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DEPARTMENT OF  
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## Shell Oil Company (Anacortes) Class II Inspection

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May 1995

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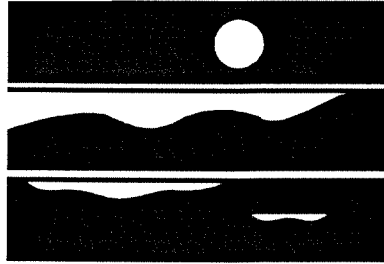
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by  
Guy Hoyle-Dodson

Environmental Investigations and Laboratory Services Program  
Olympia, Washington 98504-7710

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## Abstract

A Class II Inspection was conducted February 28 and March 1, 1994 at the Shell Oil Company Petroleum Refinery (Shell) at March Point near Anacortes, Washington. The inspection investigated the Shell process wastewater, chemical wastewater, sanitary sewage, and stormwater treatment system.

The inspection found that on the first day of the inspection Shell was not timely in containing floating oil that resulted from a stormwater contamination event. General chemistry results suggest that the system's API separator was functioning normally. Removal efficiency by the system's aeration basins and sedimentation tanks was good for all parameters except TSS. This low TSS removal efficiency was attributed to poor secondary clarifier performance, and it is suggested that Shell investigate whether the poor performance of the secondary clarifier is due to overloading. Removal efficiency across the entire system was good for most parameters with the exception of ammonia nitrogen, which showed increased concentration across the detention ponds. It is suggested that this increase may be caused by the decomposition of algae, although there are factors that may mitigate against this explanation. Cyanide concentration in the receiving water at the acute boundary was projected to exceed the State acute water quality criterion for marine receiving waters. Refinery effluent concentrations were all within NPDES permit limits. Whole effluent organic and metal concentrations were generally within state and EPA water quality criteria except for copper, mercury, and nickel. With the exception of cyanide, dilution within the receiving water reduced concentrations to below all criteria.

Ecology laboratory split sample analyses found significant differences between Shell and Ecology effluent samples and possible differences between laboratory analyses. Bioassays found toxicity in two out of four sensitive species and subacute toxicity in a third. A reasonable potential exists that the discharge violates water quality standards, and it is recommended that the source of the toxicity be identified. Sediment analyses found that organic and metal concentrations did not exceed the marine sediment quality standards. Bioassays revealed no significant toxicity in the sediment.

# Summary

## Flow Measurement

Evaluation of the Shell flow measurement device was not done during the inspection. Average flow reported by Shell over the two days of the inspection was approximately 3.6 MGD. Based upon reported rainfall during the inspection, average stormwater flow for the period was estimated to be 0.64 MGD.

## Process Wastewater Treatment System Operation

Prior to and during the inspection Shell experienced oil and phenolic contamination of their main stormwater flow. In response they diverted stormwater flow from the stormwater flume to the aeration basins. During the inspection it was observed that oil floating on the surface of the stormwater flume was allowed to enter the aeration basin. On the first day of the inspection it was observed that Shell's response to containing the floating oil was delayed until well into the afternoon. Oil was likely discharged with the effluent to the receiving water.

## General Chemistry

Solids and oxygen demand parameter concentrations in the API effluent collected after the primary clarifier were comparable to or lower than concentrations found in API effluents for typical petroleum refineries. This indicated that the API separator was functioning normally. Removal efficiencies for most general chemistry parameters across the aeration basins and the sedimentation tanks were comparable to what would be expected for similar units at typical refineries. TSS removal efficiency across these units was low compared to similar refinery treatment processes, and this may be attributed to poor secondary clarifier performance.

Removal efficiencies for most general chemistry compounds across the entire treatment system were good compared to typical refinery treatment processes, with the exception of ammonia nitrogen. The impact of stormwater loading on removal efficiencies across the treatment plant was found to be negligible. Ammonia increased in concentration across the detention ponds, but the cause of this increase was not satisfactorily identified. The ammonia final effluent concentration, based on 1992 Ecology-defined dilution ratios, did not exceed state marine water quality criteria.



The cyanide effluent concentration at the acute boundary, based on the 1992 dilution ratio, was projected to exceed state acute water chronic criterion by a factor of three. An updated dilution zone model produced revised dilution ratios, but did not appreciably change the outcome.

## **NPDES Permit Comparisons**

Refinery total effluent discharge concentrations were within NPDES permit monthly average and daily maximum loading limits.

## **Detected Organics and Priority Pollutants**

Volatile organic and BNA compounds were found in concentrations that did not exceed EPA water quality criteria for receiving waters. Most metals concentrations in the whole effluent did not exceed EPA or state water quality criteria with the exception of copper, mercury, and nickel. Dilution with the receiving water based on revised dilution ratios was projected to yield concentrations for these metals well below both acute and chronic water quality criteria.

## **Split Samples**

Ecology analysis of Ecology and Shell composite samples found significant differences between the two samples, suggesting dissimilarity in sampling protocols. Results for Ecology and Shell laboratory analyses also differed, although the small number of samples makes it difficult to determine if these differences were significant.

## **Bioassays**

One bioassay found little toxicity, while three other bioassays found sub-acute to high toxicity. *Daphnia pulex* experienced no acute toxicity (NOEC = 100% effluent and LOEC > 100% effluent) with 80% survival at 100% effluent concentration. Rainbow trout (*Oncorhynchus mykiss*) 96-hour survival test displayed 100% survival at 100% effluent concentration, although subacute toxicity was observed at this concentration. Fathead minnow 96-hour survival test found 10% survival at 100% effluent concentration. The fathead minnow test produced an NOEC = 50%, an LC50 = 73.4%, and an LOEC = 100%. The echinoderm (*Strongylocentrotus purpuratus*) marine bioassays displayed significant sperm cell toxicity, producing an NOEC, EC50, and LOEC of 17.5%, 31%, and 35% respectively.

Possible sources of toxicity are cyanide, metals and ammonia concentrations in the whole effluent. Dilution with the receiving water may mitigate some toxicity, but a reasonable potential does exist that the discharge may violate the water quality standards.

## **Sediments**

Sediment at all sample locations consisted predominately of sand. TOC in the outfall sample was low compared to typical marine sediments. Several organics were detected in appreciable concentrations at the outfall, but none exceeded the marine sediment quality standards chemical criteria. Amphipod/Rhepoxynius (*Rhepoxynius abronius*) 10-day emergence and survival bioassay detected no significant toxicity in the sediment.

# Recommendations

## Flow Measurements, Operation, and Maintenance

- To improve the accuracy of evaluating stormwater flow contributions, stormwater flow should be metered.
- To improve plant performance and effluent quality, Shell should revise its response to intermittent slugs of wastewater or contamination events to provide timely containment of contaminants.

## Process Wastewater Treatment System

- To improve plant efficiency Shell should investigate the cause of TSS increase across the aeration basins and sedimentation tanks, with an emphasis on poor secondary clarifier performance.
- To improve plant performance Shell should investigate the increase of ammonia nitrogen across the detention ponds.
- Shell should ensure that cyanide concentrations at the edge of the acute and chronic mixing zones are below State water quality criteria for marine receiving waters.
- The source of bioassay toxicity should be identified, and efforts made to reduce toxic concentrations to levels that ensure that future bioassay results do not create a reasonable potential for effluent discharges to exceed water quality standards.
- Review of composite sampling and laboratory testing protocols is advised.



# Introduction

A Class II Inspection was conducted at the Shell Oil Company Anacortes petroleum refinery on February 28 and March 1, 1994. Conducting the inspection were environmental investigator Paul Stasch and environmental engineer Marc Heffner, both of the Washington State Department of Ecology (Ecology) Toxics Investigations Section. Nancy Kmet, permit coordinator for Ecology's Industrial Section, provided technical expertise and background information to Ecology investigators and report authors. Shell plant environmental engineer Arnold Marsden represented the Shell facility, although he was not present during the inspection. Bruce Larson, Shell environmentalist, assisted on-site. Jim Cabbage and Guy Hoyle-Dodson, both with the Department of Ecology, assisted with sediment sample collection.

Wastewater generated at the Shell facility is primarily process water, with smaller amounts of stormwater, ballast water, and sanitary wastewater. The treated wastewater is discharged into Fidalgo Bay. The plant discharge is regulated under NPDES permit No. WA 000076-1 issued September 1, 1990 with an expiration date of May 1, 1994. The permit was revised May 1, 1993.

The Department of Ecology initiated the inspection to assess permit compliance and to aid in Ecology's on-going compliance strategy. The inspection was unannounced. Specific objectives of the inspection included:

1. Evaluate NPDES permit compliance and support NPDES renewal process;
2. Assess wastewater toxicity with comparisons of priority pollutant scans to EPA and Washington State water quality criteria;
3. Assess wastewater toxicity with effluent bioassays;
4. Characterize sediment toxicity with comparisons of organic priority pollutant scans to Ecology marine sediment criteria;
5. Characterize sediment toxicity with sediment bioassays;
6. Evaluate treatment plant performance with special emphasis on nutrient balance and cyanide reduction;
7. Assess permittee's self monitoring by conducting split samples; and
8. Evaluate stormwater discharge.

# Setting

## Refinery Wastewater Generation

The Shell petroleum refinery is located in Skagit County, near Anacortes. It is situated at March Point, which extends northwest into Fidalgo Bay and northeast into Padilla Bay (*Figure 1*). The locality is shared with the Texaco petroleum refinery, which also discharges to Fidalgo Bay. The Shell facility refines in excess of 100,000 barrels of crude oil per day, producing gasoline, diesel fuel, and other petroleum products. Primary refinery processes include crude distillation and desaltation, atmospheric distillation, vacuum fractionation, deasphalting, hydrotreating, catalytic cracking, catalytic reforming, gas recovery, butane isomerization, alkylation, and caustic treatment. Effluent limitations are based on guidelines published August 12, 1985 under 40 CFR Part 419 by the Environmental Protection Agency (EPA).

The refinery generates wastewater from five sources: oily process wastewater, stormwater runoff, ship ballast, chemical wastewater, and sanitary sewage. Shell process wastewater sources includes sour water (washing, mixing and stripper water), boiler condensate, crude desalter water, cooling tower blowdown (precipitation of heavy metals), lab wastewater, and oily stormwater runoff. A separate collection system can accommodate oil-contaminated stormwater runoff that originates from containment areas around storage tanks and process units. Uncontaminated runoff from these catch basins is normally drained to the stormwater collection system, but when oil contamination is detected it is mixed directly with oily process wastewater. Ballast wastewater is pumped from the tankers that serve the facility, and is added to the oily process wastewater prior to oil separation.

The main stormwater system collects surface runoff from areas of the plant not subject to oil spillage, and is usually added directly to the final detention pond. Main stormwater flows are the result of precipitation runoff from streets, parking lots, rooftops, work yards, and uncontaminated tankfarm catch basins. The chemical collection system receives acid and caustic washwaters from the units used to demineralize boiler feed water. Sanitary sewage and other wastewater is generated by facility employees. Sanitary sewage enters the process wastewater treatment system as effluent from a septic tank.

Typical pollutants for various refinery wastestreams have been identified by the Environmental Protection Agency (EPA, 1978). Sour wastewaters from catalytic cracking typically contain oil, phenols, sulfides, ammonia, and cyanide. Desalter wastewater contains ammonia, phenols, sulfides, and suspended solids. Atmospheric and vacuum fractionation wastewater contains phenols, oil, mercaptans, chlorides, ammonia, and sulfides. Hydrotreating wastewater also contains ammonia, sulfides, and phenols.

Alkylation produces spent caustic wastewater, which also contains dissolved and suspended solids. Organic constituents produce high BOD and COD concentrations in the refinery wastewater. Salts, particularly chlorides, are the major source of high dissolved solids. Most metal wastewater contaminants likely originate as natural constituents of crude oil and are concentrated in the wastewater during the refining process.

## Refinery Wastewater Treatment System

The refinery's wastewater treatment system consists of four main sections: oily wastewater oil separation system, chemical wastewater neutralization system with acid disinfection of sanitary sewage, biological treatment system, and a main stormwater passive treatment system (*Figure 2*).

Oil-contaminated process wastewater, stormwater runoff, and ballast water are mixed prior to the API separator. The two channel API separator skims floatable surface oil and settles oily sediment. Separated wastewater is pumped to the primary clarifiers. Skimmed oil residue is collected in a sump, where additional water is removed and returned to the API separator. Oil from the sump is passed to de-emulsifying beaker tanks for further water removal and additional sedimentation. Wastewater from the de-emulsifier is also returned to the head of the API separator. The condensed oil is finally returned to the plant for reprocessing. Oily sediment from the API separator and the de-emulsifier are collected for disposal by the plant's hazardous waste sludge removal system.

Chemical wastewater is directed to a neutralization pond and mixed with treated sanitary sewage. The sanitary sewage is generated by the refinery's work force, and is initially treated in a septic tank system. The septic tank effluent is pumped to the neutralization pond for disinfection by the extreme pH conditions found in the chemical wastewater. The final mixture is adjusted to a more moderate pH and then passed to the biological treatment system.

The biological treatment system consists of primary clarifiers, aeration basins, secondary clarifiers, and final detention ponds. Wastewater from the oil separation system is pumped to two parallel primary clarifiers for sedimentation. Primary sludge is removed to a sludge thickener and then sent to a Midwest hazardous waste treatment facility for use in a cement kiln. Supernatant from the clarifiers is mixed with wastewater from the chemical neutralization tank and pumped to two aeration basins operated in series. After aeration the wastewater passes through two secondary clarifiers operated in parallel and then to two large detention ponds connected in series. Sludge from the secondary clarifiers is sent to a secondary biosludge thickener and is then disposed at the county landfill.

Main stormwater runoff is collected in the stormwater flume, its surface oil skimmed, and the remaining liquid mixed with treated secondary clarifier effluent in the final detention pond. A flexible hose with a portable pump allows stormwater to be diverted from the stormwater flume directly to the aeration basin if additional treatment is required. During the inspection Shell reported that an oily water sewer line had crossed with the stormwater collection system, contaminating the stormwater. As a result a diversion of stormwater to the aeration basin had taken place.

The system also has the ability to handle surges at several points throughout the system. Wastewater can be transferred to a diversion tank and held for future treatment. Detained wastewater can be diverted to either the API separator or the aeration basins.

The final combination of treated process wastewater, ballast wastewater, chemical wastewater, and stormwater is discharge to Fidalgo Bay via a 30-inch diameter pipe that extends 3400 feet north/northwest along the refinery's shipping pier. Discharge is at a depth of approximately 34 feet below low mean tide and takes place between 12:00 AM - 4:00 AM regardless of tidal cycle.

## Procedures

Ecology set up compositors and collected composite samples from Shell's process wastewater treatment system at three locations: the effluent from the west primary clarifier unit, the effluent from the west secondary clarifier unit, and the effluent from the east detention pond prior to the outfall discharge line (Figure 2 & Appendix A). Primary clarifier effluent composite samples and secondary clarifier effluent composite samples were collected using Ecology ISCO composite samplers with equal volumes of the sample collected every 30 minutes over a 24-hour period. Equal 900 ml volumes of the east detention pond sample were collected at 12-minute intervals over a four-hour period. Temperatures of Ecology and Shell composites samples measured at the time of final partitioning were generally several degrees higher than the 4°C recommended by Manchester Laboratory as an optimal holding temperature ( Ecology, 1994). The differences in temperatures were not extreme, and are not believed to have appreciably affected the results.

Pairs of grab samples were collected at the same locations as the composite samples. The first of the grab pairs were collected in the evening of February 28 and the second grabs the morning of March 1. An additional grab-composite sample was taken for bioassay analysis at the same time grabs were taken from the final detention pond effluent. A grab-composite sample was also taken from the diverted stormwater just prior to its entry into the aeration basins. Three sediment samples were collected March 6, 1994: one at the



outfall, one approximately 30 feet east of the outfall, and an ambient background sample approximately 2000 feet northeast of the outfall.

Shell personnel collected one composite sample using their own compositor from the east detention pond effluent. Shell's effluent sample location was approximately the same as Ecology's effluent sample location. Ecology's and Shell's composite samples were each split between Ecology and Shell for analysis by each respective laboratory. Parameters analyzed, samples collected, and schedules appear in Appendix B.

Samples designated for Ecology analysis were delivered to personnel from the Ecology's Manchester Laboratory. Chain of custody procedures were observed throughout the inspection. A narrative description of all sampling stations is provided in Appendix A. Analytical procedures and laboratories performing the analyses are summarized in Appendix C. Quality Assurance / Quality Control issues are discussed in Appendix D.

## **Results and Discussion**

### **Process Wastewater Treatment System**

#### **Flow Measurement**

Independent verification of wastewater flow measurement was not performed during the inspection. Shell estimated effluent flows from pump records of the final detention pond drawdown, which was approximately four hours in duration during each day of the inspection. The average effluent flow for the two days of the inspection was 3.645 MGD.

Average stormwater flow for the same period was reported by Shell as 1.145 MGD. This figure represents the difference between measured effluent plant flow and an estimated dry weather plant flow. Stormwater is not directly metered, and actual stormwater flow for any one day can be independent of reported stormwater flow for that day. Detention of stormwater in the stormwater flume also allows stormwater additions to be independent of coinciding precipitation runoff. However, during the inspection stormwater was not being detained, but pumped to the aeration basin, and the effluent flow included stormwater flows equal to precipitation runoff. Shell reported in daily monitoring records that during the inspection daily precipitation at the site averaged 0.16 inches. A more objective approximation of inspection stormwater flow might be obtained by assuming a linear relationship between the reported monthly average stormwater flow and monthly average precipitation. The proportionality from a two-month average of reported stormwater flow to precipitation, produces a calculated stormwater flow of 0.638 MGD relative to the two-day average precipitation of 0.16 inch recorded during the inspection. It is

recommended that for more accurate evaluation of stormwater flume contributions, this flow should be metered.

### **Plant Operation and Maintenance**

Some operation and maintenance deficiencies were observed. These include:

1. Prior to the inspection Shell detected oil and phenolic contamination of their main stormwater flow, and in response Shell diverted stormwater to the aeration basins (Larson, 1995). It was observed by Ecology that the diversion allowed floating oil to enter the basins during much of the first day of the inspection;
2. Shell's response to containing the floating oil was not timely. It was observed that Shell deployed an absorbent boom to contain the oil on the surface of the stormwater flume only late on the first day of the inspection.

Although partially volatilized, floating oil likely would not be easily metabolized in the aeration basin (Metcalf & Eddy, 1991) and may be discharged with the effluent to the receiving water. Shell's past responses to contamination events have been generally thorough (Kmet, 1995), and their response to this particular event is believed to be anomalous. A systematic well-documented strategy to ensure a timely and comprehensive response to all surge or contamination events should improve plant performance and effluent quality.

### **General Chemistry**

Ecology results are shown in Table 1. Sampling which would have allowed characterization of the Shell API separator performance was not performed because of potential explosion and exposure hazards. Analysis of API separator effluent samples collected at the primary clarifier effluent produced results that were uniformly less than concentrations expected from API petroleum treatment processes at typical refineries (EPA, 1978). In particular BOD<sub>5</sub> (107 mg/L) was only 43% of the typical lowest range. These results may be an indication of excellent API separator performance, although they could also reflect primary clarifier performance.

Samples were collected upstream and downstream of the aeration basins to characterize performance. The upstream sample taken from the primary clarifier effluent did not include the neutralization pond contributions of sanitary sewage and chemical sewer wastewater. It is believed that since neutralization pond flows are small compared to process water flows, sanitary sewage is previously treated in a septic tank, and chemical wastewater is pH neutralized, the impact of these sources on aeration basin performance would be minor compared to that of the process wastewater. During the inspection Shell also diverted stormwater flow from the stormwater flume directly into the aeration basins

for treatment. Shell reported that, due to an inadvertent crossing of an oily sewer line with the stormwater collection system, stormwater runoff had for the past week been contaminated with oil and phenolics. Ecology sampled this flow prior to the aeration basin and its contribution was characterized. The downstream sample was taken from the secondary clarifier effluent and thus included the effects of clarifier sedimentation.

The secondary clarifier effluent concentrations for several critical parameters were well within expected ranges for effluents of aerated lagoon/clarifier systems typical of petroleum refineries (EPA, 1978). Compared to typical removal efficiencies for such systems, the Shell aeration basin appeared to be functioning normally, with the exception of total suspended solids (TSS) removal (EPA, 1978). Including the stormwater load, percent removals of BOD<sub>5</sub>, COD, NH<sub>3</sub> and NO<sub>3</sub> were 89%, 63%, 78%, and 99% respectively (Table 2). Total cyanide and weak acid dissociable cyanide loads were reduced 87% and 71% respectively, indicating fairly robust treatment. Both nitrification and denitrification appeared to be taking place across the basin. The TSS load across the system, however, increased 27% compared to an expected decrease of 40-65% for typical systems, and this increased TSS load appeared to be largely independent of the stormwater contribution. Since TSS would be expected to increase in the aeration basins (microorganism growth), the lack of reduction across the system is likely attributable to poor performance by the secondary clarifier. It is possible that this marginal performance is the result of hydraulic overloading, of which the stormwater addition may be a component. However, since the stormwater hydraulic load is estimated to be less than 18% of the total hydraulic load, it is not clear that the stormwater contribution would be sufficient to be the decisive contributor to hydraulic overloading in the clarifier. To improve plant efficiency Shell should investigate the cause of the TSS increase, with an emphasis on secondary clarifier performance.

The removal efficiencies across the entire plant as determined by Ecology analyses were for most parameters equivalent to efficiencies for similar treatment processes found at typical refineries (EPA 1978). When stormwater loading was considered, its impact was found to be negligible (Table 2). Ecology BOD<sub>5</sub>, COD, TOC, and TSS concentrations from the primary clarifiers to the final effluent were reduced 92%, 72%, 68%, and 82% respectively. Total cyanide and weak acid dissociable cyanide removal across the entire plant was 74% and 71% respectively. The results indicate that most removal was taking place upstream of the detention ponds. Total cyanide was found to be slightly increased across the detention ponds. This apparent increase could be due to variability in the analysis, although mixing with prior higher cyanide concentrations retained in daily turnover residual or entrainment from lagoon sediments cannot be completely excluded.

In contrast, total solids (TS), alkalinity, and conductivity increased 27%, 31%, and 35% respectively across the plant. Ammonia nitrogen concentration increased 14%, with the increase taking place exclusively across the detention ponds (>400% increase from the secondary clarifier effluent). It is common for nitrogen increases across lagoon systems to

be the result of the decomposition of algae, which can proliferate in these environments. However, mitigating against this explanation was the time of year (February has a short photo period and lower temperatures) and the presence of antimony (an algicide). Contamination by previous intermittent slugs containing higher ammonia concentrations is not likely due to the daily turnover of detention pond volumes. Nitrogen increase across the ponds is at present not fully explicable. To improve plant performance Shell should investigate the cause of the nutrient increase and take corrective action.

The whole effluent cyanide concentration (40 µg/L estimated) exceeded the Washington State acute water quality criteria for marine waters (1.0 µg/L) by a factor of 40. On the basis of EPA approved dilution models for effluent discharges (EPA, 1985) Ecology has mandated an acute dilution ratio of 13:1 at a 23-foot boundary and a chronic ratio of 162:1 at a 225-foot boundary. Based on these dilutions the mixed effluent cyanide concentration would be 3.1 µg/L at the edge of the acute boundary, which exceeds the acute criterion by a factor of three. Cyanide toxicity is of concern and steps should be taken to ensure that cyanide concentrations at the edge of the acute and chronic mixing zones are below state marine water quality criteria.

The whole effluent ammonia concentration (2.97 mg/L) was within the criteria (approximately 3.6 mg/L), calculated from ambient data collected March 3, 1994 at an Ecology sampling station located in Fidalgo Bay just east of the outfall. The station reported temperatures exceeding 8° C, pH above 7.86, and salinity between 29.9 and 30 g/Kg for this date (Eisner, 1995). The whole effluent ammonia results could exceed the calculated chronic criterion based on reported ambient data for other months at the same location (criteria below 1.6 mg/L). However, the diluted ammonia concentration at the chronic boundary was projected to be 0.018 mg/L, just slightly more than 1% of the lowest calculated chronic water quality criterion.

Data presented in a dilution zone study prepared in February 1991 (CH2M HILL, 1991) was used by Ecology to define acute and chronic dilution ratios for the Shell effluent discharge (Yee, 1992). A subsequent dilution zone was modeled based on an updated 1994 dilution model (EPA, 1994). It incorporated amended input data and projects revised dilution ratios of 18:1 and 95:1 for acute and chronic dilutions respectively (Appendix E). These new and tentative dilutions do not appreciably alter the previous conclusions, but suggest that additional dilution modeling may be necessary for future permits.

### **NPDES Permit Comparisons**

Ecology effluent loading results for BOD<sub>5</sub> (213 lbs/day), COD (1867 lbs/day), ammonia nitrogen (90 lbs/day), and TSS (152 lbs/day) were well within both the Shell permit monthly average and daily maximum loading limits (Table 3). Ecology results for permit parameters oil and grease, phenolic compounds, total and hexavalent chromium, pH, fecal

coliform, and salmonid bioassay were also within permit limits. These limitations are stipulated in the permit, based upon a plant production of three consecutive months at 93,000 bbls per day or higher (Shell three-month production levels were 99698 bbls, 101779 bbls, and 101616 bbls for Nov.-1993, Dec.-1993, and Jan.-1994 respectively). The limitations do not incorporate ballast and stormwater allocations.

### **Detected Organics and Priority Pollutant Metals**

Table 4 summarizes concentrations of organics detected with priority pollutant scans, and also summarizes priority pollutant metals. Appendix F contains results of all targeted organic compounds and metals results. Tentatively identified compounds are presented in Appendix G. A glossary of terms is provided in Appendix H.

Concentrations of VOAs, BNAs, and metals were detected in the Shell effluent (Table 4). Ecology sample results detected eight VOAs and one BNA in the plant effluent, at concentrations as high as 21.2 µg/L-estimated. None exceeded EPA or Washington State water quality criteria for receiving waters.

Seven metals were detected in the effluent sample collected and analyzed by Ecology. The Ecology whole effluent copper result (4 µg/L) exceeded the Washington State acute water quality criterion of 2.5 µg/L (Ecology, 1992). The Shell effluent mercury (0.16 µg/L) and nickel (10 µg/L) results both exceeded Washington State chronic marine water quality criteria. The Ecology sample results for both metals were non-detects at values well above the corresponding criteria values and cannot be used for confirmation. Dilution at the edge of both the acute and chronic zones, based on the revised dilution ratios, produced concentrations for these metals well below criteria.

The Ecology effluent antimony concentration (4160 µg/L) was elevated, but marine water quality criteria do not presently exist for this metal. Freshwater chronic toxicity of antimony to freshwater aquatic life has been identified in concentrations as low as 1,600 µg/L and toxicity to algae occurs at concentrations as low as 610 µg/L. Using the 1992 dilution ratio, dilution at the edge of the chronic zone is calculated to reduced the antimony concentration to approximately 26 mg/L (46 mg/L using the revised dilution ratio). A process upgrade is also anticipated that is expected to significantly reduce antimony concentrations in future effluent discharges (Kmet, 1995), although the extent of this reduction is at present unknown. Antimony's effect on marine organisms at either the diluted concentration or the anticipated lower discharge concentration is unknown and should be viewed with concern.

The whole effluent selenium concentration (17 µg/L) exceeded the 5 mg/L concentration at which it is recommended that the status of fish communities in salt water should be monitored (Ecology, 1992). Dilution at the edge of the acute dilution zone reduces this concentration to approximately 1.3 mg/L.

## Bioassays

Effluent bioassays detected acute or sub-acute toxicity in two out of three acute tests (Table 5). The *Daphnia pulex* 48-hour survival test demonstrated 80% survival at 100% effluent, with an NOEC and an LOEC of 100% effluent. It was not possible to estimate LC50 due to the variable nature of the test results. The rainbow trout (*Oncorhynchus mykiss*) 96-hour survival test exhibited 100% survival at both 65% and 100% effluent concentration. However, at 100% effluent concentration test fish exhibited symptoms of subacute toxicity after 72 hours exposure. Fish were observed swimming erratically (i.e. upside down). The fathead minnow 96-hour survival test produced significant mortality (10% survival at 100% effluent), with an NOEC, LC50, and LOEC of 50%, 73.4%, and 100% effluent respectively.

Additional acute toxicity was evidenced in a single marine organism bioassay. The echinoderm (*Strongylocentrotus purpuratus*) sperm cell toxicity (normal fertilizations) test determined an NOEC, LOEC, and EC50 of 17.5%, 35%, and 31% effluent respectively. The laboratory was unable to complete a second marine organism bioassay, the pacific oyster embryo 48-hour survival (normal embryo survival) test, because test organisms were not available at the proper life stage for the test.

Cyanide, ammonia, and metal concentrations may individually or in concert be the source of bioassay toxicity in the whole effluent and in subsequent dilutions. The cyanide concentration is known to be acutely toxic at all test dilutions and likely is a major contributor of toxicity. Effluent copper concentration exceeded the acute marine water quality criterion and would contribute to the whole effluent toxicity. Effluent mercury and nickel concentrations from the Shell effluent sample exceeded chronic criteria, and may contribute an additive effect to acute toxicity. Whole effluent ammonia concentrations may produce chronic effects at critical temperatures and pHs found in various bioassay test solutions. The effect of antimony is unknown, but highly suspect. The selenium concentration may also contribute an effect at the lower dilutions.

Although bioassays found limited toxicity at the higher dilutions, and dilution will have a mitigating effect within the receiving water, percent survival of fathead minnow was still less than the 65% performance standard required by acute whole effluent toxicity limits (Ecology, 1993). The acute critical effective concentration (ACEC) is approximately 6% effluent based on the revised dilution ratio (18:1); and although bioassay toxicity was not conspicuous at this dilution, due to violation of the performance standard, a reasonable potential to violate water quality standards exists (also cyanide exceeded the criteria by a factor of two at this dilution). The source of bioassay toxicity in the wastestream should be identified and its impact on receiving water biota evaluated by receiving water bioassays with appropriate marine test species.

## **Split Samples**

A Wilcoxon nonparametric signed ranks test was performed on Ecology lab results for Shell and Ecology effluent samples (Table 6). The test found a significant difference between the two sets of sample results at a critical level of 0.05. Relative percent difference for seven out of 13 of these parameter pairs were well outside the range of established precision variability for the corresponding analytical test (Ecology, 1991b), indicating that the difference was not just due to an inherent lack of precision of the analytical tests. The majority of the Shell sample results were higher than the Ecology results. This analysis indicates that Shell's and Ecology's composite sampling techniques may differ. Review of composite sampling protocols is advised, with particular attention paid to compositor cleaning.

Shell performed laboratory analysis on only four compounds. Relative percent differences between Ecology and Shell laboratory analyses for phenolics, NH<sub>3</sub>, TSS, and COD were 111%, 50%, 40%, and 2.1% respectively. All but the last result were outside the range of established precision variability for the respective analyses. Although the significance of these results is inconclusive due to low sample size, they may indicate differences in analytic performance between the two laboratories. Review of laboratory protocols may identify revisions in technique that will improve laboratory performance.

## **Sediments**

### **General Chemistry**

Sediment samples were collected at the effluent outfall, slightly east and down current of the outfall, and at a background location several hundred meters to the east of the shipping pier. Grain size analysis found that all sample locations were similar and consisted of approximately 75% sand, 14% silt, and 10% clay (Table 1). The outfall and background samples also contained 1% and 2% gravel size particles respectively. Percent solids at all sample locations were approximately 58% with percent volatiles about 3.5%. TOC comprised somewhat less than 1% of the total dry weight for all samples. This is less than what might be expected for typical marine sediments (Norton, 1994), but not extreme considering the sediment's sandy composition.

### **Detected Organics and Priority Pollutants**

Eleven organic compounds were detected in the effluent outfall sediment sample (Table 7). The concentrations normalized to fractional percent TOC were all well within the marine sediment quality standards chemical criteria (Ecology, 1991). Five compounds detected at the outfall -- anthracene, pyrene, dibenzofuran, fluoranthene, and chrysene --

were approximately three times the concentrations detected in the background sample, although all but dibenzofuran were reduced in the downcurrent sediments. The findings could denote the Shell effluent as the source of these compounds and suggests that attention should be paid to controlling sources of organic compounds to the wastewater treatment system.

### **Bioassays**

Bioassays with the Amphipod/Rhepoxynius (*Rhepoxynius abronius*) 10-day emergence and survival test produced a 85% and 81% average survival in the effluent outfall sediment sample and the down current sediment sample respectively (Table 8). The background sediment sample produced a 93% average survival. Average percent survival was within the marine sediment quality minimum biological effects criteria (WAC-173-204-320) and the marine sediment cleanup screening levels and minimum cleanup biological criteria (WAC-173-204-520).



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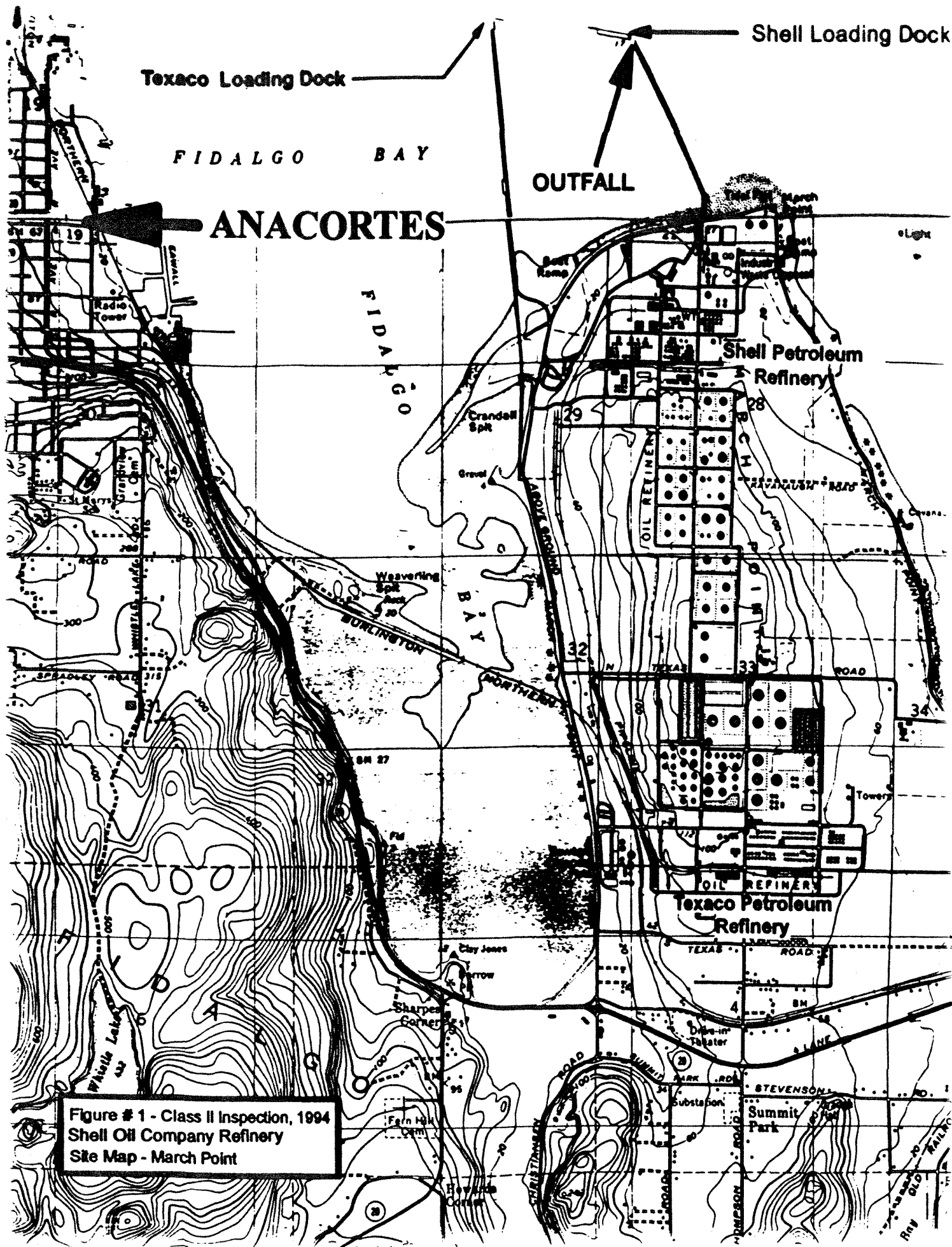


Figure # 1 - Class II Inspection, 1994  
 Shell Oil Company Refinery  
 Site Map - March Point

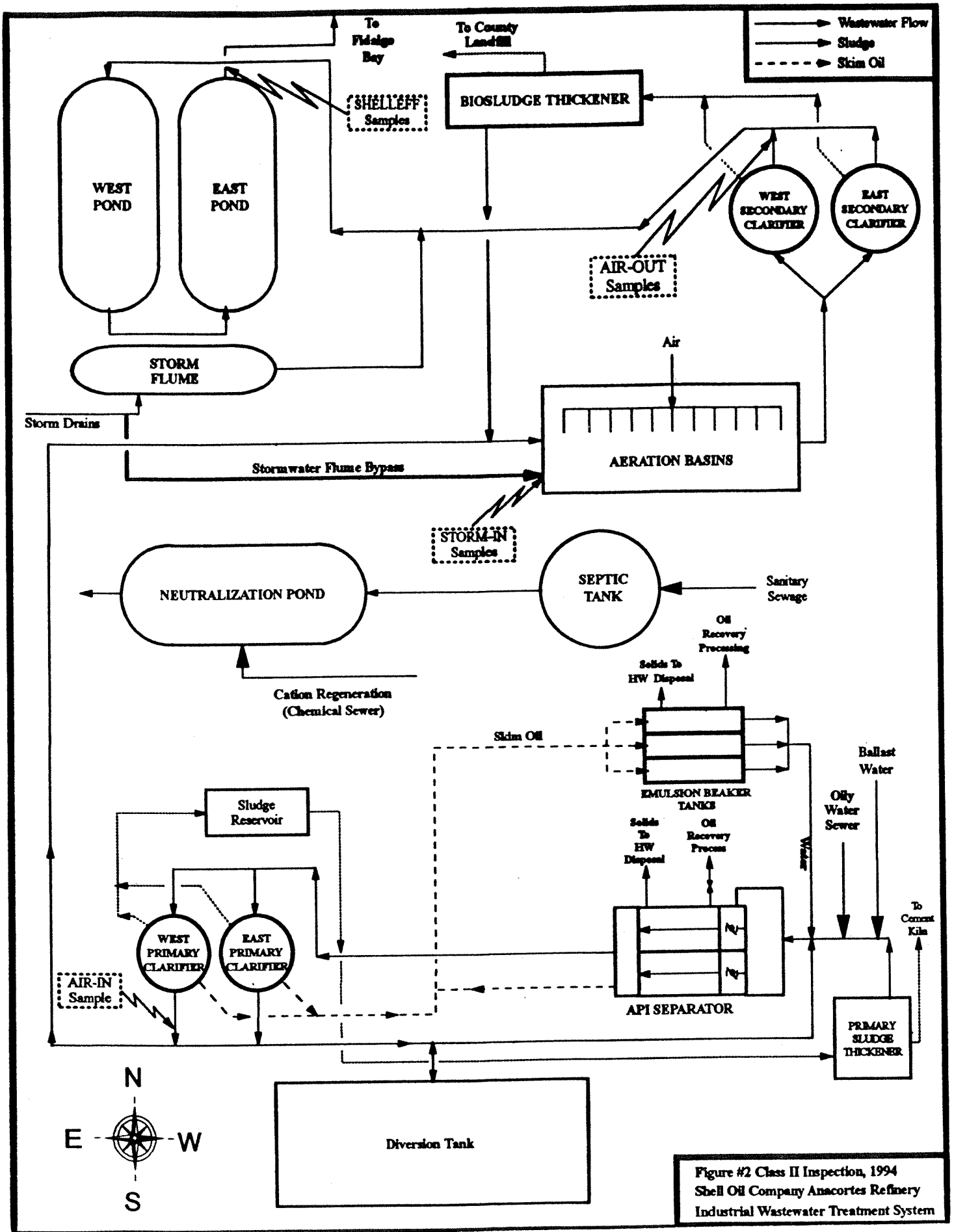


Table 1 - General Chemistry Results - Shell Oil Refinery, March 1994.

Parameter	Location:	AIR-IN	AIR-IN1	AIR-IN2	AIR-OUT	AIR-OUT1	AIR-OUT2	STORMIN	STORM-IN1	STORM-IN2
	Type:	E-comp	grab	grab	E-comp	grab	grab	grab-comp	grab	grab
	Date:	03/01	02/28	03/01	03/01	02/28	03/01	02/28&03/01	02/28	03/01
	Time:	1300-1300@	1605	1005	1230-1230@	1550	1025	1320&1015	1320	1015
	Lab Log #:	098400	098401	098402	098410	098411	098412	098420	098421	098422
<b>GENERAL CHEMISTRY</b>										
Conductivity (umhos/cm)		1810		1430				220		
Alkalinity (mg/L CaCO3)		299		196				84		
Hardness (mg/L CaCO3)										
Grain Size (%)										
Clay (<0.9-3.9 microns)										
Silt (3.9-31.2 microns)										
Fine Sand (31.2-106 microns)										
Coarse Sand (106-850 microns)										
Balance (>4750 microns)										
<b>SOLIDS</b>										
TS (mg/L)		1200		930				180		
TNVS (mg/L)		1100		810				110		
ISS (mg/L)		27	18	40	35	23	45	30	22	31
TNVS (mg/L)		19		10				25		
% Solids										
% Volatile Solids										
<b>OXYGEN DEMAND PARAMETERS</b>										
BOD5 (mg/L)		107		10				24		
COD (mg/L)		255		79.9				43.9		
TOC (water mg/L)		52.3		19.5				10.8		
TOC (soil/seed - mg/Kg-dry)									7.7	9.6
<b>NUTRIENTS</b>										
NH3-N (mg/L)		3.15	3.15	3.86	0.573	1.06	0.675			
NO2+NO3-N (mg/L)		1.17	1.35	0.634	0.01 U	0.01 U	0.01 U			
Total-P (mg/L)		0.685	1.08	0.060	0.065	0.043	0.034			
<b>MISCELLANEOUS</b>										
Oil and Grease (mg/L)									3	10
F-Coliform MF (#/100mL)										
F-Coliform MPN (#/100mL)										
Cyanide total (mg/L)		0.19 E		0.02 E						
Cyanide (wk & dis mg/L)		0.29 E		0.07 E						
Phenolics Total(water-mg/L)								0.123		
<b>FIELD OBSERVATIONS</b>										
Temperature (C)			26.3	28.5		22.9	24.2	19.8 *	18.2	21.3
Temp-cooled (C)*+		6.5		9.9						
pH		10.8	9.1	8.3	8.8	7.5	7.4	8.2 *	8.1	8.2
Conductivity (umhos/cm)		1870	1489	3240	1490	1824	1290	222 *	217	227
Sulfide (mg/L)										
AIR-IN	Ecology composite sample from primary clarifier effluent, prior to the aeration basin sample.								grab-comp	Grab composite sample.
AIR-OUT	Ecology composite sample from the aeration basin effluent.								grab	Grab sample
STORMIN	Ecology stormwater flume effluent sample.								*+	Refrigerated sample
SHELLEFF	Ecology process wastewater effluent sample.								*	Average of two grabs.
EFFLUENT	Shell process wastewater effluent sample.								E	Reported result is an estimate because of the presence of interference.
E-comp	Ecology Composite Sample.								U	The analyte was not detected at or above the reported result.
S-comp	Shell Composite Sample.								@	24-hour composite sample.

Table 1 (cont.) - General Chemistry Results - Shell Oil Refinery, March 1994.

Parameter	Location:	SHELLEFF	SHELLEFF1	SHELLEFF2	SHELLBA	EFFLUENT	SEDBACK	SOUT	SDOWN
Type:	E-comp	grab	grab-comp	S-comp	grab	grab	grab	grab	grab
Date:	03/01	03/01	03/01	03/01	03/01	03/01	04/06	04/06	04/06
Time:	0000-0400	0015	0315	0000-0400	0015&0315	0000-0400	1400	1100	1230
Lab Log #:	098430	098431	098432	098440	098433	098440	148230	148231	148232
<b>GENERAL CHEMISTRY</b>									
Conductivity (umhos/cm)	2070			2050					
Alkalinity (mg/L CaCO3)	324			325					
Hardness (mg/L CaCO3)	84			86					
Grain Size (%)			90						
Clay (<0.9-3.9 microns)							10	10	10
Silt (3.9-31.2 microns)							15	14	14
Fine Sand (31.2-106 microns)							31	29	36
Coarse Sand (106-850 microns)							42	46	43
Balance (>4750 microns)							2	1	0
<b>SOLIDS</b>									
TS (mg/L)	1300			1300					
TNVS (mg/L)	1200			1200					
TSS (mg/L)	5	11	11	21					
INVSS (mg/L)	1			12					
% Solids							58.6	57.5	58.5
% Volatile Solids							3.4	3.6	3.7
<b>OXYGEN DEMAND PARAMETERS</b>									
BOD5 (mg/L)	7			8					
COD (mg/L)	61.4			52.1					
TOC (water mg/L)	14.6		15.1	15.8			8100	9000	9100
TOC (soil/sed - mg/Kg-dry)									
<b>NUTRIENTS</b>									
NH3-N (mg/L)	2.97			3.15					
NO2+NO3-N (mg/L)	0.015			0.048					
Total-P (mg/L)	0.071			0.083					
<b>MISCELLANEOUS</b>									
Oil and Grease (mg/L)		2	3						
F-Coliform MF (#/100mL)		3 U	9						
F-Coliform MPN (#/100mL)		7.8	23						
Cyanide total (mg/L)	0.04 E			0.04 E					
Cyanide (wk & dis mg/L)	0.07 E			0.07 E					
Phenolics Total(water-mg/L)	0.0039			0.002 U					
<b>FIELD OBSERVATIONS</b>									
Temperature (C)		17.1	17.5	13.2					
Temp-cooled (C)*+	6.2			8.6					
pH	7.9	7.9	7.9	8.6					
Conductivity (umhos/cm)	2150	2160	2140	2120					
Sulfide (mg/L)		<0.1	<0.1						
AIR-IN	Ecology composite sample from primary clarifier effluent, prior to the aeration basin sample.								
AIR-OUT	Ecology composite sample from the aeration basin effluent.								
SHELLEFF	Ecology process wastewater effluent sample.								
EFFLUENT	Shell process wastewater effluent sample.								
SEDBACK	Background Sediment sample.								
SOUT	Outfall sediment sample.								
SDOWN	Down current sediment sample.								
*+	Refrigerated sample								
E	Reported result is an estimate because of the presence of interference.								
U	The analyte was not detected at or above the reported result.								
E-comp	Ecology Composite Sample.								
S-comp	Shell Composite Sample.								
grab	Grab sample								
SHELLBA	Ecology bioassay sample								

Table 2 - General Chemistry Percent Removals - Shell Oil Refinery, March 1994.

Parameter	Location: Type: Date: Time: Lab Log #:	AIR-IN E-comp 03/01 1300-1300@ 098400	AIR-OUT E-comp 03/01 1230-1230@ 098410	STORMIN grab-comp 02/28&03/01 1320&1015 098420	Percent Removal Across Aeration basins With Stormwater Load*	Percent of Aeration Basin Effluent Load Attributed to Process Wastewater
<b>GENERAL CHEMISTRY</b>						
Conductivity (umhos/cm)	1810	1430	1430	220	7%	97%
Alkalinity (mg/L CaCO3)	299	196	196			
<b>SOLIDS</b>						
TS (mg/L)	1200	930	930	180	9%	97%
TNVS (mg/L)	1100	810	810	110	13%	98%
TSS (mg/L)	27	35	35	30	-27%	81%
TNVSS (mg/L)	19	10	10	25	50%	78%
<b>OXYGEN DEMAND PARAMETERS</b>						
BOD5 (mg/L)	107	10	10	24	89%	95%
COD (mg/L)	255	79.9	79.9	43.9	63%	96%
TOC (water mg/L)	52.3	19.5	19.5	10.8	57%	96%
<b>NUTRIENTS</b>						
NH3-N (mg/L)	3.15	0.57	0.57		78%	100% #
NO2+NO3-N (mg/L)	1.17	0.01 U	0.01 U		99%	100% #
Total-P (mg/L)	0.685	0.065	0.065		88%	100% #
<b>MISCELLANEOUS</b>						
Cyanide total (mg/L)	0.19 E	0.02 E	0.02 E		87%	100% #
Cyanide (wk & dis mg/L)	0.29 E	0.07 E	0.07 E		71%	100% #
<b>FIELD OBSERVATIONS</b>						
pH	10.84	8.78	8.78	8.16	18%	**
Conductivity (umhos/cm)	1870	1490	1490	222	6%	98%

AIR-IN Composite sample from primary clarifier effluent prior to Aeration Basin.  
 AIR-OUT Composite sample after aeration basin effluent from primary clarifier effluent.  
 STORMIN Ecology stormwater flume composite effluent sample.  
 \* Based upon loads calculated with Shell's report of effluent and stormwater flows.  
 Influent concentrations do not include contributions from the neutralization pond.  
 \*\* This is percent change in pH, a logarithmic representation of active ion concentration. Assuming no buffering capacity, a linear decrease in the number of moles hydroxide ions/day exceeds 9300% across the aeration basins.  
 @ 24-hour composite sample period  
 # Assumes zero concentration in the stormwater  
 □ Assumes steady state flow and uniform removal.

E-comp Ecology Composite Sample.  
 S-comp Shell Composite Sample.

Table 2 - General Chemistry Percent Removals (cont.) - Shell Oil Refinery, March 1994.

Parameter	Location: Type: Date: Time: Lab Log #:	SHELLEFF E-comp 03/01 0000-0400 098430	Ecology Sample Percent Removal From AIR-IN to Final Effluent With Stormwater Load*	Ecology Sample Percent of Final Effluent Load Attributed to Process Wastewater <sup>o</sup>	EFFLUENT S-comp 03/01 0000-0400 098440	Shell Sample Percent Removal From AIR-IN to Final Effluent With Stormwater Load*
<b>GENERAL CHEMISTRY</b>						
Conductivity (umhos/cm)	2070		-35%	97%	2050	-34%
Alkalinity (mg/L CaCO <sub>3</sub> )	324		-31%		325	-32%
<b>SOLIDS</b>						
TS (mg/L)	1300		-27%	97%	1300	-27%
TNVS (mg/L)	1200		-29%	98%	1200	-29%
TSS (mg/L)	5		82%	81%	21	24%
TNVSS (mg/L)	1		95%		12	40%
<b>OXYGEN DEMAND PARAMETERS</b>						
BOD <sub>5</sub> (mg/L)	7		92%	95%	8	91%
COD (mg/L)	61.4		72%	96%	52.1	76%
TOC (water mg/L)	14.6		68%	96%	15.8	65%
<b>NUTRIENTS</b>						
NH <sub>3</sub> -N (mg/L)	2.97		-14% #	100% #	3.15	-21% #
NO <sub>2</sub> +NO <sub>3</sub> -N (mg/L)	0.015		98% #	100% #	0.048	95% #
Total-P (mg/L)	0.071		87% #	100% #	0.083	85% #
<b>MISCELLANEOUS</b>						
Cyanide total (mg/L)	0.04 E		74% #	100% #	0.04	74% #
Cyanide (wk & dis mg/L)	0.07 E		71% #	100% #	0.07	71% #
<b>FIELD OBSERVATIONS</b>						
pH	7.94		26% **		8.56	20% **
Conductivity (umhos/cm)	2150		-36%	98%	2120	-34%

SHELLEFF Ecology Process wastewater effluent sample.  
 EFFLUENT Shell process wastewater effluent sample.  
 \* Based upon loads calculated with Shell's report of effluent and stormwater flows.  
 \*\* Influent concentrations do not include contributions from the neutralization pond.  
 This is percent change in pH, a logarithmic representation of active ion concentration. Assuming no buffering capacity, a linear decrease in the number of moles hydroxide ions/day approaches 6E+6% across the the plant.  
 @ 24-hour composite sample period  
 # Assumes zero concentration in the stormwater  
 o Assumes steady state flow and uniform removal.



**Table 3 - NPDES Limits Inspection Results - Shell, 1994**

Parameter	NPDES Permit Effluent Limits*		Inspection Results				
			Ecology Composite	SHELL Composite	Ecology Grab		
	Monthly Average	Daily Maximum	Location: SHELLEFF	EFFLUENT	SHELLEFF-1	SHELLEFF-2	SHELLBA
			Type: E-comp	S-comp	grab	grab	grab-comp
			Date: 03/01	03/01	03/01	03/01	03/01
			Time: 0000-0400	0000-0400	0015	0315	0015&0315
			Lab Log #: 098430	098430	098431	098432	098533
<b>Effluent BOD5</b>							
Concentration (mg/L)			7	8			
Loading(lbs/day)	690	1260	213	243			
<b>Chemical Oxygen Demand</b>							
Concentration (mg/L)			61.4	52.1			
Loading(lbs/day)	4860	9330	1,867	1,584			
<b>Effluent TSS</b>							
Concentration (mg/L)			5	21			
Loading(lbs/day)	500	790	152	638			
<b>Oil &amp; Grease</b>							
Concentration (mg/L)					2	3	
Loading(lbs/day)	210	380			61	91	
<b>Phenolic Compounds</b>							
Concentration (mg/L)			0.0039	0.002			
Loading(lbs/day)	4.5	9.4	0.12	0.06			
<b>Ammonia Nitrogen</b>							
Concentration (mg/L)			2.97	3.15			
Loading(lbs/day)	440	980	90	96			
<b>Total Chromium</b>							
Concentration (mg/L)			5 U	6 P			
Loading(lbs/day)	7.5	18.7	0.15	0.19			
<b>Hexavalent Chromium</b>							
Concentration (mg/L)			6.0 U	6.0 U			
Loading(lbs/day)	0.6	1.3	0.18	0.18			
<b>Effluent pH</b>							
(S.U.)	6.0 < pH < 9.0				7.92	7.87	
<b>Effluent Fecal coliform</b>							
(#/100 mL)	200	400			3 U	9	
<b>Salmonid Acute Bioassay</b>							
(%) Survival	80% Survival at 65% Concentration						100

SHELLEFF Ecology process wastewater effluent sample.

EFFLUENT Shell process wastewater effluent sample.

SHELLBA Ecology bioassay sample

E-comp Ecology 4-hour composite sample

S-comp Shell 4-hour composite sample

grab Ecology grab sample.

P The analyte was detected above the instrument detection limit but below the established minimum quantitation limit.

U The analyte was not detected at or above the reported result.

\* Limits based upon the criteria of three preceding consecutive months of production exceeding 93,000 bbl/day and without adjustment due to the inclusion of a stormwater allocation.

Table 4 - Detected VOA, BNA, and Metals Scan Results - Shell, 1994.

Parameter	Location:		STORM-IN1		STORM-IN2		SHELLEFF1		SHELLEFF2		EPA/State Water		SEDBACK		SDOWN			
	Type:	grab	grab	ug/L	grab	ug/L	grab	ug/L	grab	ug/L	Quality Criteria Summary	Acute	Chronic	grab	ug/Kg-dry	grab	ug/Kg-dry	
<b>VOA Compounds</b>																		
Acetone																		
Chloroform																		
Benzene		1150		500		21.2 J		10.6			12000 *(a)		6400 *(a)					
1,1,1-Trichloroethane						1.4		1.3			5100 *		700 *					
Carbon Disulfide							0.071 J	0.072 J			31200 *							
2-Butanone (MEK)							0.17 J											
Naphthalene		755		1000		2.5		4.3			2350 *							
1,2,4-Trimethylbenzene		2230		1840		0.36 J		2.1										
Isopropylbenzene		37.6		24.8														
p-Isopropyltoluene		19.3		19.1														
Ethylbenzene		919		359		0.74 J		0.88 J			430 *				1.7 J			
Propylbenzene		185		120														
4-Methyl-2-Pentanone (MIBK)																		
1,3,5-Trimethylbenzene		655		569							6300 *		5000 *		0.59 J			
Toluene		5330		1310				0.82 J							4.1 J			
Total Xylenes		7690		5240			0.34 J	0.82 J							6.8 J			
m&p-Xylene		5310		3600			0.34 J	0.62 J							5.4 J			
<b>Parameter</b>																		
Location:	STORMIN		SHELLEFF		EFFLUENT		SHELLEFF		EFFLUENT		EPA/State Water		SEDBACK		SDOWN			
Type:	grab-comp		E-comp		S-comp		E-comp		S-comp		Quality Criteria Summary		grab		grab			
Date:	02/28&03/01		03/01		03/01		03/01		03/01		Acute		04/06		04/06			
Time:	1320&1015		0000-0400		0000-0400		0000-0400		0000-0400		Marine		1400		1100			
Lab Log#:	098420		098430		098440		098430		098440		Marine		148230		148231			
	ug/L		ug/L		ug/L		ug/L		ug/L		(ug/L)		ug/Kg-dry		ug/Kg-dry			
<b>BNA Compounds</b>																		
Benzo(a)Pyrene																		
Di-n-Butyl Phthalate							1.2 J											
Phenanthrene		19.0																
Fluorene		8.3																
Naphthalene		350																
2-Methylnaphthalene		462																
2-Methylphenol		83.9																
STORMIN	Ecology stormwater flume effluent sample.		J		The analyte was positively identified. The associated numerical result is an estimate.													
SHELLEFF	Ecology Process wastewater effluent sample.		*		Insufficient data to develop criteria. Value presented is the LOEL - Lowest Observed Effect Level.													
EFFLUENT	Shell Process wastewater effluent sample.		a		Total Halomethanes													
SEDBACK	Background sediment sample.		h		Total Dichlorobenzenes													
SOUT	Outfall sediment sample.		i		Total Phthalate Esters													
SDOWN	Down current sediment sample.		n		Total Polynuclear Aromatic Hydrocarbons													
E-comp	Ecology 24-hour composite sample																	
S-comp	Shell 24-hour composite sample																	
grab-comp	Grab composite sample																	
grab	Grab sample																	

Table 4 - Detected VOA, BNA, and Metals Scan Results (cont.) - Shell, 1994.

Parameter	Location: STORMIN		SHELLEFF		EFFLUENT	EPA/State Water		SEDBACK		SDOWN
	Type: grab-comp	Date: 02/28&03/01	E-comp	03/01		Quality Criteria Summary	Acute	Chronic	grab	
<b>BNA Compounds</b>	ug/L		ug/L		ug/L	(ug/L)	(ug/L)	ug/Kg-dry	ug/Kg-dry	ug/Kg-dry
Benzyl Alcohol	13.1									
2,4-Dimethylphenol	100									
Bis(2-Ethylhexyl)Phthalate	5.0 J				0.64 J	2.944 *(i)	3.4 *(i)	24.3 J	92.9 J	
Anthracene						300 *(n)		100 J	332	91.4 J
Pyrene	3.2 J					300 *(n)		7.8 J	26.0 J	20.0 J
Dibenzofuran	3.1 J					300 *(n)		22.5 J	31.7 J	
Indeno(1,2,3-cd)Pyrene						40 *	16 *	111 J	416	89.4 J
Benzo(b)Fluoranthene	1.2 J					300 *(n)			42.5 J	
Fluoranthene						300 *(n)		16.0 J	23.6 J	
Benzo(k)Fluoranthene						300 *(n)		52.1 J	181 J	
Acenaphthylene						300 *(n)		26.3 J		
Chrysene										
Retene										
<b>Metals (Total Recoverable)</b>	ug/L		ug/L		ug/L	(ug/L)	(ug/L)			
Hardness =	85									
Antimony	110 P		4160		4200					
Arsenic	3.1 P		3.4 P		3.4 P	69.0 c	36.0 d			
Trivalent						37.2 c	8.0 d			
Cadmium	0.13 P		0.16 P		0.15 P					
Chromium										
Total recoverable	5.5 P				6.1 P					
Total	5.7 P									
Hexavalent (total)										
Copper	15 P		14 P		7 P	1000.0 c,1	50.0 d			
Lead	10.6		2.0 P		3.8 P	2.5 c				
Mercury (Total)						151.0 c	5.8 d			
Nickel	12 P					2.1 c	0.025 d			
Selenium			14 J		17 PJ	71.0 c	7.9 d			
Zinc	78.3		21 P		44.8	300.0 c	71.0 d,x			
STORMIN	Ecology stormwater flume effluent sample.		J	The analyte was positively identified. The associated numerical result is an estimate.						
SHELLEFF	Ecology Process wastewater effluent sample.		P	The analyte was detected above the instrument detection limit but below the established minimum quantitation limit.						
EFFLUENT	Shell Process wastewater effluent sample.		PJ	Both P and J qualifiers apply.						
SEDBACK	Background sediment sample.		*	Insufficient data to develop criteria. Value presented is the LOEL - Lowest Observed Effect Level.						
SOUT	Outfall sediment sample.		c	A 1-hour average concentration not to be exceeded more than once every three years on the average.						
SDOWN	Down current sediment sample.		d	A 4-hour average concentration not to be exceeded more than once every three years on the average.						
E-comp	Ecology 24-hour composite sample		i	Total Phthalate Esters						
S-comp	Shell 24-hour composite sample									
grab-comp	Grab composite sample									

**Table 5 - Effluent Bioassay Results - Shell, 1994.****NOTE: all tests were run on the effluent (Shell-BA sample) - lab log # 098433****Daphnia pulex - 48 hour survival test***(Daphnia pulex)*

Sample	# Tested	Percent Survival
Control	20	90
6.25 % Effluent	20	100
12.5 % Effluent	20	70
25 % Effluent	20	55
50 % Effluent	20	75
100 % Effluent	20	80

Acute

NOEC = 100% effluent

LOEC = &gt;100% effluent

**Fathead Minnow - 96 hour survival test***(Pimephales promelas)*

Sample	# Tested	Percent Survival
Control	20	100
6.25 % Effluent	20	95
12.5 % Effluent	20	95
25 % Effluent	20	100
50 % Effluent	20	95
100 % Effluent	20	10

Acute

LOEC = 100% effluent

NOEC = 50% effluent

LC50 = 73.4% effluent

**Rainbow Trout - 96 hour survival test***(Oncorhynchus mykiss)*

Sample	# Tested	Percent Survival
Control	30	100
65% Effluent	30	100
100% Effluent	30	100*

\* fish in 100% effluent exhibited symptoms of subacute toxicity after 72 hours - fish were observed swimming erratically (e.g. upside down).

**NOTE: all tests were run on the effluent (Shell-BA sample) - lab log # 098433**

**Bivalve larvae - 48-hour survival and development test**

The laboratory was unable to complete the test. Neither test species was available at the proper life stage for the test. The blue mussel (*Mytilus edulis*) was at the end of its spawning period and the Pacific oyster (*Crassostrea gigas*) was two to three weeks from the beginning of its spawning period.

**Echinoderm Sperm Cell Toxicity Test**

*(Strongylocentrotus purpuratus)*

Sample + Concentration	% Fertilized Eggs *
	Effluent **
Brine Control	81
Control	82
4.38 % Effluent	84
8.75 % Effluent	83
17.5 % Effluent	76
35 % Effluent	53
70 % Effluent	1
Egg Control	0

**Chronic**

EC50 = 31 % effluent  
 NOEC = 17.5 % effluent  
 LOEC = 35 % effluent

\* average of 4 replicates, each with approximately 2000 eggs and a 400:1 sperm to egg ratio

\*\* salinity adjusted to 30 ppt using hypersaline brine.

NOEC - no observable effects concentration  
 LOEC - lowest observable effects concentration  
 LC50 - lethal concentration for 50% of the organisms  
 EC50 - effect concentration for 50% of the organisms

**Table 6 - Split Sample Result Comparison - Shell, 1994**

Parameter	Location:	SHELLEFF	EFFLUENT	SHELLEFF	SHELLEFF2
	Type:	E-comp	S-comp	grab	grab
	Date:	03/01	03/01	03/01	03/01
	Time:	0000-0400	0000-0400	0015	0315
	Lab Log #:	098430	098440	098431	098432
<b>General Chemistry</b>					
	Laboratory				
<b>Effluent BOD5</b> (mg/L)	Ecology	7	8		
	Shell				
<b>Effluent TSS</b> (mg/L)	Ecology	5	21		
	Shell		14		
<b>Chemical Oxygen Demand</b> (mg/L)	Ecology	61.4	52.1		
	Shell		51		
<b>TOC</b> (mg/L)	Ecology	14.6	15.8		
	Shell				
<b>Phenolic Compounds</b> (mg/L)	Ecology	0.0039	0.002 U		
	Shell		0.007		
<b>Ammonia Nitrogen</b> (mg/L)	Ecology	2.97	3.15		
	Shell		1.9		
<b>Total Chromium</b> (mg/L)	Ecology	5 U	5 U		
	Shell				
<b>Hexavalent Chromium</b> (mg/L)	Ecology	6 P	6 P		
	Shell				
<b>Effluent Fecal coliform</b> (#/100ml)	Ecology			3 U	9
	Shell		5		
<b>pH</b>	Ecology	7.94	8.56		
	Shell				
<b>Metals</b>					
<b>Antimony ( µg/L)</b>	Ecology	4160	4200		
<b>Arsenic ( µg/L)</b>	Ecology	3.4 P	3.4 P		
<b>Beryllium ( µg/L)</b>	Ecology	1 U	1 U		
<b>Cadmium ( µg/L)</b>	Ecology	0.16 P	0.15 P		
<b>Copper ( µg/L)</b>	Ecology	4 P	7 P		
<b>Lead ( µg/L)</b>	Ecology	2.0 P	3.8 P		
<b>Mercury ( µg/L)</b>	Ecology	0.1 U	0.16 P		
<b>Nickel ( µg/L)</b>	Ecology	10 U	10 P		
<b>Selenium ( µg/L)</b>	Ecology	14 J	17 PJ		
<b>Silver ( µg/L)</b>	Ecology	0.5 UN	0.05 UN		
<b>Thallium ( µg/L)</b>	Ecology	2.5 UN	2.5 UN		
<b>Zinc ( µg/L)</b>	Ecology	21 P	44.8		
E	Ecology sample	J	The analyte was positively identified. The associated numerical result is an estimate.		
S	Shell sample	P	The analyte was detected above the instrumentation limit, but below the established minimum quantitation limit.		
grab	grab sample				
comp	Composite sample	PJ	Both P and J qualifiers apply		
EFFLUENT	Shell effluent sample from final pond	U	The analyte was not detected at or above the reported result.		
SHELLEFF	Ecology effluent sample from final pond.	UN	The analyte was not detected at or above the reported result, and the spike sample recovery was not within control limits.		

**Table 7 - Comparison of Detected Sediment Organics to Marine Sediment Quality Standards - Shell, 1994**

	Location:		SOUT		SDOWN		Marine Sediment Quality Standards Chemical Criteria
	SEDBACK	grab	grab	grab	grab	grab	
<b>Organic Compounds</b>	mg/Kg TOC -dry wt.*	mg/Kg TOC -dry wt.*	mg/Kg TOC -dry wt.*	mg/Kg TOC -dry wt.*	mg/Kg TOC -dry wt.*	mg/Kg TOC -dry wt.*	
<b>Benzo(a)Pyrene</b>			6.66				99
<b>Phenanthrene</b>	12.3		19.4	9.34			100
<b>Naphthalene</b>	2.57		5.12				99
<b>2-Methylnaphthalene</b>	1.96		3.33				38
<b>Anthracene</b>	3.0		10.3				220
<b>Pyrene</b>	12.3		36.9	10.0			1000
<b>Dibenzofuran</b>	0.96		2.89	2.20			15
<b>Indeno (1,2,3-c,d)Pyrene</b>	2.78		3.52				34
<b>Fluoranthene</b>	13.7		46.2	9.82			160
<b>Acenaphthylene</b>	1.98		2.62				66
<b>Chrysene</b>	6.4		20.1				110

\* Normalized to fractional percent TOC

- SEDBACK Background sediment sample
- SOUT Ecology sediment sample taken at outfall.
- SDOWN Down current sediment sample
- grab Ecology grab sample

**Table 8 - Sediment Bioassay Results - Shell, 1994.**

**Amphipod - 10 day survival test**

*(Rheopoxynius abronius)*

Parameter	Control	Location: Type: Date: Time: Lab Log #:	SEDBACK grab 04/06 1400 148230	SOUT grab 04/06 1100 148231	SDOWN grab 04/06 1230 148232
Number Tested ***	100		100	100	100
Percent Survival	97		93	85 **	81 **
Number per Replicate Failing to Rebury	0.0 (+/- 0.0)		0.6 (+/- 0.9)	0.0 (+/- 0.0)	0.0 (+/- 0.0)
Exceeds Marine Sediment Quality Minimum Biological Effects Criteria (WAC-173-204-320)			No (Test Mean mortality > 25% on an absolute basis)	No (Test Mean mortality > 25% on an absolute basis)	No (Test Mean mortality > 25% on an absolute basis)
Exceeds Marine Sediment Cleanup Screening Levels and Minimum Cleanup Biological Criteria (WAC-173-204-520)			No (Test mean mortality > 30% higher than reference mean mortality)	No (Test mean mortality > 30% higher than reference mean mortality)	No (Test mean mortality > 30% higher than reference mean mortality)

\* Mean (standard deviation)

\*\* Difference between result and control is statistically significant (p = 0.05). Result would probably not be considered biologically significant when survival is > 80%.

\*\*\* five replicates of 20 organisms per replicate



## **Appendices**



## Appendix A - Sampling Stations Descriptions - Shell, 1994

<b>AIR-IN-#</b>	Grab sample of wastewater collected from the flow out of the West primary clarifier, upstream of the aeration basins and prior to the neutralization pond effluent - collected in both A.M. and P.M..
<b>AIR-IN</b>	Ecology 24-hour composite sample of wastewater collected from the flow out of the West primary clarifier, upstream of the aeration basins and prior to the neutralization pond effluent.
<b>AIR-OUT#</b>	Grab sample of wastewater collected from below the weir at the West secondary clarifier, upstream of the detention ponds - collected in both A.M. and P.M.
<b>AIR-OUT</b>	Ecology 24-hour composite sample of wastewater collected from below the weir at the West secondary clarifier, upstream of the detention ponds.
<b>STORM-IN#</b>	Ecology grab sample of stormwater collected from the diversion line to the aeration basins - collected in both A.M. and P.M.
<b>STORM-IN</b>	Ecology 24-hour grab-composite sample of stormwater collected from the diversion line to the aeration basins.
<b>SHELLEFF#</b>	Grab sample of effluent collected from the overflow at the East detention pond, prior to entering the discharge pipe - collected in both A.M. and P.M.
<b>SHELLEFF</b>	Ecology 4-hour composite sample of effluent collected from the overflow at the East detention pond, prior to entering the discharge pipe.
<b>SHELLBA</b>	Ecology bioassay composite grab sample of effluent collected from the overflow at the East detention pond, prior to entering the discharge pipe.
<b>EFFLUENT</b>	Shell 24-hour composite sample of effluent collected from the overflow at the East detention pond, prior to entering the discharge pipe.
<b>SOUT</b>	Sediment sample collected at the Shell loading dock outfall location (Lat: 48° 30' 30" N; Long: 122° 34' 00" W)
<b>SDOWN</b>	Sediment sample collected approximately 30 feet east of the Shell loading outfall location (Lat: 48° 30' 30" N; Long: 122° 34' 00" W)
<b>SEDBACK</b>	Background sediment sample collected approximately 2000 feet northeast of the loading dock. (Lat: 48°- 30'- 45" N; Long: 122°- 33'- 50" W)





## Appendix C - Laboratory Methods - Shell Oil Refinery, March 1994.

Parameter	MANCHESTER METHODS	APHA METHODS	Lab Used
Conductivity	EPA, Revised 1983: 120.1	APHA, 1992: 2510A.	Ecology
Alkalinity	EPA, Revised 1983: 310.1	APHA, 1992: 2320B.	Ecology
Hardness	EPA, Revised 1983: 130.2	APHA, 1992: 2340C	Ecology
Grain Size	Tetra Tech, 1986:TC-3991-04	N.A.	Soil Technology, Inc.
<b>SOLIDS</b>			
Solids <sub>4</sub>	EPA, Revised 1983: 160.2&3		Ecology
TSS	EPA, Revised 1983: 160.2	APHA, 1992: 2540D.	Ecology
% Solids	APHA, 1992: 2540G	APHA, 1992: 2540G.	Ecology
% Volatile Solids	EPA, Revised 1983: 160.4	APHA, 1992: 2540E.	Ecology
<b>OXYGEN DEMAND PARAMETERS</b>			
BOD <sub>5</sub>	EPA, Revised 1983: 405.1	APHA, 1992: 5210B	Ecology
COD	EPA, Revised 1983: 410.1	APHA, 1992: 5220B.	Analytical Resources Incorporated
TOC (water)	EPA, Revised 1983: 415.1	APHA, 1992: 5310B.	Ecology
TOC (soil/sed)	EPA, Revised 1983: 415.1	APHA, 1992: 5310B.	Analytical Resources Incorporated
<b>NUTRIENTS</b>			
NH <sub>3</sub> -N	EPA, Revised 1983: 350.1	APHA, 1992: 4500-NH <sub>3</sub> D	Ecology
NO <sub>2</sub> +NO <sub>3</sub> -N	EPA, Revised 1983: 353.2	APHA, 1992: 4500-NO <sub>3</sub> F.	Ecology
Total-P	EPA, Revised 1983: 365.3	APHA, 1992: 4500-PF.	Ecology
<b>MISCELLANEOUS</b>			
Oil and Grease (water)	EPA, Revised 1983: 413.1	APHA, 1992: 5520B	Ecology
F-Coliform MF	APHA, 1992: 9222D.	APHA, 1992: 9221D.	Ecology
F-Coliform MPN	APHA, 1989: 9221A.	APHA, 1992: 9221A.	Ecology
Cyanide (total)	EPA, Revised 1983: 335.2	APHA, 1992: 4500-CNC.	Analytical Resources Incorporated
Cyanide (wk & dis)	APHA, 1992: 4500-CNI	APHA, 1992: 4500-CNI.	Analytical Resources Incorporated
Phenolics Total(water)	EPA, Revised 1983: 420.2	APHA, 1992: 5530D.	Analytical Resources Incorporated
<b>ORGANICS</b>			
VOC (water)	EPA, 1986: 8260	APHA, 1992: 6210D.	Ecology
VOC (soil/sed)	EPA, 1986: 8240	APHA, 1992: 6210B.	Ecology
BNAs (water)	EPA, 1986: 8270	APHA, 1992: 6410B	Ecology
BNAs (soil/sed)	EPA, 1986: 8270	APHA, 1992: 6410B.	Ecology
PCB (sed)	EPA, 1986: 8080	N.A.	
PCB (water)	EPA, 1986: 8080	N.A.	
<b>METALS</b>			
PP Metals (water)	EPA, Revised 1983: 200-299	APHA, 1992: 3000-3500*.	Ecology
Total chromium	EPA, Revised 1983: 218.3	APHA, 1992: 3500-CrB.	Ecology
Hexavalent chromium	EPA, Revised 1983: 218.5	N.A.	Ecology
<b>BIOASSAYS</b>			
Salmonid (acute 65%)	Ecology, 1981.	APHA, 1989: 8910B&C.	Ecology
Salmonid (acute 100%)	Ecology, 1981.	APHA, 1989: 8910B&C.	Ecology
Bivalve Larvae (chronic)	ASTM, 1989-E724	APHA, 1989: 8610B&C	Parametrix, Inc.
Daphnia pulex (acute)	ASTM, 1986- E1193	APHA, 1989: 8711B&C.	Ecology
Fathead Minnow (acute)	EPA 1989: 1000.0	APHA, 1989: 8910B&C	Ecology
Echinoderm sperm cell	Dinnel, 1987	N.A.	Parametrix, Inc.
Rhepoximus (solid acute)	ASTM, 1990: E1367	N.A.	Ecology

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Appendix D - Priority Pollutant Cleaning Procedures and Quality Assurance /  
Quality Control - Shell (Anacortes), 1994.

## PRIORITY POLLUTANT SAMPLING EQUIPMENT CLEANING PROCEDURES

1. Wash with laboratory detergent
2. Rinse several times with tap water
3. Rinse with 10% HNO<sub>3</sub> solution
4. Rinse three (3) times with distilled/deionized water
5. Rinse with high purity methylene chloride
6. Rinse with high purity acetone
7. Allow to dry and seal with aluminum foil

## QUALITY ASSURANCE/QUALITY CONTROL DISCUSSIONS

Sampling quality assurance included priority pollutant cleaning of sampling equipment. Sampling in the field followed all protocols for holding times, preservation, and chain-of-custody set forth in the Manchester Lab Laboratory Users Manual (Ecology, 1994).

Laboratory Quality Assurance/Quality Control (QA/QC) including applicable holding times, procedural blanks, spike and duplicate spike sample analyses, surrogate recoveries, and check standards were, with several exceptions, within acceptable limits. For bioassays the conduct of testing, responses to positive and negative controls, and water quality data were generally appropriate, with the exception of the *Daphnia pulex* 48-hour survival test and the Bivalve Larvae test. Specific laboratory QA/QC concerns include:

### A. Volatile Compound Analysis

1. All sediment samples were analyzed six days over the recommended 14 day holding time. These results were qualified with "J" to indicate that the values are estimates.
2. Low levels of several volatile analytes were detected in laboratory blanks for both water and sediment matrices. Volatile compounds, acetone and methylene chloride, were detected in sediment laboratory blanks. The EPA 5 times rule was applied to the results. For those compounds detected in a sample at a concentration less than five times the concentration detected in the method blank, the result was qualified with a "U". For those compounds detected in the sample at concentration more than five times the concentration detected in the method blank, the results is not qualified.
3. The percent deviations between initial and continuing calibration standards of results for trichlorofluoromethane in all samples and for dichlorofluoromethane, acetone, and carbon disulfide in one sample exceeded the maximum. In the corresponding samples, positive results have been qualified with a "J" and non-detects with a "UJ".
4. Toluene-d<sub>8</sub> recoveries exceed the QC limits for surrogate recoveries in several samples. These samples were diluted to allow toluene concentrations to fall within the calibration range, producing acceptable recoveries. The toluene concentrations reported are from the dilution analysis and are not qualified.

5. Although matrix spike recoveries for several water matrix analytes were below QC limits, it was determined that the high concentrations present in the original samples make the spike recovery data unreliable and that no qualifier was necessary. Sediment matrix analytes that were outside the QC limits for both percent recovery and Relative Percent Difference (RPD) were qualified with a "J".

B. Semi-volatile Compound Analysis

1. Low levels of the several volatile analytes were detected in laboratory blanks for both water and sediment matrices. The EPA 5 times rule was applied, where compounds are considered real and not the result of contamination if the levels in the sample were greater than or equal to five times the amount of compounds in the associated method blank.
2. Thirteen sediment matrix compounds were outside acceptable matrix spike recoveries and RPDs. These were qualified with a "J". Three of these compounds were outside QC limits due to high native concentrations present in the sample.

C. Metals & General Chemistry Analysis

1. Spike recoveries for selenium, silver, and thallium were outside the CLP acceptance limits, and were qualified with either a "N" or a "J" depending on the analyte level and/or the severity of interference found.
2. All results for total and weak dissociable cyanide were flagged with the "E" qualifier, indicating that the value is an estimate due to interference. The source of the interference was not identified, but is thought to be characteristic of industrial effluents in general.

D. Bioassay Analysis

1. The *Daphnia pulex* test resulted in some variability in survival, unrelated to dose. It was not possible to estimate an LC50 by statistical means due to the variable nature of the test results. NOEC and LOEC were calculated. Also the LC50 estimated by potassium chloride reference toxicant exceeded the highest concentration tested, suggesting that test organisms were somewhat less sensitive than normally observed in the Manchester Laboratory.
2. The laboratory was not able to complete the Bivalve Larvae test due to insufficient development of test organisms.



## Appendix E - Dilution Zone Model

### DEPARTMENT OF ECOLOGY MEMO

Date: April 18, 1995  
To: Nancy Kmet  
From: Guy Hoyle-Dodson  
Subject: Review of Permitted 1992 Shell Dilution Zone Ratios

I modeled Shell's effluent discharge using the UDKHDEN and 3PLUMES dilution ratio modeling software. The approach was to replicate Chung Ki Yee's model results using the 1994 version of UDKHDEN, the 1994 version of 3PLUMES with the Brooks far field model, and Yee's input data. The accompanying data output file shows that our results were very similar for both far field and near field computations. The next step was to make several corrections to the input parameters that define Yee's basic model. These corrections were based on a more comprehensive characterization of the effluent and receiving water quality than was employed by Yee, and reflect improvements in the modeling software.

First, the model was corrected for effluent temperature and salinity using effluent data accumulated during the 1995 Class II Inspection. The newer UDKHDEN software also allows input of a Universal Data File (UDF) compiled from 3PLUMES, that incorporates several new parameters not found in UDF files used in the previous version. This includes automatic calculations of density from salinity and temperature, Vena Contracta corrected initial plume diameter, coefficient of contraction for the discharge port, entrainment coefficient, far field velocity, and far field dispersion coefficient. The corrected analysis also used an ambient water column profile that differed somewhat from that used by Chung Ki Yee. Data from the 1992 Shell dilution zone study collected at sample location Profile # 15 was substituted for Yee's data. This sample point was chosen on the advice of Norm Glenn as being a good representation of ambient conditions, since it was a sample point located upcurrent of the discharge and on the edge of the chronic dilution zone boundary.

Several other assumptions were made that differed from Chung Ki Yee's. Chung Ki Yee assumed a current flow perpendicular to the effluent discharge. Based upon the Shell study's current rosette and a port discharge that was directed due north, the corrected model assumed an angle 45 degrees to the perpendicular. Chung Ki Yee assumed that the effluent flow based on the

## Appendix E - Dilution Zone Model

maximum capacity of a single pump discharging over a four-hour period was suitable for both near and far field dilution calculations. Since dilutions at the edge of the chronic boundary are required to be based on a four-day average concentration, this peak flow is not suitable for calculating the chronic dilution ratio. The corrected model assumed that this flow may be used for the near field (requires a one-hour average flow), but the farfield model would require the average of four 24-hour discharges. Consequently the corrected model applied a four-day average high for total effluent discharge derived from September 1993 daily monitoring records to the 3PLUMES Brooks model. September was chosen as the month most likely to experience critical ambient condition. Assuming that concentrations detected during the inspection would remain fairly consistent year around, September's high flows would have the greatest impact on the receiving water.

Perhaps most significantly, Chung Ki Yee used a  $4/3$  power law calculation to arrive at his far field dilution ratio. The 1994 Dilution Models for Effluent Discharges promulgated by the EPA suggests that the  $4/3$  power law calculation is most suited to open coastal environments. This document suggests that the Constant Eddy Diffusion calculation offers "a conservative estimate for open coastal environments and an appropriate estimate for near coastal and inshore waters". Since the Shell discharge into Fidalgo Bay would appear to be more representative of near coastal or inshore discharge, the corrected model uses the Constant Eddy Diffusion calculation to estimate centerline (maximum) concentration at an distance X from the discharge.

The results of my modeling efforts are included in the companion printouts. My conclusions are as follows:

1. The UDKHDEN derived acute dilution ratio, based on a single pump four-hour discharge ( $0.599 \text{ m}^3/\text{s}$ ), is approximately 18 at the 6.86 meter acute boundary. The dilution ratio for the same model based on a two-pump four-hour discharge ( $0.789 \text{ m}^3/\text{s}$ ) is approximately 16.
2. The 3PLUMES Brooks model derived chronic dilution ratio based on a 4-day average flow ( $0.133 \text{ m}^3/\text{s}$ ) and using the Const. Eddy Diff. calculation is approximately 95 at the 68.6 meter chronic boundary.

Although the corrected model relies on an amalgam of data collected at different times and by different samplers, I believe that the updated algorithms and more comprehensive input data offer an improved characterization of dilution ratios.

Appendix F - VOA, BNA, PCB and Metals Scan Results - Shell, 1994.

Parameter	Location:	STORM-IN1	STORM-IN2	SHELLEFF1	SHELLEFF2	SEDBACK	SOUT	SDOWN
Type:	grab	grab	grab	grab	grab	grab	grab	grab
Date:	02/28	03/01	03/01	03/01	03/01	04/06	04/06	04/06
Time:	1320	1015	1015	0015	0315	1400	1100	1230
Lab Log#:	098421	098422	098422	098431	098432	148230	148231	148232
VOA Compounds	ug/L	ug/L	ug/L	ug/L	ug/L	ug/Kg-dry	ug/Kg-dry	ug/Kg-dry
Carbon Tetrachloride	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Acetone	5.0 U	5.0 U	5.0 U	21.2 J	10.6	12.8 UJ	12.8 UJ	14.1 UJ
Chloroform	1.0 U	1.0 U	1.0 U	1.4	1.3	1.5 UJ	1.8 UJ	1.6 UJ
Benzene	1150	500	500	1.0 U	0.092 J	1.5 UJ	1.8 UJ	1.6 UJ
1,1,1-Trichloroethane	1.0 U	1.0 U	1.0 U	0.07 J	0.072 J	1.5 UJ	1.8 UJ	1.6 UJ
Bromomethane	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Chloromethane	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Dibromomethane	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Bromochloromethane	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Chloroethane	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Vinyl Chloride	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Methylene Chloride	2.0 U	2.0 U	2.0 U	2.0 U	2.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Carbon Disulfide	1.0 U	1.0 U	1.0 U	0.17 J	1.0 U	1.6 UJ	1.8 UJ	1.6 UJ
Bromoform	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Bromodichloromethane	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,1-Dichloroethane	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,1-Dichloroethene	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Trichlorofluoromethane	1.0 UJ	1.0 UJ	1.0 UJ	1.0 UJ	1.0 UJ	1.5 UJ	1.8 UJ	1.6 UJ
Dichlorodifluoromethane	1.0 U	1.0 U	1.0 U	1.0 UJ	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,2-Dichloropropane	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
2-Butanone (MEK)	1.0 U	1.0 U	1.0 U	2.5	1.7 U	6.0 UJ	5.6 UJ	5.7 UJ
1,1,2-Trichloroethane	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Trichloroethene	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,1,2,2-Tetrachloroethane	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,2,3-Trichlorobenzene	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	7.7 UJ	8.9 UJ	8.0 UJ
Hexachlorobutadiene	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	3.1 UJ	3.6 UJ	3.2 UJ
Naphthalene	755	1000	1000	1.0 U	4.3	7.7 UJ	8.9 UJ	5.0 UJ
2-Chlorotoluene	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,2-Dichlorobenzene	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,2,4-Trimethylbenzene	2230	1840	1840	0.36 J	2.1	1.5 UJ	1.8 UJ	1.6 UJ
1,2-Dibromo-3-Chloropropane (DBCP)	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,2,3-Trichloropropane	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ

STORMIN Ecology stormwater flume effluent sample. J The analyte was positively identified. The associated numerical result is an estimate.  
 SHELLEFF Ecology process wastewater effluent sample. U The analyte was not detected at or above the reported result.  
 SEDBACK Background sediment sample. UJ The analyte was not detected at or above the reported estimated result.  
 SOUT Outfall sediment sample.  
 SDOWN Down current sediment sample.  
 grab Grab sample

Appendix F - VOA, BNA, PCB and Metals Scan Results (cont.) - Shell, 1994.

Parameter	Location	STORM-IN1	STORM-IN2	SHELLEFF1	SHELLEFF2	SEDBACK	SOUT	SDOWN
Type:	grab	grab	grab	grab	grab	grab	grab	grab
Date:	02/28	03/01	03/01	03/01	03/01	04/06	04/06	04/06
Time:	1320	1015	1015	0015	0315	1400	1100	1230
Lab Log#:	098421	098422	098422	098431	098432	148230	148231	148232
VOA Compounds	ug/L	ug/L	ug/L	ug/L	ug/L	ug/Kg-dry	ug/Kg-dry	ug/Kg-dry
tert-Butylbenzene	1.0 U	1.0 U	1.0 U	1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Isopropylbenzene	37.6	24.8		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
p-Isopropyltoluene	19.3	19.1		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Ethylbenzene	919	359		0.74 J	0.88 J	1.5 UJ	1.7 J	1.6 UJ
Styrene (Ethanylbenzene)	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Propylbenzene	185	120		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Butylbenzene	52.3 U	51.9 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
4-Chlorotoluene	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,4-Dichlorobenzene	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,2-Dibromoethane (EDB)	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,2-Dichloroethane	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
4-Methyl-2-Pentanone (MIBK)	1.0 U	1.0 U		1.0 U	1.0 U	3.1 UJ	0.59 J	3.2 UJ
1,3,5-Trimethylbenzene	655	569		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Bromobenzene	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Toluene	5330	1310		1.0 U	1.0 U	1.5 UJ	4.1 J	1.6 UJ
Chlorobenzene	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,2,4-Trichlorobenzene	1.0 U	1.0 U		1.0 U	1.0 U	3.1 UJ	3.6 UJ	3.2 UJ
Dibromochloromethane	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Tetrachloroethene	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
sec-Butylbenzene	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,3-Dichloropropane	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
cis-1,2-Dichloroethene	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
trans-1,2-Dichloroethene	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,3-Dichlorobenzene	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,1-Dichloropropene	1.0 U	1.0 U		1.0 U	1.0 U	3.1 UJ	3.6 UJ	3.2 UJ
2-Hexanone	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
2,2-Dichloropropane	1.4 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
1,1,1,2-tetrachloroethane	1.0 U	1.0 U		1.0 U	1.0 U	1.5 UJ	1.8 UJ	1.6 UJ
Total Xylenes	7690	5240		0.34 J	0.82 J	3.0 UJ	6.8 J	4.8 UJ
m&p-Xylene	5310	3600		0.34 J	0.62 J	1.5 UJ	5.4 J	3.2 UJ
cis-1,3-Dichloropropene	0.53 U	0.53 U		0.53 U	0.53 U	0.82 UJ	0.94 UJ	0.85 UJ
trans-1,3-Dichloropropene	0.47 U	0.47 U		0.47 U	0.47 U	0.73 UJ	0.83 UJ	0.75 UJ

STORMIN Ecology stormwater flume effluent sample. J The analyte was positively identified. The associated numerical result is an estimate.  
 SHELLEFF Ecology process wastewater effluent sample. U The analyte was not detected at or above the reported result.  
 SEDBACK Background sediment sample. UJ The analyte was not detected at or above the reported estimated result.  
 SOUT Outfall sediment sample.  
 SDOWN Down current sediment sample.

Appendix F - VOA, BNA, PCB and Metals Scan Results (cont.) - Shell, 1994.

Parameter	Location:	STORMIN		SHELLEFF		EFFLUENT		SEDBACK		SOUT		SDOWN	
		Type:	grab-comp	E-comp	E-comp	S-comp	grab	grab	grab	grab	grab	grab	grab
	Date:	02/28	03/01	03/01	03/01	03/01	04/06	04/06	04/06	1100	148231	04/06	04/06
	Time:	1320	1015	0000-0400	098430	0000-040	1400	1400	1400	1100	148231	1230	1230
	Lab Log#:	098420		098420	098430	098440	148230	148230	148230	148231	148231	148231	148232
BNA Compounds		ug/L		ug/L		ug/Kg-dry		ug/Kg-dry		ug/Kg-dry		ug/Kg-dry	
Benzo(a)Pyrene	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	59.9 J		214 U		214 U
2,4-Dinitrophenol	102 UJ	96.1 UJ		96.1 UJ		50.0 UJ	6960 UJ	6960 UJ	9280 U		8560 U		8560 U
Dibenzo(a,h)Anthracene	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
Benzo(a)Anthracene	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
4-Chloro-3-Methylphenol	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
Aniline	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
Dimethylnitrosamine	10.2 U	9.6 U		9.6 U		5.0 U	174 U	174 U	232 U		214 U		214 U
Benzoic Acid	25.4 UJ	96.1 UJ		96.1 UJ		50.0 UJ	6960 UJ	6960 UJ	9280 U		8560 U		8560 U
Hexachloroethane	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
Hexachlorocyclopentadiene	10.2 U	96.1 U		96.1 U		50.0 U	3480 UJ	3480 UJ	4640 U		4280 U		4280 U
Isophorone	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
Acenaphthene	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
Diethyl Phthalate	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
Di-n-Butyl Phthalate	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
Phenanthrene	19.0	1.2 J		1.2 J		2.5 U	174 U	174 U	232 U		214 U		214 U
Butylbenzyl Phthalate	5.1 U	4.8 U		4.8 U		2.5 U	100 J	100 J	175 J		84.0 J		84.0 J
N-Nitrosodiphenylamine	5.1 U	4.8 U		4.8 U		2.5 U	870 U	870 U	1160 U		1070 U		1070 U
Fluorene	8.3	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
Carbazole	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
Hexachlorobutadiene	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
Pentachlorophenol	50.8 U	48.0 U		48.0 U		25.0 U	1740 UJ	1740 UJ	2320 U		2140 U		2140 U
2,4,6-Trichlorophenol	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
2-Nitroaniline	25.4 U	24.0 U		24.0 U		12.5 U	348 U	348 U	464 U		428 U		428 U
2-Nitrophenol	5.1 U	4.8 U		4.8 U		2.5 U	348 U	348 U	464 U		428 U		428 U
Naphthalene	350	4.8 U		4.8 U		2.5 U	20.8 J	20.8 J	46.1 J		37.1 U		37.1 U
2-Methylnaphthalene	462	4.8 U		4.8 U		2.5 U	15.9 J	15.9 J	30.0 J		22.8 U		22.8 U
2-Chloronaphthalene	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
3,3-Dichlorobenzidine	10.2 U	9.6 U		9.6 U		5.0 U	348 U	348 U	464 U		428 U		428 U
Benzidine	10.2 U	9.6 U		9.6 U		5.0 U	1740 U	1740 U	2320 U		2140 U		2140 U
2-Methylphenol	83.9	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
1,2-Dichlorobenzene	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
o-Chlorophenol	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
2,4,5-Trichlorophenol	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U
Nitrobenzene	5.1 U	4.8 U		4.8 U		2.5 U	174 U	174 U	232 U		214 U		214 U

J The analyte was positively identified. The associated numerical result is an estimate.

U The analyte was not detected at or above the reported result.

E-comp The analyte was not detected at or above the reported estimated result.

S-comp Ecology composite sample

Shell composite sample

STORMIN Ecology stormwater flume effluent sample.

SHELLEFF Ecology process wastewater effluent sample.

EFFLUENT Shell process wastewater effluent sample.

SEDBACK Background sediment sample.

SOUT Outfall sediment sample.

SDOWN Down current sediment sample.

Appendix F - VOA, BNA, PCB and Metals Scan Results (cont.) - Shell, 1994.

Parameter	Location:	STORMIN		SHELLEFF		EFFLUENT		SEDBACK		SOUT		SDOWN	
		Type:	grab-comp	E-comp	grab	S-comp	grab	S-comp	grab	grab	grab	grab	grab
	Date:	02/28	03/01	03/01	04/06	03/01	04/06	04/06	04/06	1100	148230	148231	148232
	Time:	1320	1015	0000-0400	1230	0000-040	1400	1400	1400	1100	148230	148231	148232
	Lab Log#:	098420		098430		098440					148230	148231	148232
BNA Compounds		ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
3-Nitroaniline	10.2 U	10.2 U	9.6 U	5.0 U	348 UJ	464 U	428 U	428 U					
4-Nitroaniline	10.2 U	10.2 U	9.6 U	5.0 U	870 UJ	1160 U	1070 U	1070 U					
4-Nitrophenol	50.8 U	50.8 U	48.0 U	25.0 U	348 UJ	4640 U	4280 U	4280 U					
Benzyl Alcohol	13.1 U	13.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
4-Bromophenyl Phenylether	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
2,4-Dimethylphenol	100 U	100 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
4-Methylphenol	12.0 U	12.0 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
1,4-Dichlorobenzene	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
4-Chloroaniline	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
Phenol	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	25.9 U	25.9 U					
Pyridine	10.2 U	10.2 U	9.6 U	5.0 U	174 UJ	232 U	214 U	214 U					
Bis(2-Chloroethyl)Ether	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
Bis(2-Chloroethoxy)Methane	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
Bis(2-Ethylhexyl)Phthalate	5.0 J	5.0 J	4.8 U	0.64 J	174 UJ	482 UJ	788 UJ	788 UJ					
Di-n-Octyl Phthalate	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
Hexachlorobenzene	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
Anthracene	5.1 U	5.1 U	4.8 U	2.5 U	24.3 J	92.9 J	214 U	214 U					
1,2,4-Trichlorobenzene	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
2,4-Dichlorophenol	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
2,4-Dinitrotoluene	50.8 U	50.8 U	48.0 U	25.0 U	348 UJ	464 U	428 U	428 U					
1,2-Diphenylhydrazine	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
Pyrene	3.2 J	3.2 J	4.8 U	2.5 U	100 J	332 U	91.4 J	91.4 J					
Dimethyl Phthalate	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
Dibenzofuran	3.1 J	3.1 J	4.8 U	2.5 U	7.8 J	26.0 J	20.0 J	20.0 J					
Benzo(g,h,i)Perylene	5.1 U	5.1 U	4.8 U	2.5 U	80.6 UJ	232 U	214 U	214 U					
Indeno(1,2,3-cd)Pyrene	5.1 U	5.1 U	4.8 U	2.5 U	22.5 J	31.7 J	214 U	214 U					
Benzo(b)fluoranthene	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	113 J	214 U	214 U					
Fluoranthene	1.2 J	1.2 J	4.8 U	2.5 U	111 J	416 U	89.4 J	89.4 J					
Benzo(k)fluoranthene	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	23.5 J	214 U	214 U					
Acenaphthylene	5.1 U	5.1 U	4.8 U	2.5 U	16.0 J	23.6 J	214 U	214 U					
Chrysene	5.1 U	5.1 U	4.8 U	2.5 U	52.1 J	181 J	214 U	214 U					
Retene	5.1 U	5.1 U	4.8 U	2.5 U	26.3 J	232 U	214 U	214 U					
4,6-Dinitro-2-Methylphenol	102 U	102 U	96.1 U	50 U	3480 U	4640 U	4280 U	4280 U					
1,3-Dichlorobenzene	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
2,6-Dinitrotoluene	25.4 U	25.4 U	24 U	12.5 U	174 UJ	232 U	214 U	214 U					
N-Nitroso-di-n-Propylamine	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
4-Chlorophenyl Phenylether	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					
Bis(2-chloroisopropyl)-	5.1 U	5.1 U	4.8 U	2.5 U	174 UJ	232 U	214 U	214 U					

STORMIN Ecology stormwater flume effluent sample. J The analyte was positively identified. The associated numerical result is an estimate.  
SHELLEFF Ecology process wastewater effluent sample. U The analyte was not detected at or above the reported result.  
EFFLUENT Shell process wastewater effluent sample. UJ The analyte was not detected at or above the reported estimated result.  
SEDBACK Background sediment sample. SDOWN Down current sediment sample.

Appendix F - VOA, BNA, PCB and Metals Scan Results (cont.) - Shell, 1994.

Location: SHELLEFF  
 Type: E-comp  
 Date: 03/01  
 Time: 0000-0400  
 Lab Log#: 098430

PCB Compounds

ug/L  
 Aroclor-1016 0.03 U  
 Aroclor-1221 ITF  
 Aroclor-1232 ITF  
 Aroclor-1242 0.03 U  
 Aroclor-1248 0.03 U  
 Aroclor-1254 0.03 U  
 Aroclor-1260 0.03 U

Location: STORMIN  
 Type: grab-comp  
 Date: 02/28 & 03/01  
 Time: 1320 & 1015  
 Lab Log#: 098420

EFFLUENT  
 S-comp  
 03/01  
 0000-0400  
 098440

Metals (Total Recoverable)

Hardness =	85	ug/L	
Antimony	110 P	4160	4200
Arsenic	3.1 P	3.4 P	3.4 P
Pentavalent			
Trivalent			
Beryllium	1 U	1 U	1 U
Cadmium	0.13 P	0.16 P	0.15 P
Chromium			
Total recoverable	5.5 P	5 U	6.1 P
Total	5.7 P	5 U	5 U
Hexavalent (Total)	6 U	6 U	6 U
Copper	15 P	4 P	7 P
Lead	10.6	2.0 P	3.8 P
Mercury (Total)	0.1 U	0.1 U	0.16 P
Nickel	12 P	10 U	10 P
Selenium	2.0 UN	14 J	17 PJ
Silver	0.50 UN	0.50 UN	0.50 UN
Thallium	2.5 UN	2.5 UN	2.5 UN
Zinc	78.3	21 P	44.8

STORMIN	Ecology stormwater flume effluent sample.	ITF	Interference prevented analysis.
SHELLEFF	Ecology Process wastewater effluent sample.	J	The analyte was positively identified. The associated numerical result is an estimate.
EFFLUENT	Shell Process wastewater effluent sample.	P	The analyte was detected above the instrument detection limit but below the established minimum quantitation limit.
E-comp	Ecology 24-hour composite sample	PJ	Both P and J qualifiers apply.
grab-comp	Grab composite sample	U	The analyte was not detected at or above the reported result.
		UN	The analyte was not detected and the sample spike recovery was not within detection limits.

## Appendix G - Tentatively Identified Compounds - Shell (Anacortes), 1994

**Sample Location:** STORM-IN1  
**Type:** grab  
**Date:** 02/28  
**Time:** 1320  
**Sample ID:** 098421

### Volatile Organics:

Compound Name	Estimated Concentration ( $\mu\text{g/L}$ )	Qualifier
1. Cyclopentane	33.8	NJ
2. Pentane	35.6	NJ
3. Benzene, 1,2,3,4 - Tetra +	94.0	NJ
4. Benzene, 1,2,3,4 - Tetra +	131	NJ
5. 2-Butene, 2-Methyl	10.9	NJ
6. Benzene, 1,2,3-Trimeth +	310	NJ
7. Benzene, 1-Methyl-3-(1 +	173	NJ
8. Benzene, 1-Methyl-3-(1 +	160	NJ
9. Benzene, 1-Ethyl-2-Met +	262	NJ
10. Benzene, 1-Ethyl-3-Met +	565	NJ
11. 1-Pentene, 2-Methyl	36.4	NJ
12. Cyclopentene, 3-Methyl	15.8	NJ
13. 2,3-Dihydro-1-Methylin +	85.8	NJ
14. 2,3-Dihydro-1-Methylin +	89.1	NJ
15. 2,3-Dihydro-1-Methylin +	179	NJ
16. Benzene, 1,1'-(1-ethen +	260	NJ
17. Benzene, (1-methyl-2-C +	50.5	NJ

NJ There is evidence that the analyte is present. The associated numerical result is an estimate.



## Appendix G - Tentatively Identified Compounds (cont.) - Shell (Anacortes), 1994

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Sample Location: STORM-IN2  
Type: grab  
Date: 03/01  
Time: 1015  
Log Number: 098422

### Volatile Organics:

Compound Name	Estimated Concentration ( $\mu\text{g/L}$ )	Qualifier
1. Limonene	70.9	NJ
2. Benzene, 1,2,3,4-Tetra +	111	NJ
3. Benzene, 1,2,3,5-Tetra +	155	NJ
4. Benzene, 1-Methyl-3-(1 +	171	NJ
5. Benzene, 1-Methyl-3-(1 +	112	NJ
6. Benzene, 1-Ethyl-3-Met +	300	NJ
7. Benzene, 1-Ethyl-4-Met +	243	NJ
8. Benzene, 1-Propenyl-Or +	416	NJ
9. Benzene, 4-Ethyl-1,2-D +	46.3	NJ
10. Benzene, 1-Methyl-3-Pr +	232	NJ
11. Benzene, (3-Methyl-2-B +	50.5	NJ
12. 1H-Indene, 2,3-Dihydro +	67.5	NJ
13. 2,3-Dihydro-1-Methylin +	105	NJ
14. 2,3-Dihydro-1-Methylin +	91.4	NJ
15. 2,3-Dihydro-1-Methylin +	214	NJ
16. Benzene, Ethyl-1,2,3-T +	43.1	NJ
17. Benzene, (1-Methyl-2-C +	59.6	NJ

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NJ There is evidence that the analyte is present. The associated numerical result is an estimate.

Appendix G - Tentatively Identified Compounds (cont.) - Shell (Anacortes), 1994

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Sample Location: SHELEFF1  
Type: grab  
Date: 03/01  
Time: 0015  
Sample ID: 098431

Volatile Organics:

Compound Name	Estimated Concentration ( $\mu\text{g/L}$ )	Qualifier
1. 1,3-Cyclohexadiene, 1, +	4.9	NJ
2. 1,3-Cyclohexadiene, 1, +	2.5	NJ
3. 2-Hexanol, 2-Methyl	2.2	NJ
4. 1,3-Cyclohexadiene, 1, +	5.2	NJ
5. Benzene, Methyl (1-Meth +	2.1	NJ
6. Propionaldehyde, dieth +	2.9	NJ

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Sample Location: SHELEFF2  
Type: grab  
Date: 03/01  
Time: 0315  
Sample ID: 098432

Volatile Organics:

Compound Name	Estimated Concentration ( $\mu\text{g/Kg}$ )	Qualifier
1. Naphthalene, 1-Methyl-	13.2	NJ
2. Benzocycloheptatriene, 1 +	6.0	NJ
3. 1,3-Cyclohexadiene, 1, +	3.3	NJ
4. Benzene, 1,2,3-Trimeth +	5.1	NJ

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Sample Location: SOUT  
Type: grab  
Date: 04/06  
Time: 1100  
Sample ID: 148231

Volatile Organics:

Compound Name	Estimated Concentration ( $\mu\text{g/Kg}$ )	Qualifier
1. Methane, Thiobis	3.6	NJ

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## Appendix G - Tentatively Identified Compounds (cont.) - Shell (Anacortes), 1994

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**Sample Location:** STORM-IN  
**Type:** grab-comp  
**Date:** 02/28&03/01  
**Time:** 1320&1015  
**Log Number:** 098420

**Bases/Neutrals/Acids:**

Compound Name	Estimated Concentration ( $\mu\text{g/L}$ )	Qualifier
1. Naphthalene, 1-Methyl-	176	NJ
2. o-Xylene	1690	NJ
3. Isopropylbenzene (Cume +	390	NJ
4. p-Xylene	2920	NJ
5. Benzene, 1,2,3-Trimeth +	1740	NJ
6. Benzene, 1,2,3,5-Tetra +	149	NJ
7. Benzene, 1-Ethyl-2-Met +	946	NJ
8. Benzene, 1-Ethenyl-2-M +	236	NJ
9. Benzene, 1-Ethyl-3-Met +	370	NJ
10. Benzene, 1-Ethyl-4-Met +	552	NJ
11. Benzene, (1-Methyl-1-P +	131	NJ
12. Benzene, 1-Ethyl-2,4-D +	287	NJ
13. Benzene, 1-Methyl-3-Pr +	265	NJ
14. Benzene, 2-Ethyl-1,4-D +	286	NJ
15. Unknown Hydrocarbon 1	125	NJ
16. Unknown Hydrocarbon 2	120	J
17. Unknown Hydrocarbon 3	131	J
18. Unknown Hydrocarbon 4	108	J
19. Unknown Compound 1	520	J

---

NJ There is evidence that the analyte is present. The associated numerical result is an estimate.  
 J The analyte was positively identified. The associated numerical result is an estimate.

## Appendix G - Tentatively Identified Compounds (cont.) - Shell (Anacortes), 1994

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**Sample Location:** SHELLEFF  
**Type:** E-comp  
**Date:** 03/01  
**Time:** 0000-0400  
**Log Number:** 098430

### Bases/Neutrals/Acids:

Compound Name	Estimated Concentration ( $\mu\text{g/L}$ )	Qualifier
1. Unknown	28.1	NJ
2. Cyclopropane, 1,1,2,2- +	22.0	J
3. Unknown Hydrocarbon 1	9.9	J
4. Unknown Compound 1	12.2	J
5. Unknown Compound 2	42.2	J
6. Unknown Compound 3	5.8	J
7. Unknown Compound 5	67.4	J
8. Unknown Compound 6	11.6	J
9. Unknown Compound 7	5.9	J
10. Unknown Compound 8	5.1	J
11. Unknown Compound 9	11.1	J
12. Unknown Compound 10	7.4	J
13. Unknown Compound 11	18.5	J
14. Unknown Compound 12	265	J
15. Unknown Compound 13	15.4	J
16. Unknown Compound 14	9.4	J
17. Unknown Compound 15	21.5	J
18. Benzene, 1,2-Dichloro +	0.30	NJ

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NJ There is evidence that the analyte is present. The associated numerical result is an estimate.

J The analyte was positively identified. The associated numerical result is an estimate.

## Appendix G - Tentatively Identified Compounds (cont.) - Shell (Anacortes), 1994

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**Sample Location:** EFFLUENT  
**Type:** E-comp  
**Date:** 03/01  
**Time:** 0000-0400  
**Lab Number:** 098440

**Bases/Neutrals/Acids:**

Compound Name	Estimated Concentration ( $\mu\text{g/L}$ )	Qualifier
1. 1H-Pyrazole, 4,5-Dihyd +	35.6	NJ
2. Unkown	2.8	NJ
3. Unknown Compound 1	10.9	J
4. Unknown Compound 2	40.9	J
5. Unknown Compound 3	5.3	J
6. Unknown Compound 4	19.0	J
7. Unknown Compound 5	61.3	J
8. Unknown Compound 6	10.4	J
9. Unknown Compound 7	4.7	J
10. Unknown Compound 8	5.0	J
11. Unknown Compound 9	4.7	J
12. Unknown Compound 10	10.7	J
13. Unknown Compound 12	25.1	J
14. Unknown Compound 13	12.0	J
15. Unknown Compound 14	11.9	J
16. Unknown Compound 15	14.2	J
17. Unknown Compound 16	29.5	J
18. 2-Azetidinone	328	J
19. Unkown	9.6	J

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NJ There is evidence that the analyte is present. The associated numerical result is an estimate.  
J The analyte was positively identified. The associated numerical result is an estimate.

**Appendix G - Tentatively Identified Compounds (cont.) - Shell (Anacortes), 1994**

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**Sample Location:** SEDBACK  
**Type:** grab  
**Date:** 04/06  
**Time:** 14:00  
**Log Number:** 148230

**Bases/Neutrals/Acids:**

Compound Name	Estimated Concentration ( $\mu\text{g/Kg}$ )	Qualifier
1. IntStd: o,p'-DDE	480	NJ
2. Hexadecanoic Acid	1910	NJ
3. Olic Acid	687	NJ
4. Tetradecanoic Acid	404	NJ
5. 9-Hexadecenoic Acid	2510	NJ
6. Unknown Hydrocarbon 1	336	J
7. Unknown Hydrocarbon 2	442	J
8. Unknown Hydrocarbon 3	449	J
9. Unknown Compound 1	6580	J
10. Unknown Compound 2	2610	J
11. Unknown Compound 3	5380	J
12. Unknown Compound 4	591	J
13. Unknown Compound 5	560	J
14. Unknown Compound 6	509	J
15. Unknown Compound 7	728	J
16. Unknown Compound 8	369	J
17. Unknown Compound 9	1650	J
18. Unknown Compound 10	1720	J

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NJ There is evidence that the analyte is present. The associated numerical result is an estimate.  
 J The analyte was positively identified. The associated numerical result is an estimate.

## Appendix G - Tentatively Identified Compounds (cont.) - Shell (Anacortes), 1994

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Sample Location: SOUT  
Type: grab  
Date: 04/06  
Time: 1100  
Log Number: 148231

### Bases/Neutrals/Acids:

Compound Name	Estimated Concentration ( $\mu\text{g/Kg}$ )	Qualifier
1. Hexadecanoic Acid	2940	NJ
2. .Gamma.-Sitosterol	3450	NJ
3. Oleic Acid	1170	NJ
4. 4-Hydroxy-4-Methylpent +	3610	NJ
5. Tetradecanoic Acid	828	NJ
6. Cholest-5-en-3-ol (3.b +	5880	NJ
7. 9-Hexadecanoic Acid	4040	NJ
8. Unknown Hydrocarbon	747	J
9. Unknown Compound 1	9080	J
10. Unknown Compound 2	7260	J
11. Unknown Compound 3	819	J
12. Unknown Compound 4	834	J
13. Unknown Compound 5	1370	J
14. Unknown Compound 6	692	J
15. Unknown Compound 7	1540	J
16. Unknown Compound 8	700	J
17. Unknown Compound 9	1150	J
18. Unknown Compound 10	1120	J

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NJ There is evidence that the analyte is present. The associated numerical result is an estimate.  
J The analyte was positively identified. The associated numerical result is an estimate.

## Appendix G - Tentatively Identified Compounds (cont.) - Shell (Anacortes), 1994

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Sample Location: SDOWN  
Type: grab  
Date: 04/06  
Time: 1230  
Lab Log Number: 148232

### Bases/Neutrals/Acids:

Compound Name	Estimated Concentration ( $\mu\text{g}/\text{Kg}$ )	Qualifier
1. Hexadecanoic Acid	1990	NJ
2. .Gamma.-Sitosterol	3030	NJ
3. Undecanoic Acid	543	NJ
4. 9-Octadecenoic Acid (Z+	698	NJ
5. 9-Hexadecenoic Acid	2610	NJ
6. Unknown Compound 1	13100	J
7. Unknown Compound 2	4960	J
8. Unknown Compound 3	3520	J
9. Unknown Compound 4	779	J
10. Unknown Compound 5	861	J
11. Unknown Compound 6	959	J
12. Unknown Compound 7	1180	J
13. Unknown Compound 8	648	J
14. Unknown Compound 9	1120	J
15. Unknown Compound 10	1800	J

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NJ There is evidence that the analyte is present. The associated numerical result is an estimate.  
J The analyte was positively identified. The associated numerical result is an estimate.



Appendix H - GLOSSARY - Shell (Anacortes), 1995

AAS	Aeroaccelerator Activated Sludge
BNA	Base-neutral acids, semivolatiles
BOD	Biological Oxygen Demand
CLP	Contract Laboratory Program
COD	Chemical Oxygen Demand
CVAA	Cold Vapor Atomic Absorption
DAF	Dissolved Air Flootation
EPA	Environmental Protection Agency
kg	kilogram (1 X 10 <sup>3</sup> grams)
L	Liter (1 X 10 <sup>3</sup> milliliters)
LC50	Concentration which is lethal to 50% of the test organisms
LOD	Limit of Detection
LOEC	Lowest Observable Effect Concentration
m <sup>3</sup>	Cubic meter (1 X 10 <sup>3</sup> liters)
MF	Membrane Filter
mg	milligram (1 X 10 <sup>-3</sup> grams)
mL	Milliliter (1 X 10 <sup>-3</sup> liters)
NH <sub>3</sub>	Ammonia
MPN	Most Probable Number
NOEC	No Observable Effect Concentration
NPDES	National Pollution Discharge Elimination System
PCB	Polychlorinated Biphenyl
pH	Hydrogen Ion Concentration
PP	Priority Pollutant
ppm	Parts per million (1 X 10 <sup>-6</sup> ug/L or ug/kg)
ppt	Parts per thousand (1 X 10 <sup>-3</sup> ug/L or ug/kg)
PWTS	Process Water Treatment System
QA/QC	Quality Assurance/Quality Control
TIC	Total Inorganic Carbon or for GCMS Tentatively Identified Compound
TNVS	Total Non-Volatile Solids
TNVSS	Total Non-Volatile Suspended Solids
TOC	Total Organic Carbon
TP	Total Phosphorous
TPH	Total Petroleum Hydrocarbons
TS	Total Solids
TSS	Total Suspended Solids
TVS	Total Volatile Solids
ug	Microgram (1 X 10 <sup>-6</sup> grams)
ug/m <sup>3</sup>	Microgram per cubic meter
VOA	Volatile Organic Analysis
VOC	Volatile Organic Carbon