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# HYDROCARBONS ASSOCIATED WITH SUSPENDED MATTER IN THE GREEN RIVER, WASHINGTON

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# HYDROCARBONS ASSOCIATED WITH SUSPENDED MATTER IN THE GREEN RIVER, WASHINGTON

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## Abstract

In 1978 a systematic study of suspended hydrocarbons in the Green-Duwamish River was undertaken. The goal of the study was to define the suspended hydrocarbon composition both seasonally and spatially. Emphasis was placed on hydrocarbon budgets of the river and the significance of the Renton Secondary Treatment Plant.

Concentrations of total aliphatics, total "aromatics" (which were contaminated with fatty-acid esters), and the unresolved complex mixture increase downriver. The upper river above Auburn, Washington, is dominated by odd-carbon paraffins contributed by aquatic and terrestrial plants. Concentrations of the even-carbon n-alkanes, pristane, and phytane increase downriver as plant wax hydrocarbons decrease in abundance. Compositional changes in suspended hydrocarbons within the upper river are attributed to highway runoff.

Stations encompassing the sewage outfall show influence of wastewater discharge. CPI indices approach unity, demonstrating relative increases in the even-carbon paraffins. The most distinctive seasonal feature is the paucity of the algal alkanes ($C_{15}$ and $C_{17}$) in December.

A budget of suspended hydrocarbons was calculated for the lower river based on analyses of riverine suspended matter obtained by centrifugation and effluent-suspended solids recovered by filtration. Results indicate a preferential loss of the heavy hydrocarbons below the sewage outfall. The deficits may by the result of (1) flocculation or desorption of suspended hydrocarbons in the effluent as waste water mixes with river water and/or (2) an overestimation of suspended hydrocarbons in the effluent caused by retention of a lipid fraction on the glass fiber filters that is not recovered by the centrifuge. Results of a budget in the upper river suggest that sediments gained by resuspension, erosion, or runoff are diluting the suspended hydrocarbons characteristic of plant waxes.

GC-MS analyses of the "aromatic" fractions confirm the presence of retene, benz(e)pyrene, perylene, benz(g,h,i)perylene, chrysene, and fluoranthene in concentrations ranging from 0.08 to 2.2 µg/g dry weight of riverine suspended matter. Concentrations of perylene and benz (g,h,i)perylene in the effluent are approximately 40 µg/g. Esters of the even-carbon fatty acids typical of waste water and higher plants are also found in these samples.

# 1.0 INTRODUCTION

## 1.1. HYDROCARBONS--GENERAL

Hydrocarbons ($C_{12}$-$C_{35}$) are minor but ubiquitous components of water, sediment, and the biosphere. Many are not readily metabolized, and their low reactivity insures persistence in aqueous environments for long periods of time. Farrington and Meyer (1975) discuss the principal routes by which hydrocarbons enter the marine environment. Biosynthesis of hydrocarbons by marine and land organisms and the subsequent release of these compounds during metabolism and decomposition contribute 1-10 x $19^9$ kg/yr. Injection of fossil hydrocarbons geochemically from submarine and land oil seeps accounts for 0.1-10 x $10^9$ kg/yr. Natural pyrolysis from forest fires releases approximately 6 x $10^9$ kg/yr, although the relative proportions of wet and dry deposition are undetermined. Diagenesis of organic matter in soil and sediment comprises a minor geochemical source. Anthropogenic contributions, arising from fossil fuel burning and accidental spills, are responsible for another 1-10 x $10^9$ kg/yr.

Fossil fuel comsumption, municipal waste disposal, and industrial effluent are increasing the flux of petroleum hydrocarbons into the aquatic environment. Studies of acute and chronic injections of petroleum hydrocarbons have generated an abundance of literature on distributions of these compounds in the water column (Keizer et al., 1977; Levy, 1972), sediments (Blumer and Sass, 1972), biota (Blumer et al., 1970 a and b; Cowell, 1969), and the atmosphere (Lao et al., 1973; Lunde and Bjorseth, 1977). In reciprocal fashion, many investigations have been prompted by the need to distinguish anthropogenic hydrocarbons from those produced naturally by forest fires (Smith et al., 1973), by sedimentary diagenesis (Blumer and Snyder, 1965), and by recent biosynthesis (Clark and Blumer, 1967; Eglinton and Hamilton, 1963).

### 1.1.1 Compositional Characteristics of Petroleum Hydrocarbons

Petroleum hydrocarbons cover a molecular-weight range from 16 to over 20,000. Normal alkanes from $C_1$ to $C_{60}$ are present in a ratio of odd- to even-carbon chain lengths of approximate unity (Blumer et al., 1972; Farrington and Meyer, 1975). Homologous series of isoprenoid alkanes between $C_{12}$ and $C_{22}$, most notably pristane ($C_{19}$) and phytane ($C_{20}$), are also found in petroleum (Clark and Brown, 1977).

Substituted and unsubstituted cyclic compounds are present and are thought to comprise, in part, the baseline "hump" referred to as the unresolved complex mixture (UCM) in gas chromatograms of crude oils (Blumer et al., 1970b). Dewaxing of petroleum preferentially removes the n-alkanes superimposed upon this hump (Clark and Brown, 1977). Microbial degradation of crude oil in water and sediment shows a similar alteration and a concentration of the UCM (Clark and Brown, 1977).

Although olefins are rarely present in crude oils, they are formed during certain refining processes (cracking) and may occur at levels up to 30% in gasoline (Clark and Brown, 1977).

Petroleum contains a complex mixture of aromatic hydrocarbons, some of which are listed below (Clark and Brown, 1977):

| Representative Compounds | Number of Rings |
|---|---|
| benzenes | 1 |
| napthalenes, biphenyls | 2 |
| phenanthrenes, anthracenes | 3 |
| pyrenes, benzanthracenes, chrysenes | 4 |
| perylenes, benzopyrenes | 5 |

Naphthenoaromatics such as indan and tetralin comprise the higher boiling point fraction of crude oils (Clark and Brown, 1977). Polynuclear aromatic hydrocarbons (PAH) in ancient rocks and petroleum are formed from organic precursors at low temperatures over geological time spans. Compositional characteristics of such effects include extensive alkylation, clustered rings, and 5-membered naphthenic rings of intermediate strain (Blumer, 1976). Youngblood and Blumer (1975) have determined that the parent aromatic compounds in kerogen-rich shales and crude oil have an average of 3 or 4 alkyl carbons associated with them. The extent of alkylation in No. 2 fuel oil is somewhat reduced with an average of 1 to 2 carbon atoms. In contrast, aromatics in car exhaust show little alkylation (Clark and Brown, 1977). Wet and dry deposition and subsequent surface runoff ultimately transport these compounds into aquatic environments.

### 1.1.2 Compositional Characteristics of Recently Synthesized Hydrocarbons

Generally, biogenic hydrocarbons are characterized by a narrow molecular-weight range in which a single component often exceeds all others in concentration (Blumer et al., 1972). Eglinton and Hamilton (1963) summarize compositional trends found in plant waxes, a major terrestrial source of aquatic hydrocarbons. The n-alkanes of these waxes fall between $C_{25}$ and $C_{35}$ with the predominant paraffin being $C_{27}$, $C_{29}$, $C_{31}$, or $C_{33}$. Odd-carbon alkanes are more abundant than even-carbon alkanes by greater than an order of magnitude. A wide variety of gymnosperms and ferns analyzed for hydrocarbons yield $C_{29}$, $C_{31}$, or $C_{33}$ as the major paraffin (Wakeham, 1976). Principal alkanes of marsh grasses are the odd-carbon compounds between $C_{21}$ and $C_{29}$ (Burns and Teal, 1971).

Clark and Blumer (1967) found large concentrations of $C_{15}$ and $C_{17}$ in both red and brown algae. Some species contained alkanes with an odd number of carbon atoms while others exhibited an even-carbon preference. Green algae showed largest concentrations of $C_{17}$. Most algal paraffins displayed a minimum around $C_{19}$-$C_{21}$ and showed a secondary maximum near $C_{27}$-$C_{30}$. A mixed culture of zoo- and phytoplankton contained predominantly $C_{17}$ and pristane.

Alkenes are much more abundant in aquatic organisms than in crude oil. Copepods and some fish contain mono-, di-, and tri-olefins, and often sizable concentrations of heniecosahexaene (Straight-chained, 6 double bonds), (Youngblood et al., 1971; Blumer et al., 1970a).

Isoprenoid alkanes and alkenes, over a narrow molecular-weight range ($C_{19}$-$C_{20}$) are present in many marine organisms (Clark and Blumer, 1967). Pristane ($C_{19}$) is abundant in copepods where it is formed from ingested phytol and stored as a nonmetabolized buoyancy agent. As zooplankton are consumed, pristane accumulates in the fatty tissues of higher food chain members (Blumer et al., 1964), and is eventually deposited in sediments. Phytane ($C_{20}$) has been found in bacteria (Han and Calvin, 1969) and is generally present in trace amounts in modern, uncontaminated sediments (Blumer and Snyder, 1965; Giger, 1974). It is found in relatively larger amounts in ancient sediments (Meinschein, 1969), where it appears to be a diagenetic product of chlorophyll conversions (Blumer and Snyder, 1965). In that both pristane and phytane are present in both organisms and fossil fuels, they are equivocal indicators of petroleum. However, their concentrations relative to other hydrocarbon concentrations and parameters are useful source indicators in specific environments.

Polynuclear aromatic hydrocarbons are produced naturally by forest and prairie fires. This high-temperature pyrolysis produces arenes with little alkylation. Blumer and Youngblood (1975) found a relatively uniform distribution of unalkylated aromatics in various depositional environments, suggesting atmospheric transport. Analyses of atmospheric particulate organic matter from remote regions verified the presence of PAH up to chrysene and benzanthracene in addition to alkanes and isoprenoids (National Academy of Sciences, 1978). Pyrolytic processes, however, are not solely responsible for the wide variety of PAH ubiquitous to the marine environment. The suggestion that some of these compounds may be synthesized by organisms is still hotly debated (Clark and Brown, 1977). A mixed culture of anaerobic bacteria from Charles River sediments showed a bioaccumulation of polycyclic aromatic hydrocarbons, but no biosynthesis (Hase and Hites, 1976). The authors remain skeptical that a real biosynthesis has ever been measured. Blanks must be monitored with great care when dealing with organisms that are accumulating PAH as well as possibly synthesizing them. Less than one percent of the total hydrocarbons in marine organisms are aromatics, and this may be an overestimate, because the organisms analyzed have not been reliably free of contamination (Clark and Brown, 1977).

### 1.1.3 Summary of Compositional Differences Between Recently Synthesized and Fossil Fuel Hydrocarbons

In light of the preceding discussion, diagnostic differences between thermogenic hydrocarbons and those resulting from biosynthesis can be summarized. Petroleum contains a hydrocarbon mixture of greater complexity than is produced by living organisms. Many homologous series are present in fossil fuel and of these, adjacent-membered paraffins are typically found in equal concentrations. An unresolved complex mixture "hump" often characterizes gas chromatograms of samples contaminated with petroleum.

In comparison, biogenic n-alkanes have an odd-carbon predominance with one paraffin usually more abundant than all others. Petroleum contains a wide range of isoprenoids while organisms are characterized by 19- and 20-carbon homologs. Olefins are absent in crude oils, but may occur to some extent in refined products and are abundant in aquatic organisms. Alkylated aromatics and naphthenoaromatics characterize fossil fuel; unalkylated arenes spanning a narrower molecular-weight range are produced during high-temperature pyrolysis. Low concentrations of aromatics with little alkylation, which may be caused by contamination, are found in marine organisms.

## 1.2 THE ASSOCIATION OF HYDROCARBONS WITH SUSPENDED MATTER

The myriad of studies concerning hydrocarbon distributions in pristine and contaminated environments is exhaustive. These works will be referred to where they are deemed pertinent. Studies elucidating the role of suspended particulates in the accommodation and dispersal of hydrocarbons are of particular interest here.

### 1.2.1 Laboratory Experiments

Interactions between hydrocarbons and suspended solids have been explored in a number of laboratory simulations. Poirier and Theil (1941) evaluated the adsorptive behavior of several natural materials (shales, silt, humus, etc.) towards crude oil. Kaolin accommodated the greatest amount of oil (~2.2 g oil/g sed). More oil was associated with fine-grained material than with coarser particulates. In a similar study, Huang and Elliott (1977) demonstrated that mineral phases (most of which are negatively charged) accommodate similarly charged oil droplets. Apparently, the adsorption or agglutination interactions are stronger than the electrostatic repulsive forces. In an attempt to further elucidate the sorption phenomenon, Baker et al. (1978) initiated a laboratory investigation of the amount of oil that could be accommodated by riverine suspended solids. They reported decreasing oil/sediment sorptivity with increasing temperatures and showed that river sediment can assimilate up to its own weight in oil. Loadings of Prudhoe Bay crude oil on Skagit River sediments ranged from 0.07 mg oil/mg sed to 0.96 mg/mg as the amount of oil added was increased from 9 to 133 mg. Loading capacities of Fraser River sediments varied inconsistently (0.07 to 0.17 mg oil/mg sed) with amounts of oil added (18 to 89 mg).

Meyer and Quinn (1973) reported that hydrocarbon solubility affects uptake and retention of hydrocarbons by sediments. Smaller amounts of eicosane, hexadecane, anthracene, and phenanthrene were associated with sediment particles as temperature increased. Bentonite showed the greatest affinity for oil (51%), followed by kaolinite (28%), illite (12%), and finally montmorillonite (3%). In addition, removal of organic matter associated with marine sediments increased the hydrocarbon loading capacity by an average factor of 2.2. The humic fraction of the organic matter appeared to be responsible for the reduction in uptake, perhaps by occupying sorption sites or by binding particulates and reducing their effective surface area.

Meyers and Oas (1978) demonstrated that the amount of n-alkane associated with smectite increased with carbon chain length from $C_{18}$ (0.74 μg/mg; 38% uptake) to $C_{28}$ (1.41 μg/mg; 70% uptake), probably because of decreasing solubilities. Relatively greater concentrations of the isoalkane analogs were removed. Uptake of the aromatics durene (0%), acenaphthene (0%), and pyrene (19%) were low, while anthracene showed an adsorption at 46%.

### 1.2.2 Environmental Studies

Most studies concerning hydrocarbon transport and removal by suspended solids in aqueous environments have dealt with estuaries, specifically those contaminated by sewage treatment plant effluents. It has been estimated that up to 5% of the hydrocarbons entering the ocean annually are a result of domestic waste-water effluent (Van Vleet and Quinn, 1977). Farrington and Quinn (1973) reported total hydrocarbon concentrations of up to 16.2 mg/l for discharges from three waste-water plants located on the Providence River and Narragansett Bay. Although compositional parameters and concentrations of individual compounds were not reported, features of the effluent hydrocarbon chromatograms were similar to those of Wilmington crude and No. 2 fuel oils. Possible sources of these petroleum hydrocarbons include highway runoff, atmospheric fallout, and casual disposal of lubricating oils. The concentration and composition of effluent hydrocarbons ruled out thermally oxidized cooking fats as a likely source.

Schultz and Quinn (1977) reported that hydrocarbon-to-suspended-matter ratios decreased as they sampled from the Providence River (34.8 mg/g) in Narragansett Bay (1.5 mg/g). Gas chromatographic analyses on packed columns indicated the presence of both pristane and phytane, an odd/even n-alkane ratio of unity, and a high percentage of unresolved hydrocarbons, supporting the authors' argument for petroleum sources in the river (e.g., the Field Point Sewage Plant, small oil spills, and shipping activity).

Van Vleet and Quinn (1977) determined the average total hydrocarbon concentration in the Field Point Treatment Plant effluent to be 2.80 mg/l of which 95% was in the form of suspended solids. Values for total suspended hydrocarbons decreased rapidly with distance from the outfall indicating rapid particulate deposition, dilution, and/or desorption. Hydrocarbon composition was attributed to petroleum sources although individual compound concentrations and compositional parameters were not reported. On the basis of effluent hydrocarbon concentrations and daily effluent volumes discharged, it is estimated that sewage could account for 42 to 84% of the suspended hydrocarbons in the Providence River. The authors contend that if total hydrocarbon concentration in waste water (2.80mg/l) is extrapolated to sewage discharge nationwide ($3 \times 10^{10}$ l/yr), then this source of hydrocarbons to coastal waters ($31 \times 10^{6}$ kg/yr) is as important as amounts entering by direct spills ($51 \times 10^{6}$ kg/yr).

## 1.3 RESEARCH OBJECTIVES

It is evident that there is a paucity of literature concerning the importance of suspended matter in the transport of petroleum hydrocarbons and other environmentally harmful materials. Even more obvious is the lack of specific compound concentrations and compositional parameters of hydrocarbons on suspended sediment in both pristine and contaminated areas. This is largely a result of the incomplete resolution of individual compounds on packed columns previously used. In addition, the continuing need to clarify ambiguous differences between biogenic and anthropogenic hydrocarbons in systems where the two sources are present is of paramount importance. The purpose of this study is to expand our knowledge of individual compound concentrations, compositional parameters and other diagnostic features by examining the suite of hydrocarbons accommodated by suspended matter in the Green River. The Green River was chosen for study because it is a tractable environmental system: it is small in size, drains an area of low population density, and is impinged upon by only one large point source of contamination, the Renton Metro sewage outfall. Sampling strategy was designed to measure seasonal and spatial variabilities in hydrocarbon concentrations and to isolate the "signature" of the sewage outfall.

# 2.0 STUDY AREA

## 2.1 GEOGRAPHY

The combined Green-Duwamish River system, located in King County, Washington, stretches from the western slopes of the Cascade Mountains to Elliott Bay in Puget Sound. The source of the Green River lies in forested valleys near Stampede Pass. The river flows westward for 64 kilometers through forest, then northwest through farm and pastureland for 35 kilometers. At river kilometer 19 near Tukwila, the Green River is joined by the Black River forming the Duwamish River, which meanders northwest for the remaining 19 kilometers through a heavily industrialized region to Elliott Bay. (Figure 1 shows the river from its mouth to approximately river kilometer 58 southeast of Auburn.) A total of 488 square kilometers of terrain is drained by the Green-Duwamish River. (Stevens et al., 1975)

The Howard Hanson Reservoir at river kilometer 103 provides water storage for flood control in the winter. Stored flood water is usually

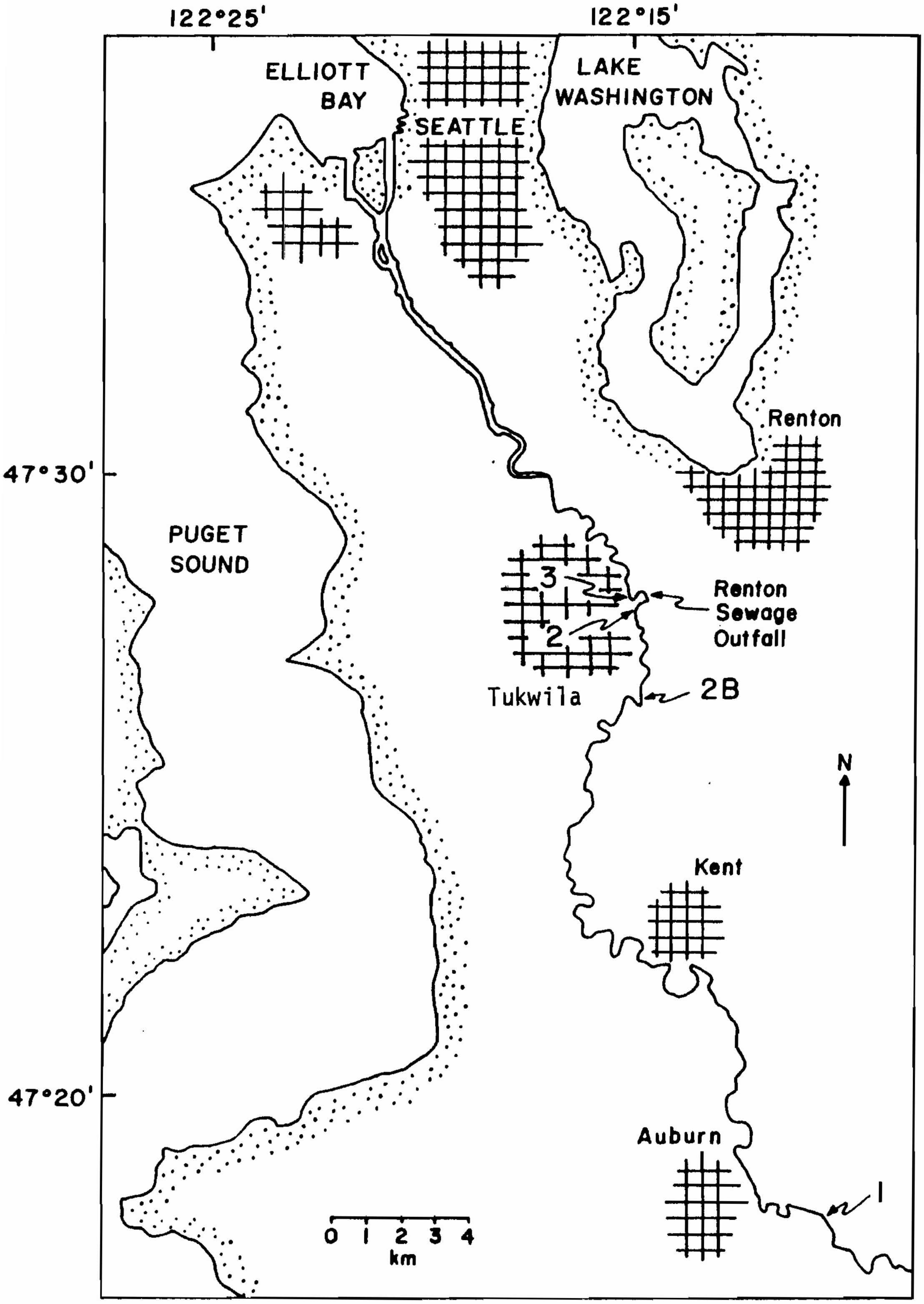

Figure 1. Locations of the sampling stations and the Renton Metro sewage outfall on the Green-Duwamish River system.

dissipated soon after a flood in order to have maximum holding capacity available for a subsequent flood (USGS, 1978). In late spring, however, runoff from snow melt is stored for augmentation of river discharge during periods of low flow in late summer. The reservoir also serves intermittently as a quiescent environment for the settling of suspended solids since the Tacoma water supply is withdrawn 5 km downstream ($CH_2M$ Hill, Inc., 1974).

## 2.2 RIVER DISCHARGE

River discharge is high during late fall and winter, responding to seasonal rains. Snow melt will extend this runoff into June, after which flow rapidly decreases to a minimum in August. This flow regime is evident in Figure 2 compiled from mean monthly discharges during 1978 (Table A-1). The United States Geological Survey (USGS) maintains eight monitoring stations along the Green-Duwamish River, two of which closely correspond to sites occupied in this study. The average annual discharge at the station near Auburn at river kilometer 52 is nearly 38.8 $m^3$/sec. The gauging station near Tukwila at river kilometer 20 records an annual average of 43.9 $m^3$/sec. (USGS, 1978). Tidal influences perturb flow during periods of low discharge up to river kilometer 21 and possibly beyond.

Suspended solids are monitored intermittently by the Municipality of Metropolitan Seattle (1978a). All available 1978 data for station A319 near Auburn and station 311 near Tukwila are shown in Figure 3 (Table A-2).

## 2.3 CLIMATE

The Green-Duwamish River lies within the west coast marine climate, typified by moderate temperatures and a definite rainy season. July is usually the driest month and December, the wettest. Most of the rainfall occurs from October through March. Located close to lower reaches of the study area is a United States Weather Bureau (Seattle-Tacoma Airport), which records an average of 98.91 centimeters of rain per year. Upper slopes of the watershed receive 254 cm/yr or more (Stevens, et al., 1975).

Average winter temperatures are in the thirties and forties (F°), (~0-5°C). Summertime temperatures average between the fifties and low

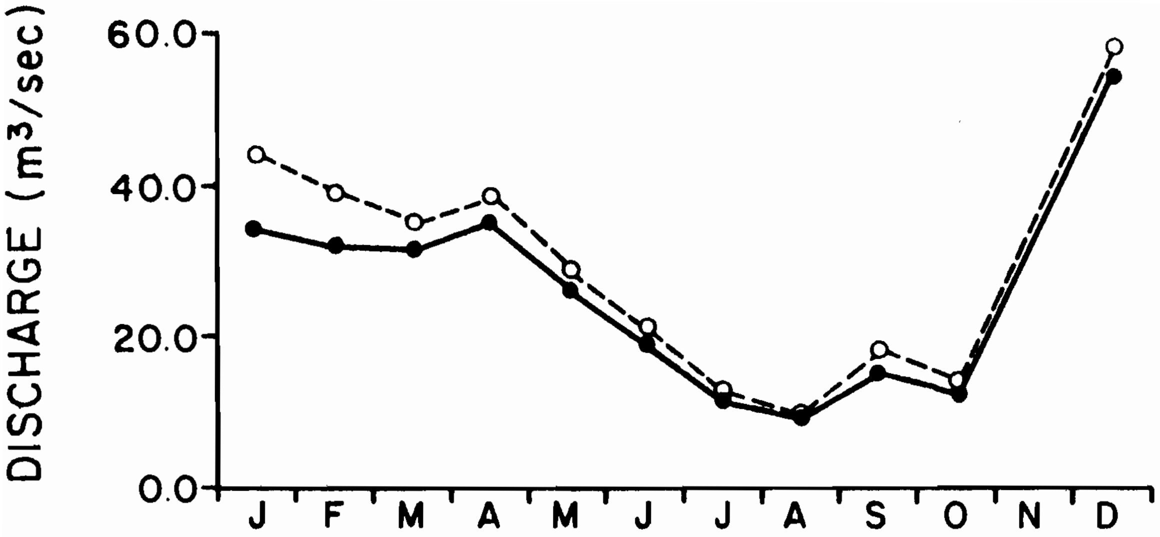

Figure 2. Mean monthly discharge (1978) of the Green River at Tukwila, river kilometer 20.0 (dotted line), and near Auburn, river kilometer 51.5 (solid line), (USGS, 1978).

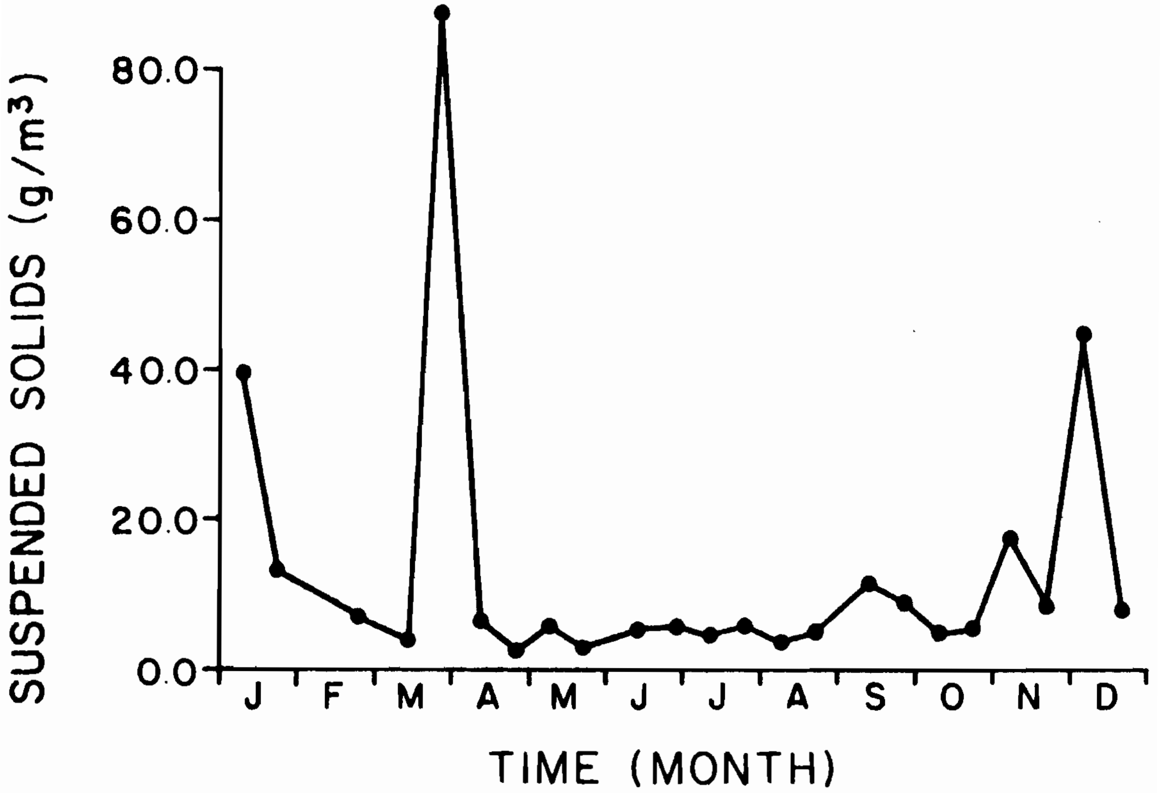

Figure 3. Profile of the suspended solids concentration in the Green River, 1978. Each point represents an average of values obtained at three Metro monitoring stations: A319 (corresponding to Station 1), 311 (corresponding to Station 2B), and 3106 (near Station 3).

eighties (F°), (~10-27°C), (Stevens et al., 1975). Table 1 lists the 1978 average monthly temperature and rainfall for two locations close to the study area.

## 2.4 VEGETATION

Douglas fir predominates in the upper reaches of the study area with western hemlock, western red cedar, and some hardwoods existing on poorly drained soils. Bigleaf maple, red alder, and willow are found at lower elevations. Black cottonwood inhabit bottom lands.

Gound cover is usually composed of shrubs, small trees, and grasses. The drier lowlands are characterized by grasses with occasional stands of Douglas fir and Oregon white oak. Freshwater marshes are covered with cattails and rushes ($CH_2M$ Hill, Inc., 1974).

## 2.5 GEOLOGY

The Green-Duwamish River valley was formed as the Vashon Glacier receded 12,000 to 14,000 years ago, leaving layers of gravel, sand, and clay ($CH_2M$ Hill, Inc., 1974).

Soils in the lower valley are composed of the Puget Series which is alluvial and contains a high proportion of silt. The uplands are characterized by glacial soils of the Everett Series (Stevens et al., 1975). More specifically, the riverbed between Auburn and Kent is gravel compacted with silt. Below Kent the river bottom is predominantly silt and rubble (Municipality of Metropolitan Seattle Water Quality Division, 1978).

## 2.6 LAND USE IN RIVER BASIN

Below river kilometer 8, the lowlands drained by the Duwamish River are used for heavy industry, while the hills above the river valley are occupied by residential and commercial sites. Shipping activities are extensive throughout this portion of the river, which is dredged to facilitate navigation. Residential and commercial developments and vacant land predominate along the remainder of the Duwamish River to Tukwila.

Table 1. Average monthly temperature and rainfall for two locations near the study area, 1978 (U.S. Environmental Data Service, 1978).

| | Kent<br>47°24'N, 122°15'W | | | | Seattle-Tacoma WSO AP<br>47°27'N, 122°18'W | | | |
|---|---|---|---|---|---|---|---|---|
| | Temperature | | Rainfall | | Temperature | | Rainfall | |
| Month | °C | °F | cm | in | °C | °F | cm | in |
| January | 6.5 | 43.7 | 14.40 | 5.67 | 6.9 | 44.4 | 10.92 | 4.30 |
| February | 7.5 | 45.5 | 9.12 | 3.59 | 7.8 | 46.0 | 9.12 | 3.59 |
| March | 8.8 | 47.9 | 7.09 | 2.79 | 9.2 | 48.6 | 6.17 | 2.43 |
| April | No Data | | | | 9.9 | 49.9 | 10.64 | 4.19 |
| May | 12.7 | 54.9 | 4.98 | 1.96 | 12.5 | 54.5 | 4.55 | 1.79 |
| June | 17.5 | 63.5 | 3.23 | 1.27 | 17.9 | 64.3 | 1.91 | 0.75 |
| July | 18.8 | 65.8 | 3.86 | 1.52 | 18.8 | 65.8 | 3.56 | 1.40 |
| August | 18.3 | 64.9 | 3.30 | 1.30 | 18.6 | 65.5 | 3.02 | 1.19 |
| September | 14.7 | 58.4 | 14.61 | 5.75 | 14.9 | 58.8 | 15.11 | 5.95 |
| October | 11.7 | 53.0 | 2.16 | 0.85 | 12.4 | 54.3 | 2.49 | 0.98 |
| November | No Data | | | | 5.1 | 41.2 | 15.37 | 6.05 |
| December | 2.4 | 36.3 | 4.72 | 1.86 | 3.1 | 37.5 | 3.48 | 1.37 |

The following data indicate land use in the lower Green River basin between Tukwila and Auburn in 1970:

| Uses | % land area |
|---|---|
| Residential | 11.5 |
| Commercial | 3.6 |
| Industrial | 1.9 |
| Streets | 15.3 |
| Open space | 33.5 |
| Agricultural (cultivated) | 2.3 |
| Agricultural (pasturage) | 3.0 |
| Forest | 27.5 |
| Inland water | 1.5 |

(Municipality of Metropolitan Seattle Water Quality Division, 1978.)

In addition, the river and its tributaries from Kent to river kilometer 104 provide excellent grounds for spawning and rearing fish. One of Washington's largest hatcheries is located on Big Soos Creek, a tributary entering the mainstream near river kilometer 54.

## 2.7 DESCRIPTION OF SITES OCCUPIED

The three stations occupied in this study depict three different riverine environments and correspond closely to Metro and USGS stations at which discharge, suspended solids, and other parameters of interest are monitored. Station 1 (Figure 1) is located near the junction of the Green Valley Highway and Auburn-Black Diamond Road--the first exit heading southeast from Auburn on Highway 18. This corresponds approximately to river kilometer 54 just upstream of the confluence with Big Soos Creek. This station represents a relatively pristine environment removed from known urban discharges and dominated by evergreen forest and ground vegetation.

Station 2 was originally located at the bridge on Interurban Avenue at the junction of Highway 1 and West Valley Road, a half kilometer upstream of the Renton Sewage Outfall. However, during the July 1978 occupation of this station, it was noted that the river slacked and flowed upstream as a result of tidal pumping, possibly contaminating this sample with sewage effluent. For the remaining two field excursions, this station (now designated 2B) was moved up the river approximately 5 kilometers to the bridge at 180th near its junction with West Valley Highway. Direction of flow remained constant at this point during subsequent samplings. This middle station serves as a monitor below the urban contributions of Auburn and Kent, yet immediately above the outfall such that the effect of the sewage effluent may be isolated.

Station 3 is located a half kilometer below the outfall at the bridge crossing into Fort Dent Park.

Latitudes and longitudes of all stations occupied are listed in Table 2. The sampling itinerary is presented in Table 3.

## 2.8 MATERIAL SOURCES

The Renton Metro Sewage Plant discharged an average of 38 mgd ($1.44 \times 10^5$ $m^3$/day) of effluent into the Green River in 1978 (Table 4). The suspended solids concentration of this effluent (Table 4) ranged from 7.9 mg/l in January to 23.0 mg/l in November with a mean monthly average of 12.5 mg/l (Municipality of Metropolitan Seattle, 1978b). The facility receives waste water from both residential and industrial sources. As much as 25% of the entering waste water may be industrial in origin (Archer, 1975). The influent is passed through a series of grit and settling tanks for removal of the large, suspended solids. The liquid is removed from the top of these tanks and proceeds to secondary treatment. At this point an activated sludge (a culture of micro-organisms) is added to the liquid to reduce organic matter. The bacteria are allowed to settle before the purified water is finally treated with chlorine gas and discharged. The quantity of chlorine which the Renton Metro plant can expell into the Green River is strictly regulated. Therefore, the effluent is dechlorinated (with $SO_2$) before final discharge. The Renton facility removes approximately 94% to 97% of the organic material in the influent (Archer, 1975).

The Green-Duwamish River has been the subject of many environmental impact studies (Stevens et al., 1975; $CH_2M$ Hill Inc., 1974; Municipality of Metropolitan Seattle Water Quality Division, 1978). Over the past few years most of the independent point sources of untreated waste have been routed to the Renton Metro Treatment Facility, the most recent being the Seattle Kent Highlands Landfill on October 4, 1978 (Mr. Richard Finger, Renton Sewage Treatment Plant, personal communication). Above Station 1 the Game Department Steelhead Hatchery and Fisheries Department Salmon Hatchery have permits to discard wastes in the Green River.

Table 2. Latitudes and longitudes of stations on the Green River and the Renton Metro Sewage Outfall.

| Station | Latitude | Longitude |
|---|---|---|
| 1 | 47° 17' 45" N | 122° 10' 30" W |
| 2 | 47° 27' 57" N | 122° 14' 50" W |
| 2B | 47° 26' 30" N | 122° 14' 43" W |
| Outfall | 47° 28' 06" N | 122° 14' 37" W |
| 3 | 47° 28' 05" N | 122° 14' 52" W |

Table 3. Itinerary of suspended sediment sampling.

| | Station 1 | Station 2(B) | Station 3 | Station 3R |
|---|---|---|---|---|
| July | July 18-19<br>1015 - 0600 | July 19-20<br>0930 - 0430 | July 20<br>0700 - 2200 | - |
| October | October 17-18<br>1145 - 0630 | October 18-19<br>1045 - 0615 | October 19-20<br>0945 - 0330 | October 20<br>0430 - 2145 |
| (Metro) | - | - | October 19-20<br>0730 - 0730 | - |
| December | December 21-22<br>1345 - 1200 | December 20-21<br>1015 - 0845 | December 18-19<br>1915 - 1145 | December 19-20<br>1300 - 0700 |
| (Metro) | December 21-22<br>1300 - 1100 | December 20-21<br>1000 - 0800 | December 18-20<br>1800 - 0600 | |

Table 4. Mean monthly discharge and suspended solids concentrations of the Renton Metro Sewage Effluent, 1978 (Municipality of Metropolitan Seattle, 1978b).

| | Discharge | | Suspended Solids |
|---|---|---|---|
| Month | $10^5$ $m^3$/day | mgd | mg/l |
| January | 1.62 | 42.75 | 7.9 |
| February | 1.55 | 40.91 | 10.1 |
| March | 1.46 | 38.58 | 8.5 |
| April | 1.49 | 39.35 | 9.5 |
| May | 1.40 | 36.87 | 9.1 |
| June | 1.34 | 35.30 | 20.1 |
| July | 1.29 | 34.11 | 9.7 |
| August | 1.29 | 34.12 | 12.3 |
| September | 1.42 | 37.55 | 12.8 |
| October | 1.32 | 34.98 | 11.1 |
| November | 1.55 | 40.82 | 23.0 |
| December | 1.53 | 40.38 | 16.2 |

# 3.0 METHODS

## 3.1 GENERAL STATEMENTS

Extreme precautions were taken while working with these environmentally low concentrations of hydrocarbons to decrease the risk of contamination. All solvents used were of nanograde quality. Gas chromatographic traces determined on reduced volumes of all solvents showed acceptably low levels of contaminants with the exception of methanol which was redistilled prior to use. Glassware, collection vessels, and stainless-steel hardware were washed in a strong dishwashing detergent, rinsed amply with deionized, filtered water, and oven dried and solvent rinsed before use. A Cahn Model 4700 Electrobalance was used for weighing filters, standards, and extract aliquots. A Sartorius Model 3716 top-loading balance was used for thimble and sediments weighings.

## 3.2 FIELD SAMPLING

The mobile field unit consisted of a covered truck 7 or 8 meters in length and a small trailer. The former housed the centrifuge, intake manifold, filtering apparatus, ice chest, and lab bench while the latter contained a 6-KW diesel generator and its fuel supply. The trailor was located at least 35 meters downwind from the truck to minimize contamination from exhaust gases.

Each station was occupied for 18 hours, during which river water was retrieved with a Peabody Barnes submersible water pump located midchannel and middepth. Water was directed through an intake manifold and prefiltered through two nylon screens, the smallest being 100 microns in mesh size. Flow rates and accumulated volume were monitored with a flow meter, flow controller, and pressure gauge. Illustration 1 shows the centrifuge, manifold, and flow monitoring system. To reduce contamination the pump, hose, manifold, and tubing were flushed with ambient water at each station for 30 minutes before the centrifuge was engaged.

Approximately every 4 hours, water was diverted at the manifold through Selas® silver filters, and Gelman® glass fiber filters for C/N analyses and suspended hydrocarbon analyses, respectively.

Sediment was recovered continuously with a Sorvall Model SS-3 high speed centrifuge. Sedimentation was accomplished at approximately

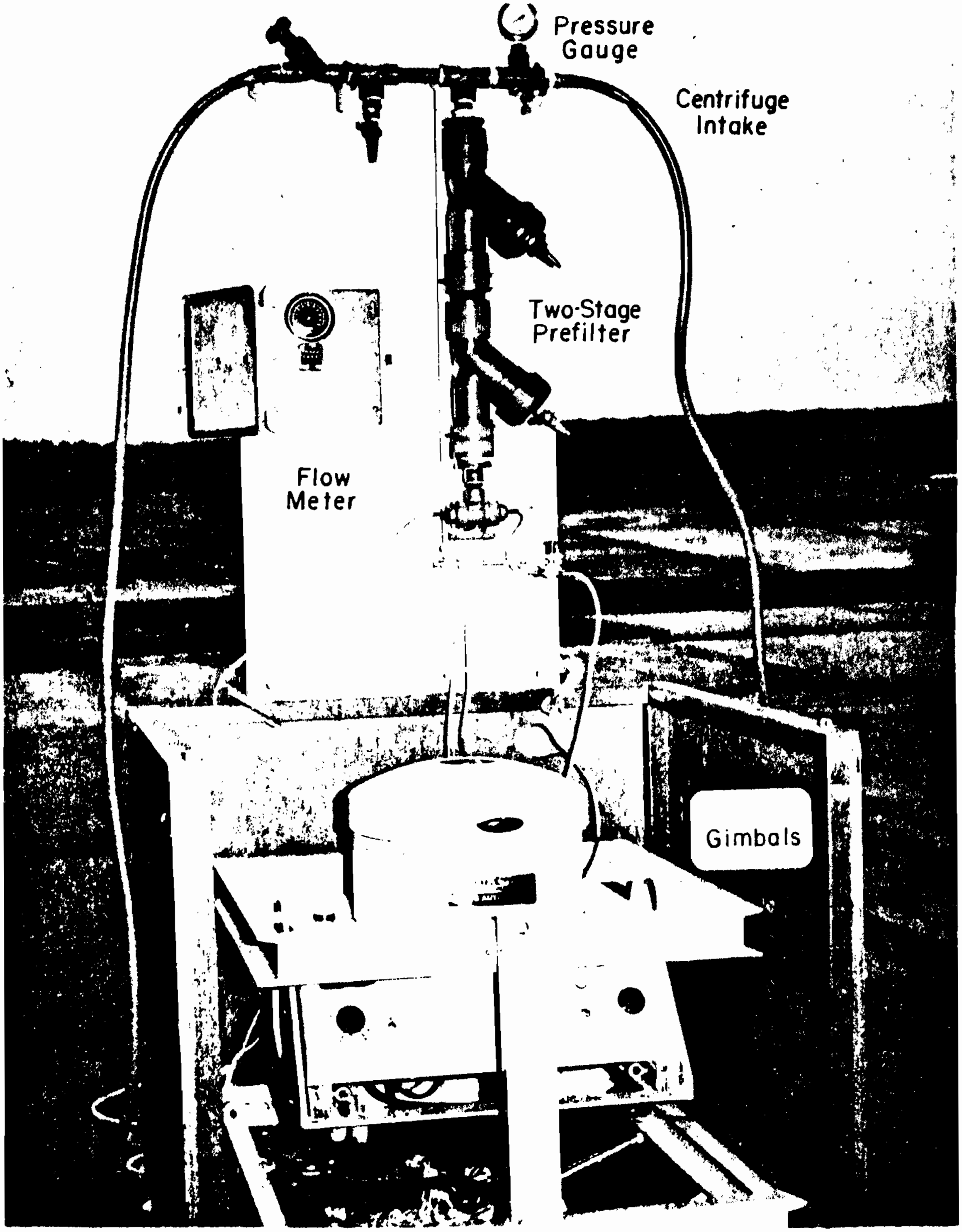

Illustration 1. Suspended matter recovery system. Suspended solids are pumped to the intake manifold and passed through a two-stage prefilter (dia ≧ 100 μm). Flow rate and accumulated volume through the centrifuge are monitored electronically. The centrifuge is shown mounted in gimbals for use at sea.

30,000 gravitational units (15,000 RPM) with supernatant being exhausted at the rate of 400-500 ml/min.

In October 1980, two years after the conclusion of this study, the centrifuge efficiency was tested at Station 3. Known volumes of centrifuge influent and effluent were filtered through 47-mm 0.4μm Nuclepore® filters. Centrifuge efficiencies and tidal variations are recorded below:

October 29-30, 1980

| Tides* | | Centrifuge Efficiency | |
|---|---|---|---|
| Time | Height (m) | Time | % |
| 1536 | 1.98 | 1700 | 89 |
| 2024 | 2.74 | 2100 | 79 |
| 0325 | 0.12 | 0100 | 63 |
| 1104 | 3.51 | 0500 | 92 |
| | | 0900 | 75 |
| | | 1300 | 68 |
| | | | $\bar{x}$ = 78± 11 |

* (U.S. Dept. of Commerce, 1980)

River flow at Station 3 is influenced considerably by tidal pumping in Elliott Bay. Over a 24-hour period, efficiencies varied from 63% to 92%. Highest efficiencies occurred close to periods of low tide. At this time, river flow is swiftest and larger particulates (more readily recovered by the centrifuge than fine particulates) are probably in suspension. At high tide river flow is reduced and often stagnant. Larger particles settle out and smaller particulates (possibly too buoyant to be recovered effectively by the centrifuge) comprise the bulk of the suspended load. At Station 3 the average recovery of particles greater than 0.4 μm was 78% ± 11%. This represents the most variable environment of the three stations since it is below the outfall (a concentrated source of particulates and possibly colloidal organics) and readily affected by tidal pumping.

Suspended matter was collected in eight 50-ml stainless-steel tubes. At the termination of sampling, excess water was decanted from each tube and the sediment was scraped into a sample jar and placed in an ice chest. During the July sampling, only regular ice was employed, keeping samples cool but not frozen. Dry ice was used during the October and December field trips and samples were frozen shortly after being recovered.

## 3.3 FILTRATION PROCEDURES

### 3.3.1 C/N Analysis

Prior to sampling, the 0.45 μm Selas® silver filters, 25 mm in diameter, were combusted in a muffle furnace at 400°C for 4 hours, cooled in a dessicator, weighed, and stored in polystyrene petri dishes. In the field a glass filtration system and vacuum pump were employed for the collection of C/N samples. Known volumes of water were also vacuum filtered through preweighed Nuclepore® filters (47 mm in diameter, 0.4 μm pore size) to determine the mass of suspended material retained by the silver filters.

Upon return to the laboratory, the silver filters were dessicated, weighed, and analyzed by the micro-Dumas combustion method (Sharp, 1974) using a Hewlett-Packard model 185B C-H-N analyzer. Total carbon and nitrogen were calculated based on combustion of known weights of NBS acetanilide standard. Table A-3 shows the analytical precision of the method based on standards run with each set of samples. This precision, based on the ratio of one standard deviation to the mean for all weights listed, was 12% for nitrogen and 9% for carbon.

Replicate filters were not taken in this study. However, replicates were filtered during a cruise in Cook Inlet, AK, and analyzed by the same technique and identical C-H-N analyzer. The average sampling precision was 20% for carbon and 15% for nitrogen (Gary Massoth, Oceanographer, NOAA/PMEL, personal communication; see Table A-4).

### 3.3.2 Filtration Procedures for Recovery of Hydrocarbons

Gelman® glass fiber filters, 47 mm, type A-E (1.0 μm nominal pore size with liquids) were prepared by Soxhlet extraction for 48 hours in a 65% methylene chloride/35% methanol solution with a solvent change after 24 hours. Filters were subsequently oven dried and stored in cleaned glass jars. In the field during the July sampling these filters were enclosed in solvent-rinsed plastic holders. Suspended matter was recovered by pressure filtration (14-20 psi) directly from the manifold. Filtered water was collected in a graduated cylinder for volume measurement. In October and December, water was vacuum filtered in an all-glass system. The volume of water filtered, together with the TSM concentration (determined from centrifuge data), was used to calculate the amount of sediment collected on each filter. Filters were stored frozen in glass petri dishes pending analyses by the methods described in the laboratory methods section below.

## 3.4 METRO EFFLUENT SAMPLING

Metro sewage effluent samples were taken concurrently with the October and December field excursions. One-gallon, glass reagent bottles, formerly containing nanograde methylene chloride, were delivered to the Renton Metro Sewage Treatment Plant. In October, 4 g mercuric chloride and 2 g sodium azide were added to the sample to retard bacterial growth. The four December samples each contained approximately 1.5 g mercuric chloride. Each Metro effluent sample totaled about 3200 ml and was comprised of 200- to 300-ml aliquots of treated effluent withdrawn every 2 hours. These samples were vacuum filtered through 4 to 8 Gelman® glass fiber filters which were then frozen. The filtrate in 600-ml aliquots was poured into a one-liter glass separatory funnel and extracted with two 60-ml and one 30-ml portions of methylene chloride. A total of 150 µl of recovery standard containing 5.93 ng/µl 1,3,5 tri-isopropyl benzene and 5.64 ng/µl n-decylcyclohexane was added to each sample during the extraction. The extracts were stored in one-liter, glass-stoppered bottles in the ice chest.

The suspended solid concentrations of the METRO effluent samples used in later budget calculations (chapter 5) are measured daily by METRO. Reeve Angel glass fiber filters (type 934 A-H, 2.1 cm in diameter, .75 µm to 1.25 µm nominal pore size) are combusted at 550°C, cooled, and weighed. Each filter is placed in a Gooch crucible and a known volume of effluent is passed through it. The filter is then dried, reweighed, and the suspended particulate concentration is calculated from the weight change and the volume filtered.

## 3.5 LABORATORY METHODS FOR HYDROCARBON ISOLATION AND IDENTIFICATION

The extraction of hydrocarbons from a sediment matrix has long been a subject of controversy with methods running the entire spectrum from sonication and tumbling to the more traditional Soxhlet extraction.

Rohrback and Reed (1975), in their comparison of various methodologies, found that Soxhlet extraction released the greatest amount of lipid material, thus this method was used in this study. The remaining procedures for sample clean-up, separation, and analysis follow those developed by the Northwest and Alaska Fisheries Center (MacLeod et al., 1976) with some minor changes. The flow diagram shown in Figure 4 outlines the extraction, separation, and concentration procedures adopted.

### 3.5.1 Extraction

Whatman® cellulose thimbles (25 x 80 mm) were used to contain the sediment in the Soxhlet extractors. The entire Soxhlet apparatus with thimbles was preextracted by cycling them for 48 hours in approximately 80 ml of a 65% methylene chloride/35% methanol mixture. Thimbles were then oven dried and weighed, and the thawed sediment was transferred into them. Fresh solvent and 150 μl of recovery standard were added to the boiling flasks before Soxhlet extraction resumed. After 24 hours the sediment was agitated with a stainless-steel spatula, and fresh solvent was placed in the boiling flask. Extraction continued for another 24 hours before thimbles were oven dried and weighed for the calculation of sediment dry weight.

The relative efficiency of this method was demonstrated by extracting one sediment sample for an additional 24 hours with fresh solvent. Approximately 97% of the extractable hydrocarbons were recovered in the original 48-hour period.

Solvent extracts were combined in a 250-ml separatory funnel to which 100 ml of distilled, deionized, filtered water was added to remove methanol. The two-phase system was agitated for 2 to 3 minutes and allowed to separate before the organic layer was drained and the water was back-extracted twice with 20 ml each of methylene chloride. The organic layer was returned to the separatory funnel and the entire procedure repeated. If the sample still appeared to contain water, anhydrous sodium sulfate, preextracted with methylene chloride, was added to the flask overnight. Such samples were then either carefully decanted or filtered through a glass-wool plug before proceeding to the concentration step.

SAMPLE

↓

SOXHLET EXTRACTION

(48 hrs; 65% $CH_2Cl_2$/35% $CH_3OH$)

↓

ELIMINATION OF METHANOL

(distilled water wash)

↓

CONCENTRATION → MICROGRAVIMETRY

(heat) (total extractables)

↓

CLEAN-UP COLUMN CHROMATOGRAPHY

($CH_2Cl_2$ on silica gel)

↓

SEPARATION COLUMN CHROMATOGRAPHY

(petroleum ether, $CH_2Cl_2$ on silica gel)

SATURATED HYDROCARBONS

↓

CONCENTRATION → MICROGRAVIMETRY

(heat, $N_2$)

↓

GAS CHROMATOGRAPHY

↓

(glass capillary, SP-2100)

UNSATURATED HYDROCARBONS

↓

CONCENTRATION → MICROGRAVIMETRY

(heat, $N_2$)

↓

GAS CHROMATOGRAPHY

↓

(glass capillary, SE-54)

Figure 4. Flow diagram of procedures employed to isolate and identify hydrocarbons associated with suspended solids.

The extracts, in round-bottomed flasks, were fitted with Snyder® distillation columns, placed in a hot water bath, and reduced to approximately 15 ml. Extracts were then transferred to 25-ml Kuderna-Danish concentrator tubes (Kontes®) and reduced in a tube heater to 1-2 ml. Samples were transferred to 5-ml volumetric flasks and brought to volume for microgravimetry.

### 3.5.2 Microgravimetry

Aliquots varying between 20 µl and 90 µl were transferred to preweighed aluminum pans with Hamilton syringes. Variations in volumes used depended upon whether the more concentrated extracts of sediment or the less concentrated extracts from filters were being weighed. These aliquots were allowed to evaporate for 10 to 15 minutes, previously determined to be the interval necessary to evaporate the solvent and attain a nearly constant weight. Triplicates of each sample showed an average relative standard deviation of 7.6%.

### 3.5.3 Liquid Chromatography

#### A. Silica Gel

The total organic extract was eluted through a clean-up column designed to remove residual water and interfering pigments. Twenty milliliters of silica gel, 100- to 200-mesh size was combined with 25 ml of methylene chloride. The slurry was swirled and permitted to degas for 5 minutes before quickly being transferred to a liquid chromatographic column. When the settling front was one centimeter high, the stopcock was opened, delivering solvent at 1 to 2 drops per second. Tapping the column aided the settling process. Solvent-washed sand (1.7 g) was added to the top of the column and two 25-ml rinses of methylene chloride were eluted before the sample was chromatographed. Two 25-ml and one 10-ml aliquots were used to elute the sample. The eluate was reduced to 1-2 ml as previously described. Two milliliters of hexane were added, and the solvent was concentrated again to approximately 1 ml in preparation for separation chromatography.

Columns were poured as before but with 15 ml of silica gel and 4.5 grams of activated copper on top of the sand to remove elemental sulfur and reduced sulfur compounds. The copper was washed with hydrochloric acid and rinsed first with acetone, then with petroleum ether. The column was flushed with 50 ml of methylene chloride followed by 40 ml of petroleum ether.

The sample was applied to the column and eluted with 15 ml of petroleum ether, 5 ml of 20% methylene chloride in petroleum ether, and finally 23 ml of methylene chloride. The saturates eluted within the first 18-ml fraction and the unsaturates were contained in the second 25-ml cut. These were reduced to 1-ml volumes, transferred to 2-ml vials and "blown down" with purified $N_2$ to approximately 100 μl. One hundred microliters of GC internal standard, hexamethylbenzene (5 ng/μl) in iso-octane was added, and the sample was again reduced to approximately 100 μl before the final capping and refrigeration, pending gas chromatographic analysis.

Solvent blanks were run concurrently with each set of Soxhlet extractions. These blanks were corrected for recovery efficiency and subtracted from sediment samples. Corrected blanks comprised an average of 4% of the individual n-alkanes in the centrifuge sediment sample. Filter blanks are discussed in appendix C.

### B. Sephadex® Chromatography

Large quantities of hydrocarbons suspected to be nonaromatics were interfering with GC identification of aromatic compounds. For this reason, a few samples were chromatographed on Sephadex®. Techniques employed follow those of Prahl and Carpenter (1979). Samples were transferred to the top of a Sephadex® LH-20 column (20 g, 2.1 cm i.d.) and eluted with 50% benzene in methanol. The initial 20 ml was discarded, then a second fraction (35 ml) containing the unsaturates and a final cut (45 ml) containing aromatics were collected. Samples were concentrated by rotary evaporation, transferred to small vials and reduced further by evaporation under $N_2$. Fifty microliters of the GC internal standard, hexamethylbenzene (5 ng/μl) in iso-octane, were added to each of these samples before they were reduced again under $N_2$.

### 3.5.4 Gas Chromatography

Saturate hydrocarbons were analyzed by a Hewlett Packard model 5730A gas chromatograph interfaced to a Hewlett Packard model 3385 integrator. Component separation was accomplished by splitless injection on an SP-2100 WCOT glass capillary column, 30 m x 0.25 mm i.d. (J & W Scientific, Inc.) equipped with a flame ionization detector. Temperature was programmed from 70°C to 270°C at 4°C/min after an initial 4-minute hold. Approximately 2 μl of each sample (in iso-octane) was injected manually.

A standard (Table 5) containing 25 aliphatic compounds in iso-octane solvent was injected daily or more often when conditions appeared unstable. A chromatogram of this standard (Alk-25) is presented in Figure 5. Concentrations in samples were calculated using response factors determined from the composite standard. These were corrected for differences in detector behavior and injection technique by the use of internal standard, hexamethylbenzene. The following equation used by the microprocessor shows the computation:

$$\text{Mass }(X)_{sa} = \frac{\text{Area }(X)_{sa}\left(\dfrac{\text{Mass X}}{\text{Area X}}\right)_{std}}{\text{Area }(\text{ISTD})_{sa}\left(\dfrac{\text{Mass ISTD}}{\text{Area ISTD}}\right)_{std}} \times \text{Mass }(\text{ISTD})_{sa} \times \text{D.F.}$$

where:

X = compound of interest
sa = sample
std = standard
ISTD = internal standard
D.F. = dilution factor, incorporating recovery and sediment weight

Table 5 also reports the precision of the gas chromatographic analysis calculated from triplicate injections (on different dates) of the aliphatic standard. Relative standard deviations range from 5.2% to 8.1%.

The chromatographic "hump," referred to as the unresolved complex mixture (UCM) in saturate samples, is defined here as the area enclosed by the baseline and a tangential skim at the base of each peak from $C_{14}$ to $C_{32}$. The UCM area was measured by dividing the "hump" into 20 slices, digitizing the baseline and tangential heights at each point, and applying Simpson's rule, (Hornbeck, 1975). A response factor relating the Simpson's rule area to the integrator area was determined by applying the digitization method to well-shaped standard peaks of known

Table 5. Compounds comprising the alkane standard, concentrations of these components, and the precision of three nonconsecutive injections on the gas chromatograph.

| Component | Concentration (ng/μl) | Mean Response Factor [$10^{-3}$ (ng/area)] | σ | $(\sigma/\bar{x}) \times 100$ (%) |
|---|---|---|---|---|
| $C_{12}$ dodecane | 5.36 | 1.062 | .086 | 8.1 |
| $C_{13}$ tridecane | 5.30 | 0.990 | .076 | 7.6 |
| $C_{14}$ tetradecane | 5.66 | 1.009 | .080 | 7.9 |
| hexamethylbenzene (HMB) | 5.00 | 1.019 | .083 | 8.1 |
| $C_{15}$ pentadecane | 5.38 | 1.007 | .072 | 7.1 |
| $C_{16}$ hexadecane | 5.42 | 1.017 | .068 | 6.7 |
| n-decyl cyclohexane (DCH) | 5.64 | 0.947 | .064 | 6.8 |
| $C_{17}$ heptadecane | 5.44 | 0.981 | .065 | 6.6 |
| pristane | 5.38 | 1.010 | .066 | 6.6 |
| $C_{18}$ octadecane | 5.36 | 0.929 | .061 | 6.6 |
| phytane | 5.38 | 0.976 | .061 | 6.3 |
| $C_{19}$ nonadecane | 5.44 | 1.006 | .059 | 5.8 |
| $C_{20}$ eicosane | 5.04 | 0.985 | .054 | 5.5 |
| $C_{21}$ heneicosane | 5.03 | 0.977 | .053 | 5.4 |
| $C_{22}$ docosane | 5.00 | 0.978 | .051 | 5.2 |
| $C_{23}$ tricosane | 5.02 | 0.966 | .053 | 5.5 |
| $C_{24}$ tetracosane | 5.01 | 0.993 | .053 | 5.4 |
| $C_{25}$ pentacosane | 5.13 | 1.017 | .056 | 5.6 |
| $C_{26}$ hexacosane | 5.01 | 1.041 | .060 | 5.8 |
| $C_{27}$ heptacosane | 5.02 | 1.057 | .062 | 5.9 |
| $C_{28}$ octacosane | 8.02 | 1.073 | .070 | 6.5 |
| $C_{30}$ triacontane | 5.03 | 1.148 | .075 | 6.5 |
| $C_{31}$ hentriacontane | 5.21 | 1.446 | .087 | 5.9 |
| $C_{32}$ dotriacontane | 5.39 | 1.347 | .093 | 6.9 |

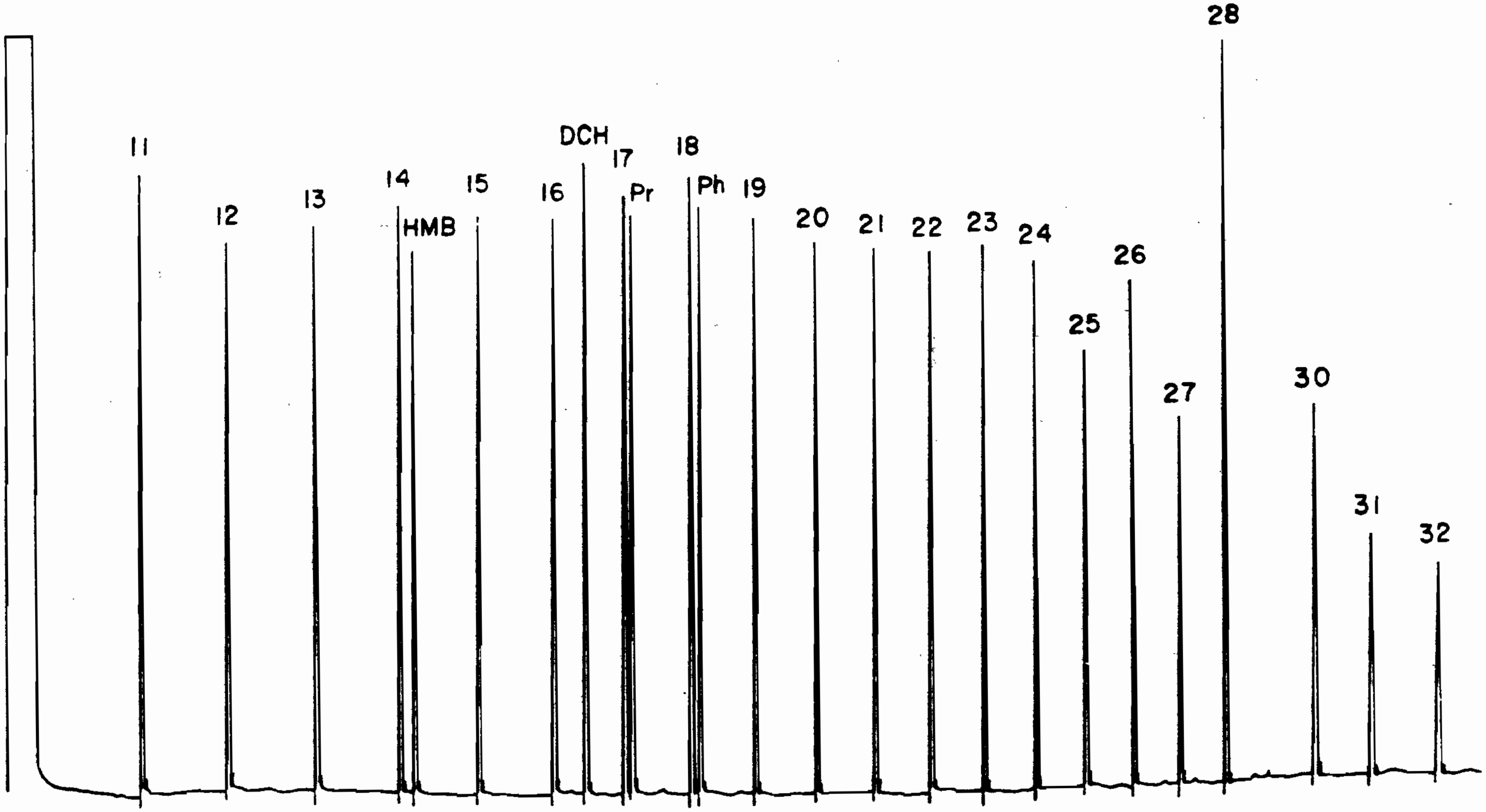

Figure 5. Gas chromatogram of the aliphatic standard. Compounds and their concentrations are listed in Table 3-1. Chromatographic conditions are given in section 3.5.4.

areas. The weight of hydrocarbons comprising the UCM was calculated using an average response factor (weight/area) from standards of n-alkanes covering the UCM range.

The unsaturate fractions (in iso-octane) were injected (splitless) into a Hewlett Packard 5840A gas chromatograph equipped with an SE-54 WCOT glass capillary column, 30 m x 0.25 mm i.d. (J & W Scientific, Inc.). A standard containing 21 aromatic compounds in iso-octane was used for identification and quantification (Table 6). A chromatogram of this standard is presented in Figure 6. Again, the analytical precision of the instrument is reported with standard deviations relative to the mean ranging from 2.2% to 7.4% (Table 6).

Compound concentrations were corrected for evaporative and other losses using a combination of recovery standards spiked in each sample (n-decylcyclahexane in the aliphatic fraction; tri-isopropylbenzene in the aromatic fraction) and an alkane recovery curve determined in the following manner. A representative sediment sample and the same sediment spiked with the alkane standard ($C_{11}$-$C_{32}$, pristane, phytane) were concurrently carried through the extraction procedure. Recoveries were determined by difference, and steadily increased from 40% to 90% for the compounds $C_{13}$ through phytane, and averaged 90-95% for compounds $C_{19}$-$C_{32}$. Alkane recovery efficiencies were applied to aromatic compounds with similar boiling points.

### 3.5.5 GC-MS Analysis

Identity verifications and additional data on individual compounds were obtained by electron impact GC-MS analyses of selected samples. An HP 5992 GC-MS system equipped with an SP-2100 glass capillary column for saturate fractions and an SE-54 glass capillary column for the unsaturate fractions was used.

Three aromatic samples were selected for GC-MS analysis at the Institute of Geophysics and Planetary Physics at UCLA. The samples were run on a Finnigan model 4000 GC-MS in the electron impact mode. The instrument was equipped with an INCOS Data system and an OV-101 WCOT glass capillary column (30 m).

Table 6. Compounds comprising the aromatic standard, concentrations of these components, and the precision of three injections on the gas chromatograph.

| Component | Concentration | Mean Response Factor | σ | $(\sigma/\bar{x})$ x 100 |
|---|---|---|---|---|
| | (ng/µl) | [$10^{-3}$ (ng/area)] | | (%) |
| propyl benzene (PRB) | 24.42 | 1.933 | .063 | 3.2 |
| indan (IND) | 19.29 | 1.886 | .042 | 2.2 |
| naphthalene (NPH) | 20.24 | 1.812 | .049 | 2.7 |
| benzothiophene (BTP) | 24.23 | 2.958 | .076 | 2.6 |
| 1-methyl naphthalene (IMN) | 20.50 | 1.885 | .054 | 2.9 |
| biphenyl (BPH) | 20.54 | 1.819 | .054 | 3.0 |
| 2,6 dimethyl naphthalene (DMN) | 20.10 | 1.853 | .059 | 3.2 |
| hexamethylbenzene (HMB) | 19.99 | 1.869 | .049 | 2.6 |
| fluorene (FLU) | 20.14 | 1.892 | .063 | 3.3 |
| dibenzothiophene (DBT) | 20.66 | 2.189 | .072 | 3.3 |
| phenanthrene (PHN) | 20.00 | 1.821 | .073 | 4.0 |
| anthracene (ANT) | 20.26 | 2.065 | .140 | 6.8 |
| 2 methyl anthracene (2MA) | 20.49 | 2.052 | .145 | 7.1 |
| fluoranthene (FLA) | 20.02 | 1.839 | .066 | 3.6 |
| pyrene (PYR) | 19.92 | 1.846 | .054 | 2.9 |
| chrysene (CHR) | 10.28 | 3.246 | .206 | 6.3 |
| benz(e)pyrene (BEP) | 20.14 | 2.053 | .139 | 6.8 |
| benz(a)pyrene (BAP) | 20.17 | 2.225 | .164 | 7.4 |
| perylene (PER) | 37.44 | 1.920 | .141 | 7.3 |
| o-phenylene pyrene (OPP) | 16.48 | 2.372 | .174 | 7.4 |
| benz(g,h,i)perylene (BGP) | 23.68 | 2.454 | .092 | 3.8 |

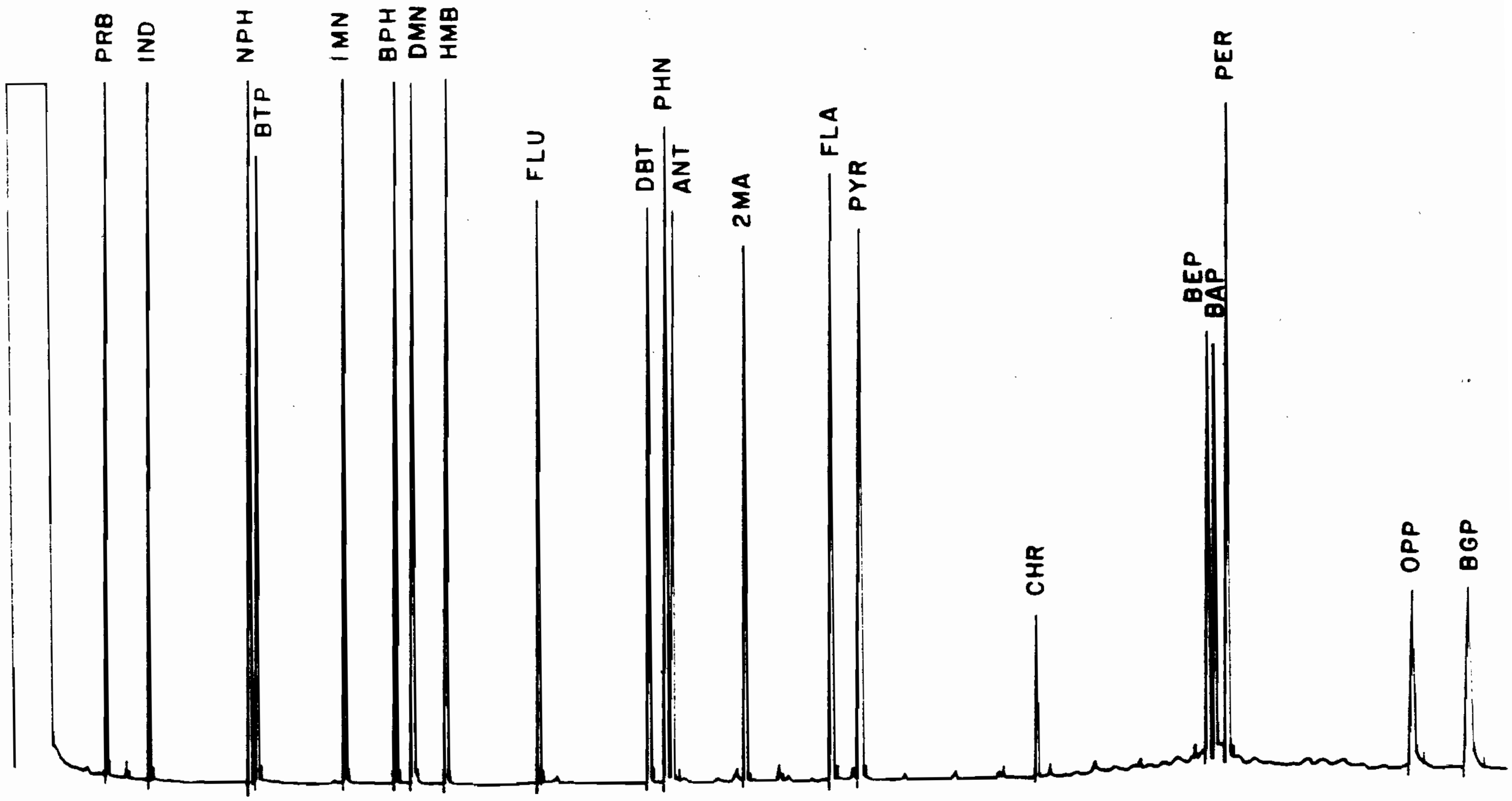

Figure 6. Gas chromatogram of the aromatic standard. Compounds and their concentrations are listed in Table 3-2. Chromatographic conditions are described in section 3.5.4

## 3.6 ANALYTICAL PRECISION AND SAMPLING VARIABILITY

In December, Station 3 was occupied for 36 hours to recover enough sediment for triplicate analyses. The sediment was homogenized and divided into 3 aliquots for analyses. The aliphatic-hydrocarbon concentrations determined in these replicates, their means, standard deviations, and percent deviations from the mean are reported in Table 7. The mean relative standard deviation for all compounds was 9%; the range extends from 19% ($C_{16}$) to 2% ($C_{22}$ and $C_{32}$). The low-molecular-weight hydrocarbons ($C_{13}$ to $C_{20}$) showed significantly greater variabilities ($\sigma/\bar{x}$ = 13%) than the heavy hydrocarbons ($C_{21}$ to $C_{33}$ ; $\sigma/\bar{x}$ = 7%), presumably due to their higher volatility.

Station 3 was occupied for two consecutive 18-hour periods in October. Although these duplicates actually represent river variability, they are the closest measure of sampling variability determined in this study. The duplicate values, their means, and the ratios of their differences to their means are listed in Table 8. The difference between the values obtained at Stations 3 and 3R divided by their mean averaged 24% for all the aliphatics. The variability of the volatiles ($C_{13}$ to $C_{20}$; $\Delta/\bar{x}$ = 33%) is markedly higher than that of the heavier components ($C_{21}$ to $C_{32}$; $\Delta/\bar{x}$ = 16%). Hydrocarbons containing an even number of carbon atoms between $C_{22}$ and $C_{32}$ exhibited a significantly greater average variability (25%) than the odd-carbon compounds within the same range (7%). This is in part a result of the lower concentrations of the even-carbon compounds from $C_{22}$ to $C_{32}$. In addition, Station 3 is below the outfall which appears to be a major source of the heavy, even-carbon alkanes (chapter 4). Daily variation in the quantity and characteristics of the effluent is probably reflected in the larger deviations of the even-carbon compounds. The heavy, odd paraffins are far more abundant than the even-carbon alkanes, and the major sources of these odd-carbon compounds, terrestrial plant waxes, are encountered before the outfall is reached. For this reason the heavy, odd hydrocarbons do not fluctuate as greatly relative to the even-carbon compounds. The sampling variability listed in Table 8 represents an upper limit since Station 3, immediately below the outfall, is the most variable site among the stations selected for study.

Table 7. Analytical reproducibility of the saturate fraction based upon triplicate analyses of a single homogenized sediment sample retrieved in December 1978 at Station 3.

| Alkane | R-1 (ng/g) | R-2 (ng/g) | R-3 (ng/g) | $\bar{x}$ (ng/g) | $\sigma$ (ng/g) | $(\sigma/\bar{x}) \times 100$ (%) |
|---|---|---|---|---|---|---|
| 13 | 1020 | 1340 | 1340 | 1230 | 190 | 15 |
| 14 | 1380 | 1570 | 1610 | 1580 | 130 | 8 |
| 15 | 3050 | 2340 | 2430 | 2600 | 390 | 15 |
| 16 | 3340 | 2340 | 2550 | 2740 | 530 | 19 |
| 17 | 3960 | 2840 | 3120 | 3310 | 580 | 18 |
| pr | 2110 | 2200 | 2430 | 2250 | 170 | 7 |
| 18 | 2290 | 1810 | 1990 | 2030 | 240 | 12 |
| phy | 1300 | 1010 | 1460 | 1250 | 230 | 18 |
| 19 | 1280 | 1110 | 1210 | 1200 | 80 | 7 |
| 20 | 950 | 1050 | 1130 | 1040 | 90 | 9 |
| 21 | 730 | 740 | 800 | 760 | 30 | 5 |
| 22 | 600 | 620 | 630 | 610 | 10 | 2 |
| 23 | 1480 | 1220 | 1430 | 1380 | 140 | 10 |
| 24 | 800 | 770 | 820 | 800 | 30 | 3 |
| 25 | 6700 | 5560 | 6190 | 6150 | 580 | 9 |
| 26 | 1230 | 1050 | 1170 | 1150 | 90 | 8 |
| 27 | 7020 | 6350 | 6990 | 6780 | 380 | 6 |
| 28 | 1120 | 1140 | 1400 | 1220 | 150 | 13 |
| 29 | 7130 | 6370 | 6740 | 6740 | 380 | 6 |
| 30 | 1090 | 990 | 900 | 990 | 90 | 9 |
| 31 | 6710 | 6080 | 6490 | 6430 | 320 | 5 |
| 32 | 530 | 720 | 680 | 640 | 100 | 2 |
| Sample Weight (g) | 1.70 | 1.88 | 1.68 | | | |

Table 8. Approximation of suspended hydrocarbon sampling variability based upon two consecutive occupations of Station 3 in October 1978.

| Alkanes | R-1 (ng/g) | R-2 (ng/g) | $\bar{x}$ (ng/g) | $\Delta$ (ng/g) | $(\Delta/\bar{x}) \times 100$ (%) |
|---|---|---|---|---|---|
| 13 | 3240 | 5420 | 4330 | 2180 | 50 |
| 14 | 4660 | 6860 | 5760 | 2200 | 38 |
| 15 | 14230 | 19200 | 16710 | 4970 | 30 |
| 16 | 3710 | 5620 | 4670 | 1910 | 41 |
| 17 | 10280 | 12450 | 11360 | 2170 | 19 |
| pr | 2890 | 3540 | 3210 | 650 | 20 |
| 18 | 1480 | 2710 | 2090 | 1230 | 59 |
| phy | 2300 | 2180 | 2240 | 110 | 5 |
| 19 | 1340 | 2050 | 1700 | 720 | 42 |
| 20 | 1410 | 1860 | 1640 | 460 | 28 |
| 21 | 1280 | 1150 | 1220 | 130 | 11 |
| 22 | 960 | 1300 | 1130 | 340 | 30 |
| 23 | 1690 | 1570 | 1630 | 130 | 8 |
| 24 | 1010 | 1060 | 1040 | 50 | 5 |
| 25 | 3320 | 3290 | 3300 | 30 | 1 |
| 26 | 1390 | 1790 | 1590 | 400 | 25 |
| 27 | 5420 | 5610 | 5510 | 190 | 3 |
| 28 | 1350 | 1930 | 1640 | 580 | 34 |
| 29 | 5490 | 6120 | 5800 | 630 | 11 |
| 30 | 1170 | 1720 | 1440 | 550 | 38 |
| 31 | 3440 | 3610 | 3530 | 170 | 5 |
| 32 | 940 | 1090 | 1010 | 160 | 15 |

# 4.0 AREAL DISTRIBUTION OF HYDROCARBONS, RESULTS, AND DISCUSSION

## 4.1 JULY 1978

Concentrations and compositional parameters of suspended hydrocarbons retrieved at the three stations occupied in July are summarized in Table 9. Concentrations of total suspended matter (TSM) were determined by dividing the centrifuge sample weight by the volume of water centrifuged. TSM and total particulate organic carbon (TPC) were negatively correlated, spacially. Station 1 showed the lowest TSM value (2.6 mg/l) and the highest carbon content (8.4%), whereas Stations 2 and 3 exhibited higher suspended loads, averaging 4.6 mg/l and lower carbon values, averaging 6.0%.

### 4.1.1 Total Extractables and Aliphatics

Total solvent extractables ranged from 8.4 mg/g dry sediment at Station 1 to 28.6 mg/g at Station 3. These values fall within the range reported by Schultz and Quinn (1977) for Narragansett Bay suspended matter (1.5 to 34.8 mg/g at the most pristine and contaminated stations, respectively).

Abundance of hydrocarbons in the alkane fraction varied between 0.25 mg/g at Station 1 and 1.09 mg/g at Station 3. These values are higher than those reported for surface sediment in the Gulf of Mexico (0.1-7.5 μg/g; Gearing et al., 1976), the Northwest Atlantic slope and shelf (37 μg/g; Farrington and Tripp, 1977), Narragansett Bay (173 μg/g; Wade and Quinn, 1979), and Puget Sound (4-350 μg/g; Barrick et al., 1980). Values measured in this study are within concentrations determined in sediment from the New York Bight, an area highly contaminated by petroleum hydrocarbons (25-1800 μg/g; Farrington and Tripp, 1977). Total aliphatic concentrations in surface sediments of Lake Washington, a local, freshwater environment near Seattle, varied from 0.28 to 1.70 mg/g. Stations located near the Cedar and Sammamish Rivers in the lake showed the lowest concentrations ranging from 0.28 to 0.55 mg/g (Wakeham, 1976).

Table 9. Concentrations and compositional parameters of hydrocarbons associated with suspended matter retrieved from the Green River by centrifugation in July 1978.

| | Station 1 | Station 2 | Station 3 |
|---|---|---|---|
| TSM* (mg/l) | 2.6 | 5.1 | 4.1 |
| TPC (wt.%) | 8.5 ± 1.7 | 5.4 ± 3.2 | 6.6 ± 3.4 |
| Total Extractables (mg/g) | 8.4 ± 0.3 | 12.7 ± 0.8 | 28.7 ± 1.5 |
| Total Saturates (mg/g) | 0.25 | 0.56 | 1.09 |
| UCM (ug/g)<br>(ug/g C) | 109<br>(1280) | 176<br>(3250) | 380<br>(5750) |
| $\sum_{12}^{32}$ n-alkanes (ug/g) | 73.2 | 83.6 | 77.3 |
| $\sum_{13}^{20}$ n-alk/ $\sum_{21}^{32}$ n-alk | 0.28 | 1.70 | 1.39 |
| $CPI_{14-20}$ | 18.2 | 19.8 | 11.1 |
| $CPI_{20-32}$ | 10.9 | 7.0 | 3.9 |
| $(C_{15} + C_{17})/2\ C_{16}$ | 25.5 | 19.4 | 11.9 |
| Phytane/$C_{17}$ | 0.01 | 0.01 | 0.08 |
| Pristane/$C_{17}$ | 0.02 | 0.02 | 0.10 |
| Pristane/Phytane | 1.7 | 1.9 | 1.3 |

* Calculated from the centrifuge sample weight and volume of water centrifuged.

### 4.1.2 Unresolved Hydrocarbons

The unresolved complex mixture (UCM), containing cycloalkanes, naphthenoaromatics, and other unresolved compounds was estimated in each sample. Typical chromatograms of the saturate hydrocarbon fractions at Stations 1, 2, and 3 are presented in Figure 7. The UCM is unimodal and reaches a maximum at $C_{27}$. Concentrations increase from 109 μg/g (1280 μg/g carbon (C)) at Station 1 to 380 μg/g (5750 μg/g C) at Station 3. Despite the differences in concentrations, the UCM comprises 39% of the total gravimetric saturates at Station 1, 30% at Station 2, and 34% at Station 3. Values at Stations 2 and 3 are on the order of those measured in post-1955-dated sediments of Puget Sound (3700 μg/g organic carbon (OC)) by Barrick et al., 1980.

### 4.1.3 The Normal Paraffins

The sums of the n-alkane concentrations ( $\sum_{13}^{32}$ n-alkanes) are relatively uniform for the three July stations, averaging 78.0 μg/g (1190 μg/g C). The mean value for Puget Sound surface sediments ( $\sum_{14}^{34}$ n-alkanes) is much lower, 260 μg/g OC (Barrick et al., 1980), as is the average Lake Washington concentration, 9.27 μg/g (Wakeham, 1976).

The distributions of the individual n-alkanes are presented in Figure 8. Concentrations are tabulated in Table C-1. Station 1 displays the classical "fingerprints" of biogenic hydrocarbons. Heptadecane and pentadecane, products of plankton and algae, dominate the low-molecular-weight fraction ($C_{13}$-$C_{20}$) at concentrations of 1.3 and 13.1 μg/g, respectively. A concentration minimum between $C_{18}$ and $C_{22}$ is followed by a preferential increase in the heavy, odd-carbon compounds, $C_{23}$ through $C_{31}$, reaching a maximum at $C_{27}$ (15.5 μg/g). This high-molecular-weight suite is indicative of terrestrial plant waxes.

Station 2 exhibits a striking increase in $C_{15}$ (7.8 μg/g) and $C_{17}$ (41.0 μg/g) compared to values at Station 1. The concentration of $C_{16}$ is greater by a factor of 4. The heavy, odd-carbon compounds again peak at $C_{27}$ (7.6 μg/g) in a pattern similar to that of Station 1. Concentrations, however, are significantly lower.

The pattern of volatile and high-molecular-weight, odd-carbon com-

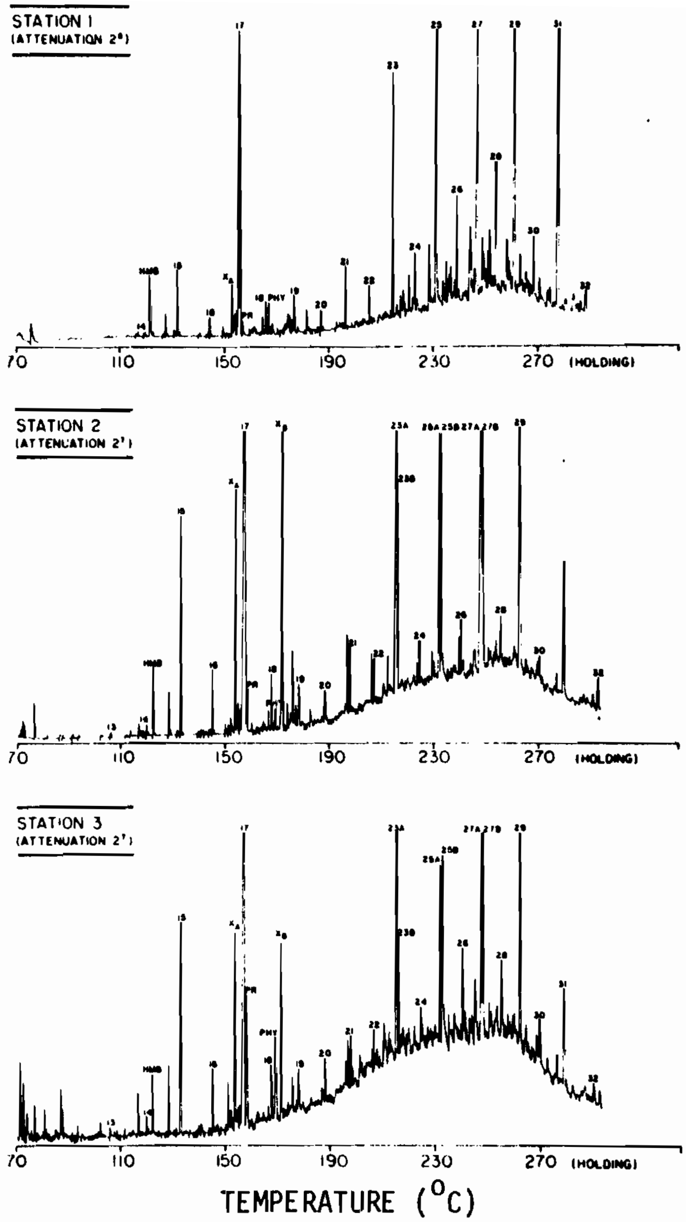

Figure 7. Gas chromatograms of the aliphatic hydrocarbon fractions extracted from Green River suspended matter. Samples were retrieved by centrifugation in July 1978. Chromatographic conditions are given in section 3.5.4.

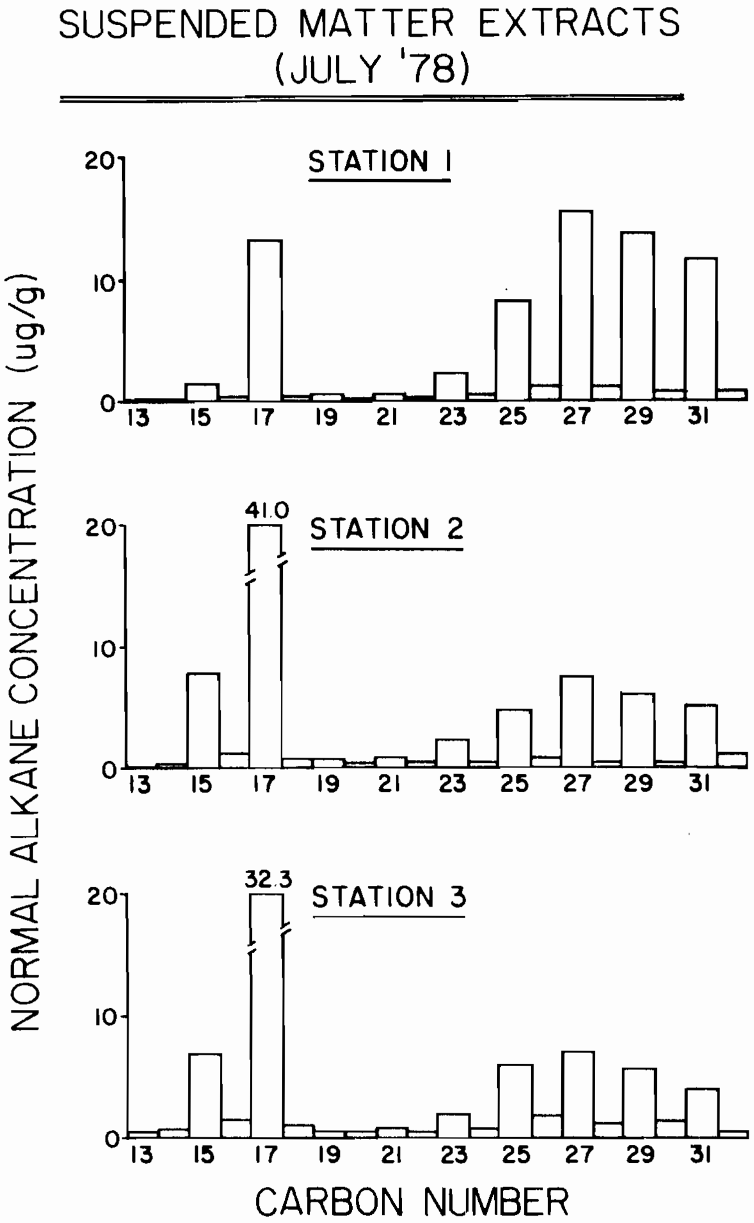

Figure 8. Concentrations of the normal paraffins associated with suspended matter in the Green River. Samples were retrieved by centrifugation in July 1978.

pounds at Station 3 is nearly identical to that at Station 2 although the even-carbon alkanes have increased in relative importance at the latter station.

### 4.1.4 Compositional Characteristics

Diagnostic parameters, reflecting source differences, are summarized in Table 9. The first of these parameters is the ratio of the volatile hydrocarbons to the heavier constituents ( $\sum_{13}^{20}$ n-alk/ $\sum_{21}^{32}$ n-alk). This ratio is lowest at Station 1 (0.28) and highest at Station 2 (1.70). The value at Station 1 falls within the general range for vascular plants, 0 to 0.5 (Gearing et al., 1976) and corresponds to the mean value found for Puget Sound sediments, 0.27 (Barrick et al., 1980). The increase in $C_{15}$ and $C_{17}$, and the simultaneous decrease in the heavy, plant wax hydrocarbons account for the higher ratios at Stations 2 and 3. These values are well below the range for plankton and nonvascular plants (Gearing et al., 1976).

The carbon preference index (CPI) is a weighted ratio of odd- to even-carbon n-alkanes over a specified molecular-weight range. The index is usually calculated over two fractions, the volatiles, $C_{14}$ through $C_{20}$ (equation 4-1), and the heavy hydrocarbons, $C_{20}$ through $C_{32}$ (equation 4-2) (Clark and Finley, 1973).

$$CPI_{14-20} = 1/2 \left( \frac{\sum_{15}^{19} [odd]}{\sum_{16}^{20} [even]} + \frac{\sum_{15}^{19} [odd]}{\sum_{14}^{18} [even]} \right) \qquad (4-1)$$

$$CPI_{20-32} = 1/2 \left( \frac{\sum_{21}^{31} [odd]}{\sum_{22}^{32} [even]} + \frac{\sum_{21}^{31} [odd]}{\sum_{20}^{30} [even]} \right) \qquad (4-2)$$

Stations 1 and 2 show similar high values for the low-molecular-weight ratio (~19). Between Stations 2 and 3 the $CPI_{14-20}$ drops sharply, reflecting the relative increase in the concentrations of the even-carbon compounds: $C_{14}$, $C_{16}$, $C_{18}$. The simultaneous decrease in $C_{15}$ and

$C_{17}$ concentrations from Stations 1 to 3 may be the result of reduced aquatic plant production and/or dilution. Crude oils and their refined products, demonstrate $CPI_{14-20}$ values of approximate unity, with n-alkane concentration maxima between $C_{14}$ and $C_{17}$ (Clark and Brown, 1977). The injection of refined products through the Renton outfall or diffuse local sources may account for the relative increases in the even-carbon compounds at Station 3. Wakeham (1976) reports a $CPI_{14-20}$ of 1.10 for the West Point Sewage Effluent.

The $CPI_{20-32}$ varies from 10.9 at Station 1 to 3.9 at Station 3. Values between 4 and 10 usually indicate vascular land plant alkanes (Clark and Blumer, 1967). Station 1 shows a pronounced dominance of the odd-carbon, plant wax compounds, reflecting a forested drainage basin. The decrease in this ratio downriver corresponds to the increase in concentrations of heavy, even-carbon compounds and a decrease in the terrestrial plant wax components. Ratio values of about 1 are typical of petroleum and bacteria. Wakeham (1976) reports a value of 1.08 for the West Point effluent. The lower value at Station 3 may be the result of material introduced by the Renton effluent, although the ratio 3.9 still falls at the lower end of the range for land plant sources. Numbers in this study can be compared with the $CPI_{20-34}$ values for the Skagit and Snohomish River delta sediments, which are 5.3 and 3.9, respectively (Barrick et al., 1980).

The ratio $(C_{15} + C_{17})/2\ C_{16}$ compares the predominant aquatic plant constituents to hexadecane, a compound abundant in crude oil and its refined products, but not generated in significant amounts biologically. This parameter drops stepwise from 25.5 at Station 1 to 11.9 at Station 3 as the concentration of $C_{16}$ increases. Despite the decrease in this ratio, the lowest value is much higher than the Puget Sound mean of 1.7 (Barrick et al., 1980) and the average Port Angeles value, 1.35 for sediments thought to be contaminated by fuel oil seepage (MacLeod, et al., 1976).

The phytane/$C_{17}$ ratio is another compositional indicator of hydrocarbon sources in the environment. Phytane is abundant in ancient sediments where it is produced by diagenetic altering of chlorophyll (the splitting of the phytol chain). It is absent from most aquatic organisms and found in only trace amounts in uncontaminated sediments.

Phytane is a constituent of crude oils, their refined products, and some bacteria. The dominant source of $C_{17}$ is aquatic organisms. Thus, increases in the ratio of these two compounds (phytane/$C_{17}$) in a given environment may reveal injections of hydrocarbons derived from a petrogenic source. Concentrations of phytane increase from Station 1 to Station 3 (0.18 to 2.51 µg/g). The phytane/ $C_{17}$ ratio remains the same at Stations 1 and 2 (0.01), but is significantly higher at Station 3 (0.08). These ratios are well below the Puget Sound mean of 0.39 (Barrick et al., 1980) and the Lake Washington surface sediment value of 0.20 (Wakeham, 1976).

Pristane is present in petroleum, but in uncontaminated marine environments, it is thought to be produced by organisms from the phytol chain of chlorophyll. Pristane/$C_{17}$ ratios show an increase only between Station 2 (0.02) and Station 3 (0.10), with the highest value a factor of 20 below the average Puget Sound ratio (Barrick et al., 1980).

Pristane/phytane ratios fall between 1.25 (Station 2) and 1.94 (Station 3). These values are comparable to ranges reported by Gearing et al., (1976) for the Gulf of Mexico (0.77-2.81) and by Keizer et al., (1978) for the Scotian Shelf (1.03-10.21), but lower than the Puget Sound mean of 6.8 (Barrick et al., 1980).

### 4.1.5 Unknown Aliphatic Hydrocarbons

It is evident from the chromatograms of the aliphatic fractions (Figure 7) that there are a number of dominant unidentified peaks ($X_A$, $X_B$, $23_A$, $25_A$, $27_A$). GC and GC-MS analyses revealed the following information.

| Compound Label | Mass of Major Ion | Probable Carbon # | Probable Degree of Unsaturation | Kovats Index (SP-2100) | Concentration (µg/g) Station 2 | Concentration (µg/g) Station 3 |
|---|---|---|---|---|---|---|
| $X_A$ | 238 | 17 | 1 | 1671 | 4.92 | 7.00 |
| $X_B$ | 278 | 20 | 2 | 1836 | 6.24 | 3.50 |
| $23_A$ | 322 | 23 | 1 | 2294 | 17.20 | 11.30 |
| $25_A$ | 350 | 25 | 1 | 2491 | 6.21 | 4.05 |
| $27_A$ | 378 | 27 | 1 | 2693 | 15.00 | 12.00 |

The three compounds $23_A$, $25_A$, and $27_A$ are thought to comprise a homologous series of mono-olefins. A plot of KI versus carbon number for these unknowns is linear and parallel to a similar plot for the corresponding n-alkanes. Upon hydrogenation (procedure follows Barrick et al., 1980), these unknowns shifted to their corresponding saturate homologs. Wakeham (1976) reported a $C_{27}$ olefin in Lake Washington sediments which is also found in plankton indigenous to the lake. Giger et al., (1980) have noted the presence of mono-olefins from $C_{21}$ through $C_{27}$ in sediments of the Greifensee, Switzerland. The odd-carbon alkenes predominated, and their concentrations were similar to those of the saturated homologs.

Alkenes are known to be biologically abundant (Blumer et al., 1970b). Moreover $23_A$, $25_A$, and $27_A$ are not present in the October and December suspended sediment samples, suggesting a biological origin. They may be the result of a July bloom near the outfall, a known source of nutrients.

Barrick et al., (1980) have tentatively identified a compound present in Puget Sound sediment samples as phytadiene (MW 278) at KI SP-2100 1879. The unknown, $X_B$ (MW 278) also has 2 degrees of unsaturation, but a KI SP-2100 of 1836. Hydrogenation of the samples showed a shift in the retention time of $X_B$ to that of phytane. In addition, $X_A$ shifted to heptadecane.

### 4.1.6 Summary

TSM and TPC were negatively correlated as one proceeded downriver, indicating a dilution of the high TPC material measured at Station 1. Highest concentrations of total extractables (28.6 mg/g) and aliphatics (1.09 mg/g) were measured at Station 3. The UCM concentration was three times higher at Station 3 than at Station 1, although the unresolved mixture comprised an average of 34% ± 5% of the saturate fractions measured at all stations. Heptadecane and pentadecane, the algal and planktonic indicators, dominated the low-molecular-weight fraction at each station. Concentrations of volatile compounds increased between Stations 1 and 2 although the internal ratios ($CPI_{14-20}$, $(C_{15} + C_{17})/2C_{16}$) remained similar. From Stations 2 to 3 the concentrations of the volatile odd-carbon compounds decreased as concentrations of the even-carbon compounds increased. This was reflected in the decrease in the $CPI_{14-20}$ between these two stations. The plant wax constituents dominated the heavy hydrocarbons at each station. Concentrations of these odd-carbon compounds at Stations 2 and 3 were less than half the values measured at Station 1. The $CPI_{20-32}$ steadily decreased downriver indicating that proportionally greater concentrations of the heavy, even-carbon paraffins were being added. Generally the odd-to-even bias, distinctive at Station 1, was gradually attenuated with distance downriver, especially between Stations 2 and 3. Pristane and phytane both increased with respect to $C_{17}$ over the same distance. Surface runoff and sewage effluent containing fuel oil (CPI values of approximately unity) are likely sources of these compositional changes. Microbial activity indigenous to the river and/or the secondary treatment process could also be a contributing factor.

## 4.2 OCTOBER 1978

Results obtained for the stations occupied in October and the Metro effluent filter sample are presented in Table 10. Suspended matter concentrations (determined from the centrifuge sample) increased progressively from 1.4 mg/l at Station 1 to 2.6 mg/l at Station 3R. The outfall injected an average concentration of 8.3 mg/l during the occupation of Stations 3 and 3R. Triplicate particulate carbon measurements at Station 1 ranged from 9% to an anomalous 83%. Excluding the extreme result, the average of the remaining two values was 12%. Carbon concentrations were highest at Stations 3 and 3R; ($\overline{TPC}$ = 19.4%).

### 4.2.1 Total Extractables and Aliphatics

Total solvent extractables varied from 7.1 mg/g at Station 2B to 53.1 mg/g at Station 3R. Values at Stations 3 and 3R are greater than those measured by Schultz and Quinn (1977) at their most contaminated station in Narragansett Bay (34.8 mg/g). The October Metro effluent concentration of extractables was 337 mg/g (2.8 mg/l). This value is consonent with the average total suspended hydrocarbon value determined by Van Vleet and Quinn (1977) in Fields Point effluent, 2.7 mg/l.

Total aliphatic hydrocarbon abundance varied from 0.10 mg/g at Station 1 to 2.5 mg/g at Station 3R; the outfall injected a concentra-

Table 10. Concentrations and compositional parameters of hydrocarbons associated with suspended matter retrieved from the Green River (by centrifugation) and the Renton Metro effluent (by filtration) in October 1978.

| | Station 1 | Station 2B | Effluent | Station 3 | Station 3R |
|---|---|---|---|---|---|
| TSM* (mg/l) | 1.4 | 2.2 | 8.3** | 2.4 | 2.6 |
| TPC (wt.%) | 12.0 | 9.3±1.2 | N.D. | 17.5 | 21.3 |
| Total Extractables (mg/g) | 8.2±0.5 | 7.1±1.0 | 337±6 | 41.6±0.4 | 53.1±0.8 |
| Total Saturates (mg/g) | 0.10 | 0.30 | 8.69 | 1.49 | 2.47 |
| UCM (µg/g) | 51.8 | 116 | 3480 | 620 | 702 |
| $\sum_{13}^{32}$ n-alkanes (µg/g) | 79.3 | 59.0 | 973 | 67.8 | 86.4 |
| $\sum_{13}^{20}$ n-alk/ $\sum_{21}^{32}$ n-alk | 0.35 | 0.82 | 0.26 | 1.47 | 1.86 |
| $CPI_{14-20}$ | 11.1 | 2.6 | 2.3 | 3.3 | 2.8 |
| $CPI_{20-32}$ | 7.5 | 8.0 | 1.1 | 2.9 | 2.3 |
| $(C_{15} + C_{17})/2\ C_{16}$ | 12.0 | 2.2 | 3.0 | 3.3 | 2.8 |
| Phy/$C_{17}$ | 0.02 | 0.06 | 0.33 | 0.22 | 0.18 |
| Pr/$C_{17}$ | 0.04 | 0.17 | 0.42 | 0.28 | 0.28 |
| Pr/Phy | 2.2 | 2.9 | 1.3 | 1.3 | 1.6 |

* Calculated from centrifuge sediment weight and volume of water centrifuged.

** Average for sampling period (Municipality of Metropolitan Seattle, 1978b).

tion of 8.7 mg/g. These values are all higher than those reported for sediments in Narragansett Bay (Wade and Quinn, 1979) and Puget Sound (Barrick et al., 1980). Concentrations of aliphatic hydrocarbons at Stations 3 and 3R are greater than those measured in Lake Washington sediments (Wakeham, 1976) and in the surficial sediments of the New York Bight (Farrington and Tripp, 1977).

### 4.2.2 Unresolved Hydrocarbons

The unresolved complex mixture reaches a maximum near $C_{27}$ (Figs. 9 and 10). Values vary from 51.8 μg/g (430 μg/g C) at Station 1 to 3480 μg/g near the outfall, with intermediate values, averaging 660 μg/g (3420 μg/g C), below the outfall. The UCM comprises approximately 50% of the total saturate fraction at Station 1, 40% of the effluent, and an average of 35% below the outfall. In Puget Sound sediments (post 1875), the UCM accounted for an average of about 70% of the total aliphatic hydrocarbon (Barrick et al., 1976).

### 4.2.3 The Normal Paraffins

The sum of the n-alkanes is lowest at Station 2, 59 μg/g (634 μg/g C) and highest in the effluent, 973 μg/g. Concentrations at Stations 1, 3, and 3R are intermediate: 79 μg/g (658 μg/g C), 69 μg/g (394 μg/g C), and 86 μg/g (404 μg/g C), respectively. These values are all greater than the average for Puget Sound surface sediments, 260 μg/g OC (Barrick et al., 1980), Lake Washington sediments, 9.27 μg/g (Wakeham, 1976), and the range reported for intertidal sediments in Port Angeles Harbor, 1.3 to 10.9 μg/g (MacLeod et al., 1976).

Figure 11 presents the distributions of individual n-alkanes at each station. Concentrations are listed in Table C-2. As in July, Station 1 reflects aquatic and terrestrial plant hydrocarbon sources. Pentadecane and heptadecane dominate the volatile fraction with concentrations of 2.7 μg/g and 14.5 μg/g, respectively. The heavy, odd-carbon compound abundances, $C_{23}$ to $C_{31}$ form a smooth normal distribution, reaching a maximum concentration of 16.7 μg/g at $C_{27}$. Concentrations of the heavy, even-carbon compounds, $C_{24}$-$C_{32}$, are relatively constant, varying between 0.8 and 1.9 μg/g.

Station 2 shows a dramatic increase in $C_{13}$, $C_{14}$, and $C_{16}$. The concentration of pentadecane has increased to 6.0 μg/g, while that of hep-

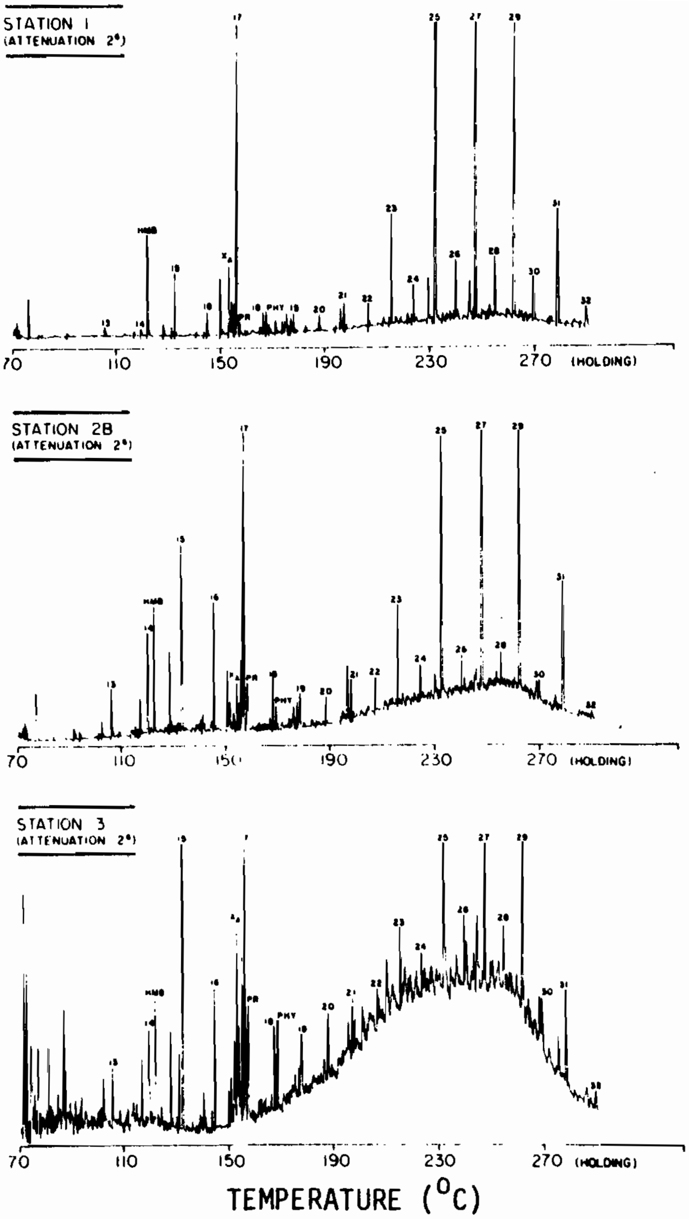

Figure 9. Gas chromatograms of the aliphatic hydrocarbon fractions extracted from Green River suspended matter. Samples were retrieved by centrifugation in October 1978. Chromatographic conditions are given in section 3.5.4

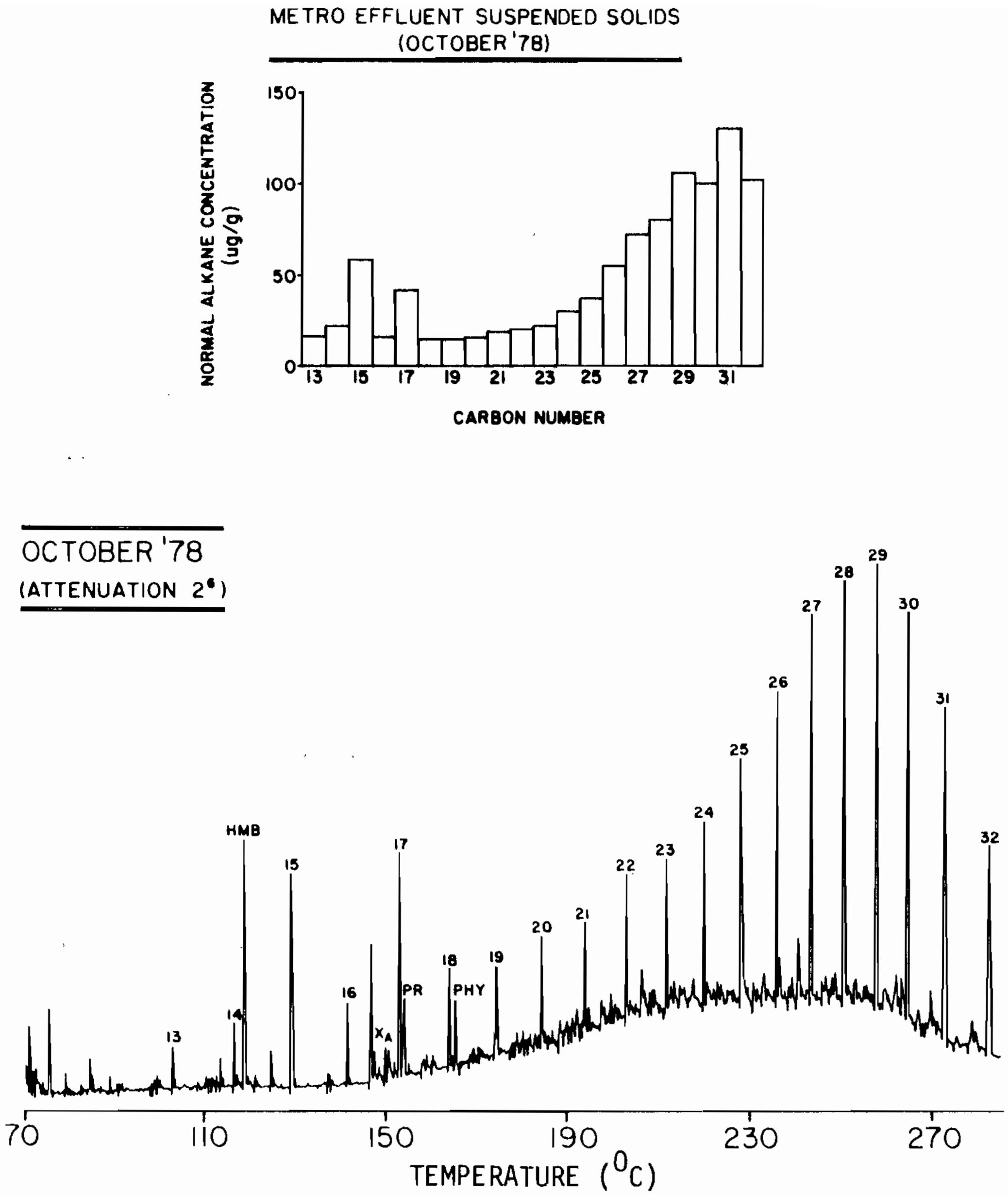

Figure 10. Top: Concentrations of the normal paraffins associated with suspended solids in Renton Metro sewage effluent. This sample was retrieved by filtration of an effluent composite taken October 19-20, 1978 (0730-0730 hrs). Bottom: Gas Chromatogram of the aliphatic hydrocarbon fraction extracted from the sample identified above. Chromatographic conditions are given in section 3.5.4.

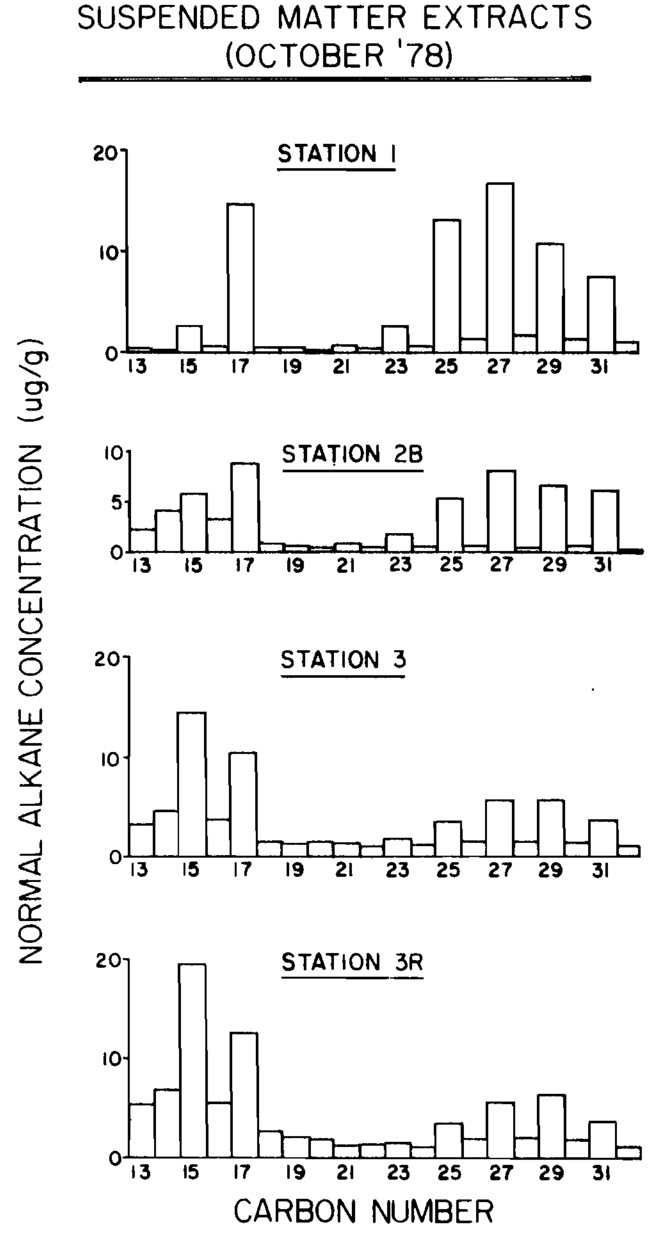

Figure 11. Concentrations of the normal paraffins associated with Green River suspended matter. Samples were recovered by centrifugation in October 1978.

tadecane has decreased to 8.9 μg/g. The heavy, odd-carbon compounds attain a maximum at $C_{27}$ with a concentration of 8.0 μg/g, half the value measured at Station 1.

Duplicate samples taken at Station 3 display the similar high concentrations of $C_{13}$, $C_{14}$, and $C_{16}$ exhibited at Station 2. There is a reversal in dominance between $C_{15}$ ($\bar{C}_{15}$ = 16.7 μg/g) and $C_{17}$ ($\bar{C}_{17}$ = 11.4 μg/g). The concentration minimum at $C_{19}$-$C_{22}$ has increased relatively as have the concentrations of heavy, even-carbon compounds, $C_{24}$-$C_{32}$. The odd-carbon suite shows highest concentrations at $C_{27}$ ($\bar{C}_{27}$ = 5.5 μg/g) and $C_{29}$ ($\bar{C}_{29}$ = 5.8 μg/g).

Figure 10 (top) presents a bar diagram of n-alkanes distribution associated with suspended solids in the October Metro Composite Sample (Oct. 19-20, 1978). Pentadecane and heptadecane dominate the low-molecular-weight compounds. Concentrations increase stepwise from $C_{18}$ (14 μg/g) to a maximum at $C_{29}$ (105 μg/g) with nearly equal amounts of odd- and even-carbon compounds present.

### 4.2.4 Compositional Characteristics

Compositional parameters for the October data are summarized in Table 10. The $\sum_{13}^{20}$ n-alk/ $\sum_{21}^{32}$ n-alk ratio is increasing from 0.35 at Station 1 to 1.9 at Station 3R. The Renton outfall is contributing material with the lowest value (0.26). The ratios determined in the effluent and at Station 1 fall within the 0 to 0.5 range characteristic of vascular land plants (Gearing et al., 1976). The downstream increase in this ratio reflects both an increase in the volatile compound concentrations and a decrease in the major heavy hydrocarbons.

The carbon preference indices, $CPI_{14-20}$, decrease dramatically between Station 1 (11.1) and Station 2 (2.6) responding to the large increases in $C_{14}$ and $C_{16}$. This precipitous change may reflect the contributions of surface runoff contaminated with fossil fuel hydrocarbons ($CPI_{14-20}$ ~1.0). The outfall is injecting volatile compounds ($CPI_{14-20}$ = 2.3) in a proportion similar to that observed at Station 2B. Values remain low below the outfall ($CPI_{14-20}$ ~ 3.0).

The carbon preference indices of the heavy compounds, $CPI_{20-32}$, at Stations 1 and 2B are similar (7.5 and 8.0) and fall within the range vascular land plants (Clark and Blumer, 1967). The outfall injects an n-alkane mixture with a $CPI_{20-32}$ near unity, comparable to the primary discharge from the West Point treatment facility (Wakeham, 1976). The ratios at Stations 3 and 3R are intermediate ($CPI_{20-32} = 2.6$), presumably reflecting a dilution of the effluent hydrocarbons with ambient hydrocarbons.

The ratio $(C_{15} + C_{17})/2\ C_{16}$ decreases between Station 1 (12.0) and Station 2B (2.2) reflecting the increase in $C_{16}$. The effluent and Stations 3 and 3R show values from 2.8 to 3.3. The trend of this ratio is similar to that of the $CPI_{14-20}$, emphasizing that the changes in the composition of the low-molecular-weight compounds are not caused by effects of the Metro effluent (i.e., the ratio changes between Station 1 and 2B, upstream of the treatment plant).

The phytane/$C_{17}$ ratio increases from 0.02 at Station 1 to 0.22 below the outfall. The outfall is injecting material with the highest ratio, 0.33. Pristane/$C_{17}$ follows a similar trend, lowest at Station 1 (0.04), highest at the outfall (0.42), and intermediate below the outfall (0.28). Although concentrations of $C_{17}$ vary considerably, concentrations of pristane increase monotonically downstream. The variability in $C_{17}$ and the trends in pristane and phytane indicate that the source of these latter two compounds is different from that of $C_{17}$, usually produced by aquatic organisms. Pristane/phytane ratios do not vary greatly. Values above the outfall average 2.5 while the mean below the outfall is 1.4. Again, the consistency in this ratio suggests similar sources of pristane and phytane, the major one being the outfall.

### 4.2.5 Unknown Aliphatic Hydrocarbons

Figures 9 and 10 show chromatograms of the aliphatic samples extracted from suspended matter collected at Stations 1, 2, 3, and from the effluent. A number of unidentified peaks are evident. Of the five described in the July results, only $X_A$ was apparent in a significant amount. This compound was present in the Renton Metro effluent, and greater concentrations were measured below the outfall than above it:

| | | | | | Concentrations at Stations (μg/g) | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Hydrocarbon | Mass of Major Ion | Probable Carbon # | Probable Degree of Unsaturation | KI SP-2100 | 1 | 2 | Outfall | 3 | 3R |
| $X_A$ | 238 | 17 | 1 | 1673 | 1.93 | 1.02 | 9.6 | 5.66 | 3.94 |

### 4.2.6 Summary

The highest concentrations of total extractables and aliphatic hydrocarbons were measured in the effluent. Riverine suspended matter at Stations 3 and 3R below the outfall exhibited the next largest concentrations of the extractables and aliphatics. The UCM comprised a greater proportion of the total saturates at Station 1 (50%) than below the outfall (35%) despite the elevated concentration measured in the effluent.

Pentadecane and heptadecane dominated the volatile fraction of all samples although the concentrations of $C_{13}$, $C_{14}$, and $C_{16}$ at Stations 2B, 3, and 3R were considerably greater relative to their aquatic algal counterparts. This is reflected in the dramatic decrease in $CPI_{14-20}$ and $(C_{15} + C_{17})/2\ C_{16}$ values between Stations 1 and 2B (before the outfall was reached). The abrupt changes in these parameters and the concurrent increase in pristane and phytane may be a result of microbial activity in the river or diffuse sources of petroleum products, such as those contained in surface runoff. A cruise up the Green River in February 1980 located 49 pipes between Stations 1 and 2B of which 29 are known to transport highway runoff. Fuel oils contain high concentrations of $C_{14}$ through $C_{17}$ with concentrations of individual hydrocarbons decreasing as molecular weight increases. Wakeham (1976) reported the following average storm water and bridge runoff values (water and particulates combined): $CPI_{14-20} \sim 1.22$, $CPI_{20-36} \sim 1.28$, $Pr/C_{17} \sim 0.87$.

The heavy hydrocarbons at Stations 1 and 2B reflect regimes dominated by vascular land plants. An abrupt decrease in $CPI_{20-32}$ values between Stations 2B and 3 implicates the outfall as a source of heavy, even-carbon compounds.

## 4.3 DECEMBER 1978

The results of the December river samples and the effluent suspended solid samples obtained concurrently are presented in Tables 11 and 12. Station 3 hydrocarbon values represent averages of triplicate analyses. Suspended matter concentrations in the river increased stepwise from 3.2 mg/l at Station 1 to 6.9 mg/l at Station 3. The outfall contributed an average of 14.2 mg/l of suspended solids over the 4-day sampling period. TCP was highest (15.4%) at Station 1. Low values were

Table 11. Concentrations and compositional parameters of hydrocarbons associated with suspended matter retrieved from the Green River by centrifugation in December 1978.

| | Station 1 | Station 2B | Station 3 |
|---|---|---|---|
| TSM* (mg/l) | 3.2 | 5.1 | 6.9 |
| TPC (wt.%) | 15.4 | 3.1 ± 0.5 | 3.6 ± 2.0 |
| Total Extractables (mg/g) | 5.9 ± 0.1 | 5.4 ± 0.1 | 17.4 ± 0.5 |
| Total Saturates (mg/g) | 0.63 | 0.41 | 0.74 ± .16 |
| UCM (μg/g) | 237 | 122 | 323 ± 52 |
| $\sum_{12}^{32}$ n-alkanes (μg/g) | 71.3 | 43.3 | 52.4 |
| $\sum_{13}^{20}$ n-alk/ $\sum_{21}^{32}$ n-alk | 0.08 | 0.27 | 0.56 |
| $CPI_{14-20}$ | 2.5 | 1.6 | 1.0 |
| $CPI_{20-32}$ | 14.3 | 10.2 | 5.0 |
| $(C_{15} + C_{17})/2\ C_{16}$ | 2.3 | 1.2 | 1.1 |
| Phytane/$C_{17}$ | 0.46 | 0.40 | 0.38 |
| Pristane/$C_{17}$ | 0.50 | 0.60 | 0.68 |
| Pristane/Phytane | 1.1 | 1.5 | 1.8 |

* Calculated from centrifuge sediment weight and volume of water centrifuged.

Table 12. Concentrations and compositional parameters of hydrocarbon associated with suspended solids retrieved from Renton Metro effluent via filtration in December 1978.

| | Sample 1 | Sample 2 | Sample 3 | Mean |
|---|---|---|---|---|
| TSM (mg/l) | 17.3* | 12.7* | 12.8* | 14.2 ± 2.6 |
| Total Extractables (mg/g) | 376 | 439 | 375 | 397 ± 37 |
| Total Saturates (mg/g) | 10.8 | 13.2 | 8.2 | 10.7 ± 2.5 |
| UCM (μg/g) | 3430 | 4690 | 3420 | 3850 ± 730 |
| $\sum_{13}^{32}$ n-alkanes (μg/g) | 507 | 690 | 224 | 474 ± 234 |
| $\sum_{13}^{20}$ n-alk/ $\sum_{21}^{32}$ n-alk | 0.30 | 0.21 | 0.59 | 0.37 ± 0.20 |
| $CPI_{14-20}$ | 1.1 | 1.1 | 1.0 | 1.1 ± 0.1 |
| $CPI_{20-32}$ | 1.1 | 2.0 | 1.2 | 1.4 ± 0.5 |
| $(C_{15} + C_{17})/2\ C_{16}$ | 1.5 | 1.3 | 1.3 | 1.4 ± 0.1 |
| Phytane/$C_{17}$ | 1.0 | 1.6 | 1.6 | 1.4 ± 0.4 |
| Pristane/$C_{17}$ | 1.1 | 1.9 | 1.8 | 1.6 ± 0.4 |
| Pristane/Phytane | 1.2 | 1.2 | 1.2 | 1.2 ± 0.00 |

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* Average for each sampling period (Municipality of Metropolitan Seattle, 1978b).

measured at Stations 2B and 3 (3.1% and 3.6%, respectively). It appears that most of the suspended matter increase is caused by the addition of material low in carbon.

### 4.3.1 Total Extractables and Aliphatics

Total extractables were low (5-6 µg/g) at Stations 1 and 2B, whereas total lipids at Station 3 were much higher, averaging 17.4 mg/g. The high value at Station 3 may reflect the average outfall contribution of 397 mg/g. Total saturated hydrocarbon concentrations varied from 0.63 mg/g far above the outfall to 0.74 mg/g below the outfall with a minimum of 0.41 mg/g at Station 2B. The average contribution of total saturates by the Renton Secondary Treatment plant was 10.7 mg/g.

### 4.3.2 Unresolved Hydrocarbons

The unresolved complex mixture extends from $C_{14}$ to beyond $C_{32}$, reaching a maximum at approximately $C_{27}$ (Figures 12 and 13). The concentration of the UCM was highest at the outfall, averaging 3850 µg/g and lowest at Station 2B (122 µg/g; 3990 µg/g C). The highest river value was at Station 3 below the outfall (323 µg/g; 8950 µg/g C), and Station 1 exhibited an intermediate value of 237 µg/g (1540 µg/g C). These values bracket those found in recent Puget Sound surface sediments, (3700 µg/g OC; Barrick et al., 1980). The UCM comprised 38% of the total gravimetric aliphatics at Station 1, 30% at Station 2B, and 44% at Station 3.

### 4.3.3 The Normal Paraffins

The sum of the n-alkanes varies from 71.3 µg/g at Station 1 to 43.3 µg/g at Station 2B. Normal paraffins averaged 474 µg/g in the Metro effluent decreasing to a value at Station 3 (52.4 µg/g) similar to those measured upstream. Bar graphs illustrating the distribution of the individual alkanes in the river samples and Metro composite samples are presented in Figures 14 and 15. The most notable feature is the paucity of low-molecular-weight compounds usually associated with aquatic plants ($C_{15}$ and $C_{17}$) at all three stations. Station 1 shows a slight odd-carbon dominance among the low level of volatile hydrocarbons, and a progressive increase in the heavy, odd-carbon compounds $C_{23}$-$C_{31}$, con-

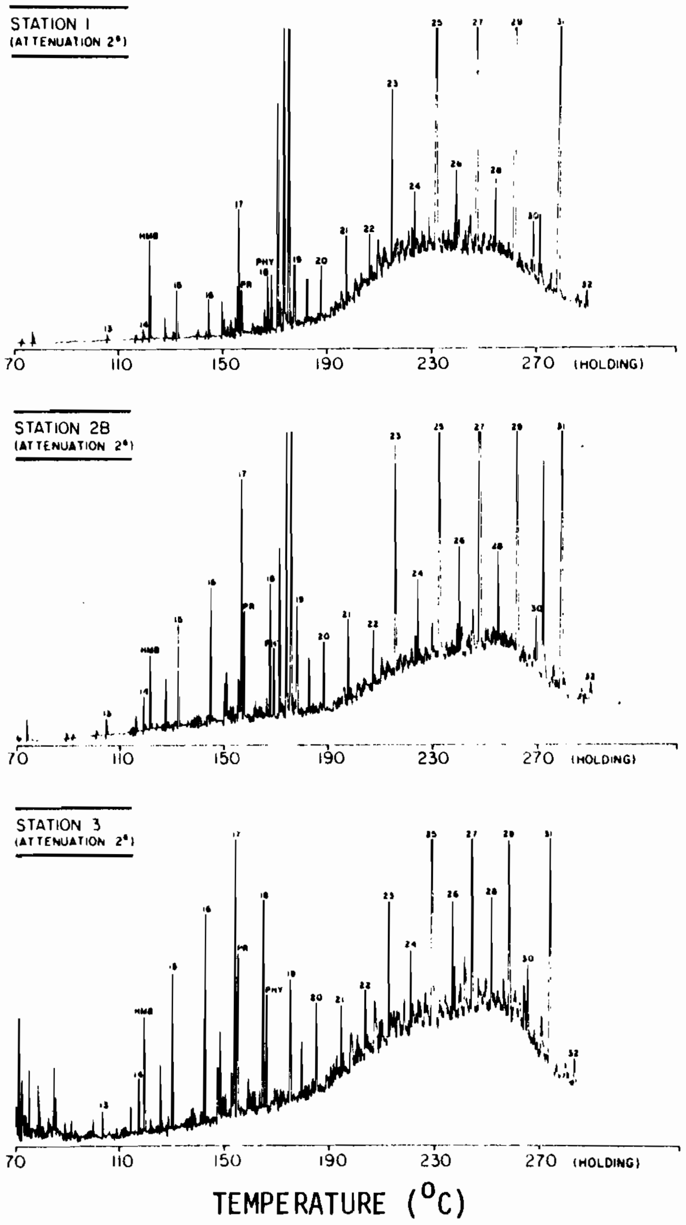

Figure 12. Gas chromatograms of the aliphatic hydrocarbon fractions extracted from Green River suspended matter. Samples were retrieved by centrifugation in December 1978. Chromatographic conditions are given in section 3.5.4.

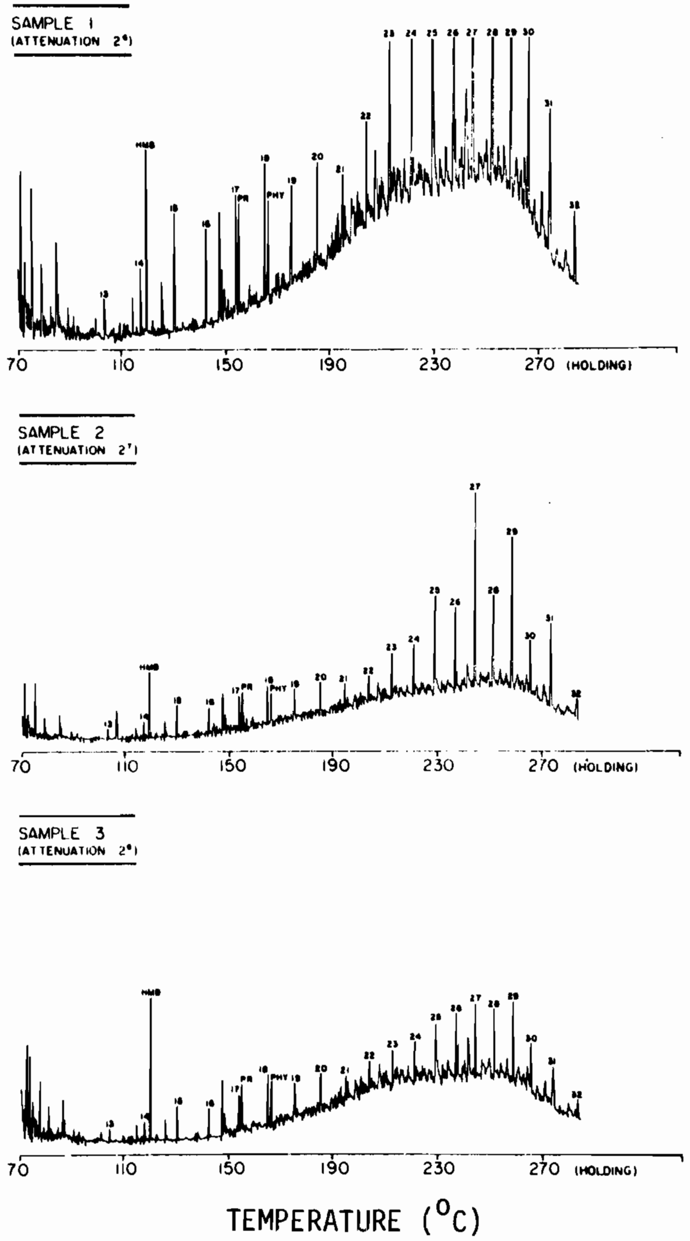

Figure 13. Gas chromatograms of aliphatic hydrocarbon fractions extracted from suspended solids retrieved by filtration from consecutive Renton effluent composites: Sample 1-- December 18-20, 1978 (1800-0600 hours), Sample 2--December 20-21, 1978, (1000-0800 hours), Sample 3--December 21-22, 1978 (1300-1100 hours). Chromatographic conditions are described in section 3.5.4.

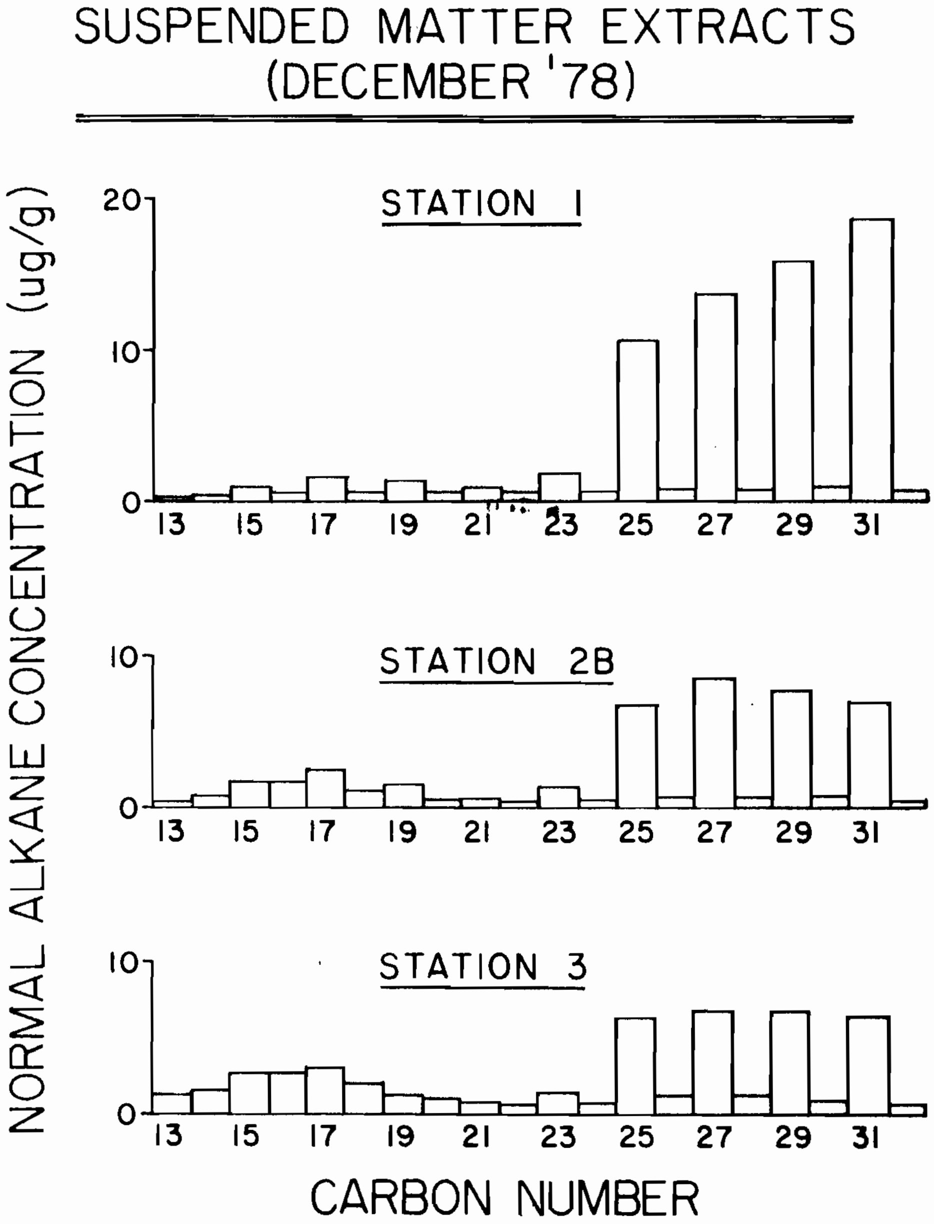

Figure 14. Concentrations of the normal paraffins associated with suspended matter in the Green River. Samples were obtained by centrifugation in December 1978.

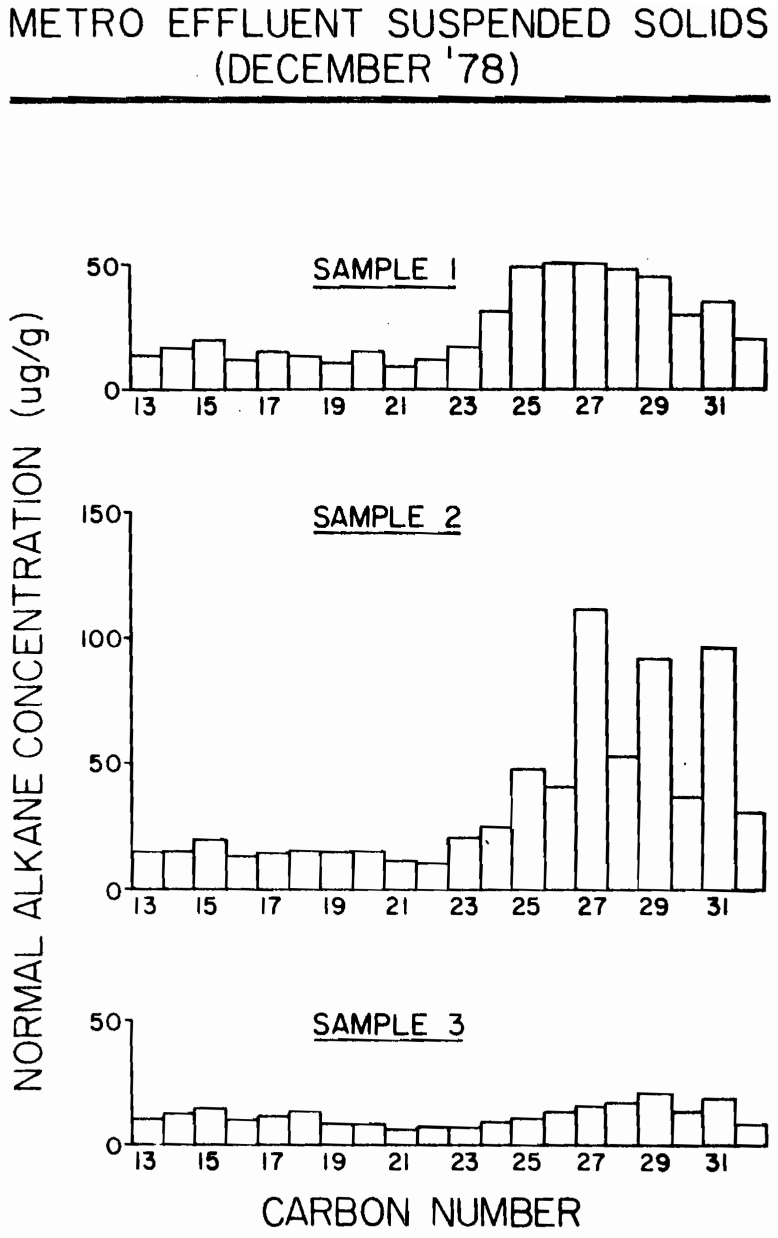

Figure 15. Concentrations of the normal paraffins associated with suspended solids retrieved from Renton Metro sewage effluent. Samples were retrieved by filtration of effluent composites obtained on the consecutive dates given in Figure 13.

tributed by plant waxes. The highest concentration was reached at $C_{31}$ (18.6 µg/g). Station 2B exhibits a slight increase in the $C_{15}$-$C_{18}$ volatiles ($C_{17}$ = 2.3 µg/g), and a decrease in the plant wax constituents. Heptacosane shows the highest concentration, 8.3 µg/g. Below the outfall (Station 3), the concentration of the low-molecular-weight hydrocarbons is slightly greater (e.g., $C_{17}$ = 3.3 µg/g). The concentrations of the heavy, odd-carbon compounds $C_{25}$, $C_{27}$, $C_{29}$, and $C_{31}$ are all similar, averaging 6.5 µg/g. The heavy, even-carbon compounds increased relative to Station 2B values.

The variation in the aliphatic profiles of the three sewage effluent samples is extreme (Table C-5). In Sample 1, the alkanes fall into two natural divisions: $C_{13}$ to $C_{23}$ compounds shows similar concentrations averaging 14 µg/g and the $C_{25}$ to $C_{32}$ hydrocarbons exhibit consistent concentrations, averaging 44 µg/g. There is no dominant compound in the profile and the odd-to-even compounds are equally balanced. The volatile fraction of Sample 2 shows little variation with compound concentrations averaging 15 µg/g ($C_{13}$ to $C_{23}$). Concentrations of the heavier compounds increased dramatically with a striking odd dominance of $C_{27}$, $C_{29}$, and $C_{31}$. The highest concentration was exhibited by $C_{27}$ (112 µg/g). Sample 3 displayed similar low levels of all compounds $C_{13}$ to $C_{32}$ averaging 11 µg/g.

### 4.3.4 Compositional Characteristics

Compositional parameters for river and Metro samples are summarized in Tables 11 and 12. The ratio $\sum_{13}^{20}$ n-alk/ $\sum_{21}^{32}$ n-alk varies from 0.08 at Station 1 to 0.56 at Station 3. Station 2B and average effluent values are intermediate, 0.27 and 0.37, respectively. All values fall within the range reported for hydrocarbon of vascular plants, 0 to 0.5 (Gearing et al., 1976).

The $CPI_{14-20}$ values decrease from 2.5 at Station 1 to 1.0 below the outfall. Effluent values fluctuate slightly around unity and appear to be reflected in the low value observed at Station 3. The decrease in the $CPI_{14-20}$ from Station 1 to the intermediate value at Station 2B may reflect an input of petroleum products from surface runoff.

The $\mathrm{CPI}_{20-32}$ values decrease from 14.3 at Station 1 to 5.0 at Station 3. The decrease in this ratio as one proceeds downriver parallels the relative decrease in the odd-carbon, plant wax constituents. The index change between Stations 2B and 3 also reflects a relative increase in heavy, even-carbon compounds. The outfall is injecting suspended hydrocarbons with an average $\mathrm{CPI}_{20-32}$ of 1.5 ± 0.5.

The $(C_{15}-C_{17})/2C_{16}$ ratio shows little variability. Values vary between 2.3 at Station 1 and 1.1 at Station 3, reflecting the lack of volatile hydrocarbon ($C_{15}$ and $C_{17}$) produced biologically. These ratios are similar to the Puget Sound mean, 1.7 (Barrick et al., 1980) and the average for Port Angeles Harbor sediments, 1.35 (MacLeod et al., 1976).

The phytane/$C_{17}$ ratios decrease slightly as one proceeds downstream with values averaging 0.41. Pristane/$C_{17}$ ratios increase slightly from Station 1 to 3 $(\overline{\mathrm{Pr/C}}_{17} = 0.59)$, while the outfall injects material of a higher ratio $(\overline{\mathrm{Pr/C}}_{17} = 1.6 \pm 0.4)$. Pristane/phytane ratios range from 1.1 at Station 1 to 1.8 at Station 3. The outfall average of 1.2 is intermediate.

### 4.3.5 Unknown Aliphatic Hydrocarbons

The unknown compounds identified as $X_A$ and $X_B$ in July and October aliphatic fractions were also found in December samples. Data obtained by GC and GC-MS analyses are given below.

| Compound Label | Mass of Major Ion | Probable Carbon # | Probable Degree of Unsaturation | KI SP-2100 | Concentrations at Stations (µg/g) 1 | 2B | 3 |
|---|---|---|---|---|---|---|---|
| $X_A$ | 238 | 17 | 1 | 1671 | 0.28 | 0.14 | 0.29 |
| $X_B$ | 278 | 20 | 2 | 1836 | 2.49 | 1.13 | N.D. |

Concentrations of $X_A$ in December were an order of magnitude lower than concentrations measured in July and October. This seasonal decrease may imply a biological source of this compound. Concentrations of $X_B$ at Stations 1 and 2B were lower in December than in July. Unknown $X_B$ was not detected (N.D.) at Station 3 in December.

### 4.3.6 Summary

TSM increased with distance downriver as TPC decreased, confirming the negative correlation found in July. The highest riverine concentrations of extractable lipids and total saturates were measured at Station 3. The outfall effluent contributed concentrations 15 to 20 times higher than these values. The UCM was also highest in the effluent and an order of magnitude lower at Station 3. Station 2B exhibited minima in all of the extensive parameters (except TSM) listed in Table 11. The December river samples were characterized by low concentrations of $C_{15}$ and $C_{17}$, reflecting the lack of biological activity in the winter. Plant wax constituents continued to dominate the heavy-molecular-weight fraction at all stations although concentrations were greatly reduced with distance downriver. Both carbon preference indices decreased from Stations 1 to 3 reflecting the relative increase in even-carbon compounds. Waste water contributions to heavy, odd-carbon compounds were superimposed upon the much higher concentrations of these compounds delivered by terrestrial plant matter (measured at Stations 1 and 2B). The changes between Stations 1 and 2B may be attributed to surface runoff resulting from December rainfall. In the lower Green River, the hydrocarbon signature is significantly influenced by the sewage outfall.

## 5.0 HYDROCARBON MASS BALANCE

Compositional differences notwithstanding, it is evident that the concentrations of the n-alkanes vary greatly with distance down the river. Concentrations of the volatile and heavy, even-carbon compounds have increased from Stations 1 to 3 while the heavy, odd-carbon paraffins have simultaneously decreased. To identify and quantify diffuse sources along the river, a mass balance of hydrocarbons was constructed. River fluxes were calculated at each station from a knowledge of hydrocarbon concentrations, the magnitude of the suspended load, and river discharge. Imbalance between stations implies sources or sinks.

### 5.1 LOWER GREEN RIVER

Quantitative data are available for one source, the Renton outfall, in addition to the end members, Stations 2B and 3. For each hydrocarbon, the transport measured at Station 3 should equal the sum of three terms: the transport measured at Station 2B, the input resulting from the outfall, and the amount contributed by diffuse sources between these stations. Biological oxidation of the hydrocarbons is ignored because of the relatively short distances involved. It is also assumed provisionally that preferential flocculation has not occurred, that is, hydrocarbons have not been removed by settling to the bottom. Later in the discussion these assumptions will be examined more closely.

The transport of each component at Station 3 is given by the expression below.

$$T_3 = T_{2B} + T_0 + T_D \qquad (5\text{-}1)$$

The subscripts indicate Stations 3, 2B, Renton outfall, and other diffuse sources or sinks between Stations 2B and 3. Rearranging equation (1), we obtain the magnitude of the diffuse source.

$$T_D = T_3 - T_{2B} - T_0 \qquad (5\text{-}1a)$$

The hydrocarbons are presumed to be associated with suspended solids (i.e., expressed as mass hydrocarbon/mass suspended solids), and thus both the suspended particulate concentrations (mass suspended sediment/volume of water) and the discharge (volume of water/time) are incorporated in the conservation of mass equation.

$$T_D = C_3P_3D_3 - C_{2B}P_{2B}D_{2B} - C_0P_0D_0 \qquad (5\text{-}2)$$

where: $C_3C_{2B}C_0$ = hydrocarbon concentrations (ug/g)

$P_3P_{2B}P_0$ = suspended particulate concentrations (g/m$^3$)

$D_3D_{2B}D_0$ = discharge (m$^3$/sec)

and subscripts 3, 2B, 0 refer to Stations 3, 2B, and the effluent outfall, respectively.

In July the centrifuge sample at Station 2 was believed to be contaminated with sewage effluent from the outfall located only 0.5 km downstream. Flood tide caused one observed river reversal and another similar episode likely occurred (Figure 16). Moreover, Metro effluent was not analyzed for suspended hydrocarbons in July. For these reasons the hydrocarbon budget will be calculated only for October and December data.

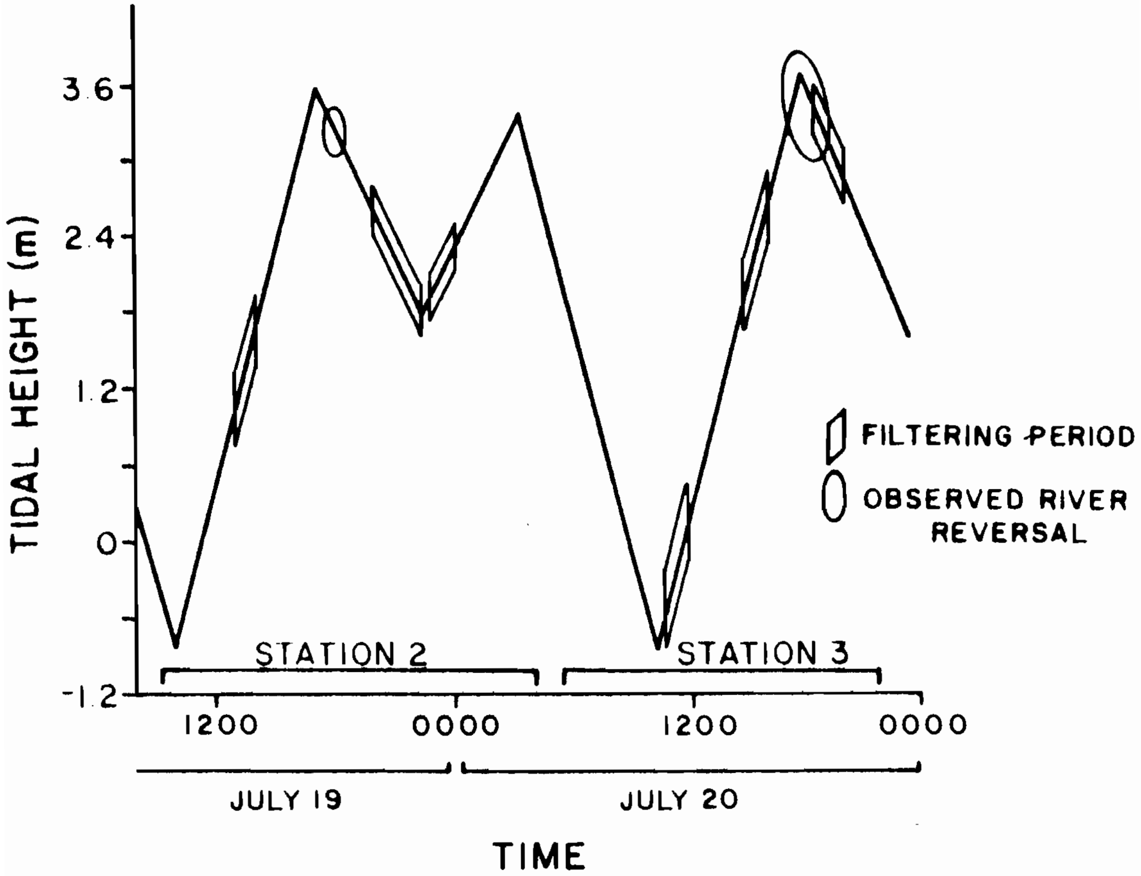

Figure 16. Tidal amplitudes at Elliott Bay (U.S. Dept. of Commerce, 1978) and the schedule of suspended matter sampling on the Green River in July 1978. Observed reversals in river discharge are noted.

### 5.1.1 Water Budget

Discharges are known near Stations 1 and 2B (Table A-1) and at the outfall (Municipality of Metropolitan Seattle, 1978b), but not at Station 3. The latter can be approximated, however, by adding the outfall discharge to the river discharge near Station 2B. Discharge values used in the budget are reported in Table 13. In October the outfall comprised 12% of the total river discharge at Station 3. By December, seasonal rainfall had increased river discharge threefold such that the outfall contributed only 4% of the river volume at Station 3.

### 5.1.2 Suspended Particulate Budget

Applying the conservation of mass equation (5-2) to both water and suspended particulate concentrations, the surplus transport of suspended matter between Stations 2B and 3 was calculated. Riverine suspended matter concentrations determined from centrifuge sample weight and volume of water centrifuged, and the effluent concentrations reported by Metro were substituted for $P_{2B}$, $P_3$, and $P_0$. Data are listed in Table 13. The outfall contributed 41% of the suspended particulate transport measured at Station 3 in October and 9% in December. A suspended matter deficit of 6.5 g/sec was calculated from October concentrations. That is, the outfall contributed 196% toward the net TSM increase between Stations 2B and 3. In contrast, December data showed a suspended matter surplus of 56.1 g/sec from sources other than the outfall. During this period, the outfall contributed 32% of the net TSM increase between Stations 2B and 3. Possible sources of the surplus include riverbank erosion, resuspension of bottom sediments, and surface runoff, resulting from autumn rains. A survey of river outfalls in February 1980 located 14 pipes between these two stations, of which at least five transport street runoff.

### 5.1.3 Normal Alkane Mass Balances

The budgets of the aliphatic hydrocarbons and the UCM are calculated by substituting known TSM concentrations, water discharges, and the UCM and hydrocarbon concentrations listed in Tables 10, 11, 12, B-2, B-4, and B-5 into equation (5-2). Hydrocarbon and UCM concentrations in Samples 1 and 2 of the December effluent were averaged for the calcula-

Table 13. Results of the hydrocarbon mass balance calculations for the lower Green River, October and December 1978. Transports resulting from the outfall and diffuse sources are also compared to the transports measured at Station 3 (see $T_0/T_3$ and $T_D/T_3$). Discharges and suspended particulate concentrations used in the calculations are reported here. The hydrocarbon concentrations are given in Tables B-2, B-4, and B-5. UCM concentrations are reported in Tables 10, 11, and 12.

October

$D_3 = 13.7\ m^3/sec$
$D_0 = 1.6\ m^3/sec$
$D_2 = 12.1\ m^3/sec$

$P_3 = 2.5\ g/m^3$
$P_0 = 8.8\ g/m^3$
$P_{2B} = 2.2\ g/m^3$

December

$D_3 = 40.8\ m^3/sec$
$D_0 = 1.7\ m^3/sec$
$D_2 = 39.1\ m^3/sec$

$P_3 = 6.9\ g/m^3$
$P_0 = 15.3\ g/m^3$
$P_{2B} = 5.1\ g/m^3$

| Hydrocarbon | $T_D$ (µg/sec) | $T_0/T_3$ | $T_D/T_3$ | $T_D$ (µg/sec) | $T_0/T_3$ | $T_D/T_3$ |
|---|---|---|---|---|---|---|
| 15 | -403 | 1.4 | 0.7 | -67 | 0.7 | 0.1 |
| 16 | -154 | 1.4 | 1.0 | +139 | 0.4 | 0.2 |
| 17 | -437 | 1.5 | 1.1 | +102 | 0.4 | 0.1 |
| Pr | -184 | 2.3 | 1.7 | -199 | 0.9 | 0.3 |
| Phy | -135 | 2.6 | 1.8 | -298 | 1.3 | 0.9 |
| 25 | -552 | 4.6 | 4.9 | -826 | 0.7 | 0.5 |
| 26 | -725 | 14.0 | 13.3 | -983 | 3.7 | 3.0 |
| 27 | -1040 | 5.4 | 5.5 | -1850 | 1.1 | 1.0 |
| 28 | -1080 | 20.1 | 19.3 | -1060 | 3.8 | 3.1 |
| 29 | -1460 | 7.4 | 7.3 | -1380 | 0.9 | 0.7 |
| 30 | -1370 | 28.2 | 27.6 | -696 | 3.0 | 2.5 |
| 31 | -1870 | 15.2 | 15.5 | -1210 | 0.9 | 0.7 |
| 32 | -1410 | 41.3 | 40.5 | -527 | 3.5 | 2.9 |
| UCM | -29400 | 2.2 | 1.3 | -39000 | 1.2 | 0.4 |

tion of the December budget because these samples together represent the period during which suspended sediment was retrieved at Stations 2B and 3. The results of the budget calculations are summarized in Table 13.

In October all individual paraffin transports decreased between Stations 2B and 3 when corrected for the contribution from the outfall. Deficits for individual components ranged from -135 to -1870 ug/sec. There appears to have been a preferential loss of the heavier alkanes.

The ratio of the outfall's contribution to the transports measured at Station 3 ($T_0/T_3$; Table 5-1) ranged from 1.4 to 41.3. The Renton outfall is apparently a greater relative source of the heavy, even-carbon compounds, $C_{26}$-$C_{32}$ ($T_0/T_3$: 14.0 to 41.3) than the plant wax compounds ($T_0/T_3$: 4.6 to 15.2) measured at Station 3.

A comparison of the apparent hydrocarbon deficits (sinks) and the transports below the outfall are also reported in Table 13 (see $T_D/T_3$). The similarity between the two ratios, $T_D/T_3$ and $T_0/T_3$ in October is striking. The calculated loss of heavy hydrocarbons between Stations 2B and 3 appears to be related to the theoretical effluent contributions of these compounds.

The UCM also shows a transport deficit in October. The ratio of the UCM deficit to the transport measured at Station 3 ($T_D/T_3$) is similar to the ratios calculated for the low-molecular-weight alkanes.

The disparities noted in the hydrocarbon transports have a number of plausible explanations. The composite effluent samples analyzed represent the effluent before the final dechlorination step in the secondary treatment process. After dechlorination, microbial and other biological activities are free to resume as the waste water is transported through a pipe 0.5 km in length to the outfall. Modifications of the hydrocarbons within such a short time period seem unlikely. Similarly, the possibility of heavy alkane reduction by biological processes within the river environment between the outfall and Station 3 (another 0.5 km) seems equally improbable.

Desorption is not likely a dominant process since it is the heavy compounds that are being preferentially lost. The heavy hydrocarbons are more hydrophobic than the volatile compounds, and they therefore should bind more tenaciously with the particulate phase. If desorption were occurring, a preferential loss of the low-molecular-weight compounds would be expected. The UCM transports appear to behave in a manner similar to the low-molecular-weight compounds. However, the individual compounds comprising the UCM have not been identified. Without knowledge of the chemical properties of these constituents, an adequate explanation of the UCM results is improbable.

The heavy hydrocarbon deficit between Stations 2B and 3 may also be largely the result of an exaggerated estimation of the suspended hydrocarbon concentrations present in the effluent, an artifact of the filtering procedure. The Gelman® filters, coated with the effluent's complex suspended solid matrix, may act as scavenging mats, retaining colloidal or even dissolved hydrocarbons on their surfaces. Despite their frequent use in the study of suspended hydrocarbons, glass fiber filters have proved inadequate for separating dissolved and particulate phases in a number of studies. A significant amount of what has been called POC (or a portion of the TPC in this case) is actually dissolved organic carbon (DOC) adsorbed on the glass fiber mesh (Menzel, 1966; Loder, 1971).

Feely (1975) reported that 23% of the POC he measured was actually DOC. Glass fiber filters consist of thick layers of glass fibers with large surface areas that may retain particles much smaller than the nominal pore size of the filters (Sheldon, 1973). The filters may retain effluent particulates that are too bouyant to be recovered efficiently by the centrifuge.

In order to determine whether the amounts of suspended matter recovered from METRO effluent by the centrifuge and by filter were significantly different, a grab sample of METRO effluent was obtained in December 1980. The sample was stirred continuously while aliquots were passed through preweighed Nuclepore® membrane filters, Gelman® glass fiber filters, and the continuous flow centrifuge (operating at 15,000 RPM and 400-500 ml/min). Portions of the centrifuge effluent were also filtered through preweighed Gelman® and Nuclepore® filters. Gravimetrically, the centrifuge retained 94% ± 2% of the suspended material recovered by the glass fiber filters and 87% ± 17% of the material recovered by membrane filters. In a similar experiment the centrifuge and Gelman® filter samples of METRO effluent particulates were extracted for hydrocarbons. This single comparison showed that the individual concentrations of the n-alkanes in the filter samples were an average of 1.4 times greater than concentrations in the centrifuge sample. The deficits of most compounds, especially of the heavy hydrocarbons, remain significant even if a correction for this bias is applied to the budget.

The loss of hydrocarbons between Stations 2B and 3 is most likely the result of flocculation and subsequent precipitation of organic matter as the complex effluent matrix mixes with river water. The less soluble, heavy hydrocarbons would be deposited in a solid phase more readily than the volatile compounds, thus explaining the greater deficits of the heavier ($C_{25}$-$C_{32}$) hydrocarbons reported here. Elevated concentrations of these alkanes in a sample of bottom sediments near the outfall may confirm the occurrence of such a precipitation process.

The imbalances in the budget calculated for the December paraffins range from +121 μg/sec to -1860 μg/sec (Table 13). The low-molecular-weight compounds show surpluses or relatively small deficits while the heavy alkanes, $C_{26}$-$C_{32}$, show marked depletions.

Suspended hydrocarbons in the effluent contributed relatively less to the budget in December than in October, primarily because of increased river flow. Relative to the transports observed at Station 3, the outfall material was enriched in the even-carbon compounds, $C_{26}$ through $C_{32}$. Surplus transports and small deficit transports of low-molecular-weight compounds, and the lower proportion of these compounds apparently contributed by the outfall, suggest that surface runoff from diffuse sources was important. The heavy alkane fraction was again preferentially lost from the suspended material.

## 5.2 UPPER GREEN RIVER

The effects of dilution may reveal additional reasons for the biased hydrocarbon transports that are observed. The dilution model is applied to the data collected at Stations 1 and 2B, since major point sources of sediment and hydrocarbons between these stations are unknown. The simple hydrocarbon transport equation (5-3) describes the upper portion of the river.

$$C_{2B}P_{2B}D_{2B} = C_1P_1D_1 + C_DP_DD_D \qquad (5\text{-}3)$$

To determine whether dilution is important, the aliphatic hydrocarbon contribution from eroded or resuspended sediments between Stations 1 and

2B is assumed negligible. With this assumption, equation (5-3) reduces to equation (5-4).

$$C_{2B} = \frac{C_1 P_1 D_1}{P_{2B} D_{2B}} \qquad (5\text{-}4)$$

Using hydrocarbon and UCM concentrations measured at Station 1 (Tables B-2, B-4, 10, and 11), expected concentrations at Station 2B can be calculated and compared to observed values. Results of this calculation are shown in Table 14. In October the calculated values of the heavy paraffins ($C_{25}$-$C_{32}$) and $C_{17}$ were in reasonable agreement with their measured concentrations. The UCM imbalance was similar to the values calculated for the low-molecular-weight compounds excluding $C_{17}$. These observations suggest that surface runoff was an important contributor to the low-molecular-weight fraction. The near balance of heptadecane implies that this paraffin is of a different origin (algal or planktonic). Ratios in gross excess of 100% ($C_{28}$ and $C_{32}$ values) are evidence of a "sink" not yet accounted for.

In December, the situation was somewhat different. The calculated values for the UCM, $C_{29}$, $C_{31}$, and $C_{32}$ were near their calculated concentrations. Apparently the river sediments eroded during periods of higher runoff contain appreciable amounts of the remaining hydrocarbons. The dilution hypothesis applies more aptly to the October data than to the December concentrations.

## 5.3 SUMMARY

In the lower Green River the transport of suspended particulates in October were conserved. In December the outfall contributed only 32% of the gain in suspended matter transport between Stations 2B and 3, indicating that resuspension of bottom sediments and erosion of the riverbank contributed significantly to the increased suspended load. Calculations of the hydrocarbon transports showed deficits for all alkanes and the UCM in October and for most of the paraffins in December. During both sampling periods the outfall theoretically contributed more toward the transports of the heavy, even-carbon compounds than toward the plant wax constituents measured at Station 3.

Table 14. A comparison of measured and calculated hydrocarbon concentrations at Station 2B in October and December (1978), assuming that only dilution with pristine suspended material is occurring in the upper Green River.

| October | December |
|---|---|
| $D_1 = 11.02\ m^3/sec$ | $D_1 = 32.31\ m^3/sec$ |
| $D_{2B} = 12.52\ m^3/sec$ | $D_{2B} = 36.82\ m^3/sec$ |
| $P_1 = 3.0\ g/m^3$ | $P_1 = 5.4\ g/m^3$ |
| $P_{2B} = 5.4\ g/m^3$ | $P_{2B} = 11.5\ g/m^3$ |

|  | Station 2B |  | Station 2B |  |
|---|---|---|---|---|
| Hydrocarbons | Calculated Concentrations (μg/g) | $\frac{\text{Calculated}}{\text{Measured}}$ (%) | Calculated Concentrations (μg/g) | $\frac{\text{Calculated}}{\text{Measured}}$ (%) |
| 15 | 1.33 | 22 | 0.36 | 24 |
| 16 | 0.35 | 11 | 0.21 | 14 |
| 17 | 7.11 | 80 | 0.61 | 27 |
| Pr | 0.28 | 18 | 0.31 | 23 |
| Phy | 0.13 | 24 | 0.28 | 31 |
| 25 | 6.42 | 118 | 4.31 | 65 |
| 26 | 0.70 | 99 | 0.35 | 56 |
| 27 | 8.23 | 103 | 5.62 | 68 |
| 28 | 0.92 | 177 | 0.32 | 56 |
| 29 | 5.29 | 79 | 6.52 | 86 |
| 30 | 0.73 | 83 | 0.38 | 58 |
| 31 | 3.64 | 60 | 7.63 | 113 |
| 32 | 0.60 | 207 | 0.30 | 86 |
| UCM | 25.38 | 22 | 97.17 | 80 |

The calculated hydrocarbon deficits are not likely the result of biological modification occurring within the outfall pipe or river. The apparent loss of hydrocarbons may be attributable to an overestimate of the suspended hydrocarbons in the effluent, a result of filtration. Glass fiber filters are known to adsorb dissolved organics and to retain particles smaller than their nominal mesh size. Results of a single experiment showed that concentrations of n-alkanes extracted from filter samples of a bulk METRO effluent sample were an average of 1.4 times greater than concentrations in the centrifuge sample. However, the deficits of most compounds (especially the heavier hydrocarbons) remain significant despite an incorporation of this factor into the budget calculation. Flocculation and subsequent deposition of organic matter as the effluent mixes with the river water would provide a sink for these compounds.

Dilution appeared to play a substantial role in controlling the concentrations of heavy paraffins between Stations 1 and 2B in October. Effects of dilution appeared somewhat less pronounced in December indicating that the sediments eroded during this period of high discharge contained concentrations of hydrocarbons comparable to the ambient levels measured at Station 1. The volatile fraction and the UCM were insignificantly affected by dilution (except $C_{17}$ in October). Surface runoff was probably the major source of the low-molecular-weight compounds and the UCM.

# 6.0 SEASONAL VARIATIONS

## 6.1 NORMAL ALKANE CONCENTRATIONS

Figure 17 summarizes the seasonal and spatial hydrocarbon distributions for all centrifuge sediment samples. December samples at all three stations displayed minimal concentrations of those hydrocarbons produced by aquatic organisms, namely $C_{15}$ and $C_{17}$. The decrease in light and the concomitant hiatus in biological activity during winter are responsible for the loss of these compounds. Station 2 exhibited the precipitous decrease in $C_{17}$ between the July and October samplings

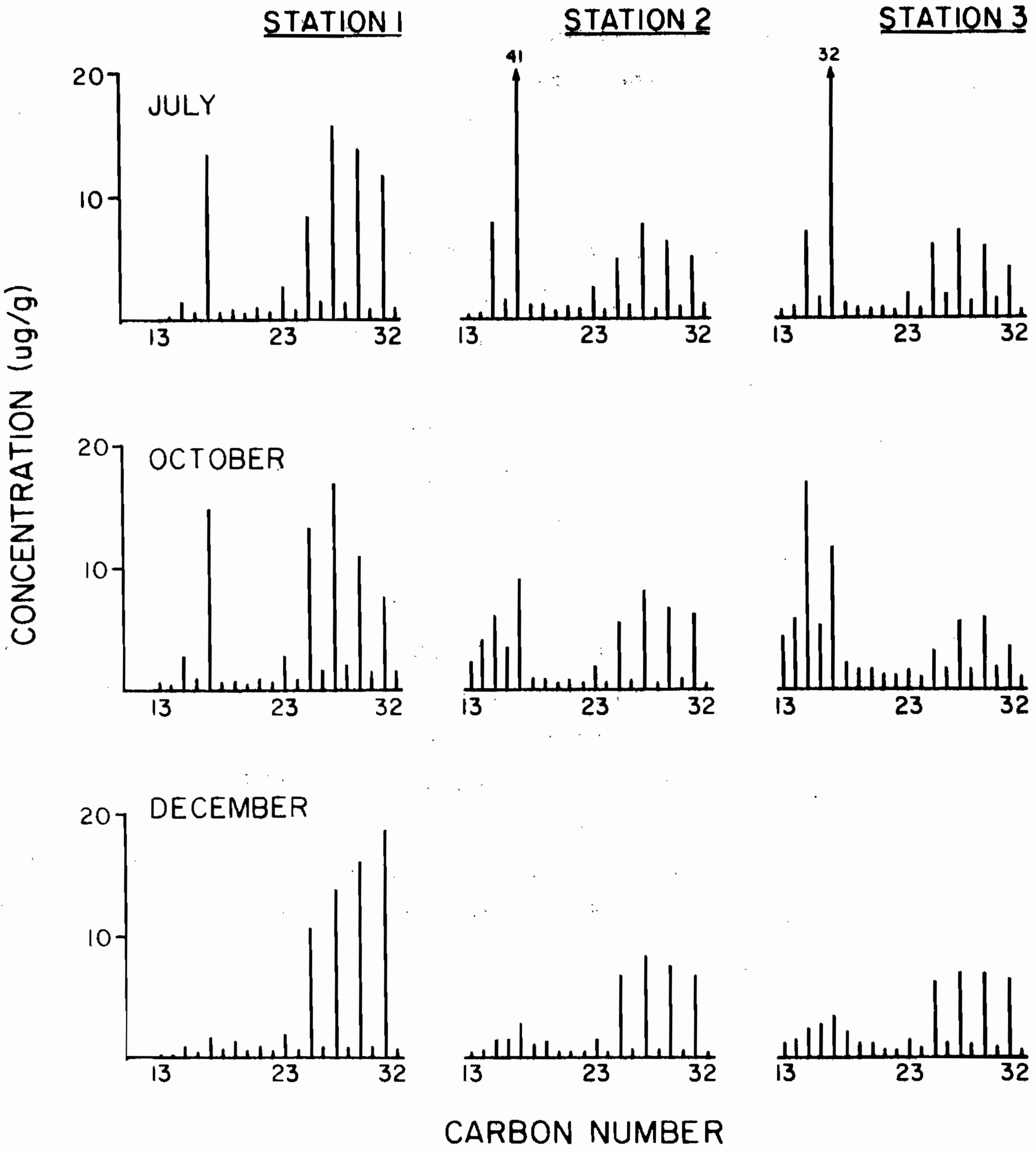

Figure 17. Summary figure displaying concentrations of the normal paraffins associated with Green River suspended matter in 1978.

while Station 3 showed a reversal in the $C_{17}$-$C_{15}$ dominance over the same period, possibly reflecting relative changes in the dominant populations providing these compounds. Both of these stations displayed increased concentrations of $C_{13}$, $C_{14}$, and $C_{16}$ from summer to fall. Bridge and highway runoff would be a likely source of these low-molecular-weight compounds; however, October received less precipitation than any other month in 1978 (Table 1). These changes could also be the result of microbial activity. The concentrations of all low-molecular-weight compounds decreased from October to December, accompanying increases in suspended loads.

The heavy hydrocarbons were consistently dominated by the plant wax constituents during the three sampling periods. Stations 2 and 3 showed little seasonal change in concentrations of these compounds. Station 1 in December was an exception to this generalization, displaying a stepwise increase in the heavy, odd-carbon paraffins to a maximum at $C_{31}$ instead of the normal distribution centered about $C_{27}$ that characterized July and October samples. This may be a reflection of seasonal differences in plant waxes available for scavenge by runoff.

## 6.2 COMPOSITIONAL PARAMETERS

Ancillary information and diagnostic parameters are summarized in Table 15 for a seasonal comparison. TSM concentrations at the three stations showed minima in October (again, repercussions of the low rainfall) and maxima in December. Total particulate carbon increased from summer to fall at all three stations. The autumn to winter trends, however, showed differences. TPC increased to a maximum at Station 1 in December while it showed minima downstream at Stations 2B and 3 simultaneously. The increased suspended loads at Stations 2B and 3 had a proportionately lower carbon content, presumably because of dilution with sediments eroded from the river bank and/or resuspended by turbulence. The threefold increase in river discharge between October and December was likely responsible for the higher concentrations of suspended matter.

Concentrations of total extractables were consistently low in December, another consequence of dilution with suspended matter of lower hydrocarbon concentrations. At Stations 1 and 2B, concentrations of

Table 15. A seasonal summary of selected data and compositional parameters for suspended matter obtained at Stations 1, 2(B), and 3 on the Green River, 1978.

| | JULY | OCTOBER | DECEMBER |
|---|---|---|---|
| | | STATION 1 | |
| TSM (mg/l) | 2.6 | 1.4 | 3.2 |
| TPC (wt.%) | 8.5 | 12.0 | 15.4 |
| Total Extractables (mg/g) | 8.4 | 8.2 | 5.9 |
| Total Saturates (mg/g) | 0.25 | 0.10 | 0.63 |
| $CPI_{14-20}$ | 18.2 | 11.1 | 2.5 |
| $CPI_{20-32}$ | 10.9 | 7.5 | 14.3 |
| | | STATION 2(B) | |
| TSM (mg/l) | 5.1 | 2.2 | 5.1 |
| TPC (wt.%) | 5.4 | 9.3 | 3.1 |
| Total Extractables (mg/g) | 12.7 | 7.1 | 5.4 |
| Total Saturates (mg/g) | 0.56 | 0.30 | 0.41 |
| $CPI_{14-20}$ | 19.8 | 2.6 | 1.6 |
| $CPI_{20-32}$ | 7.0 | 8.0 | 10.2 |
| | | STATION 3 | |
| TSM (mg/l) | 4.1 | 2.5 | 6.9 |
| TPC (wt.%) | 6.6 | 19.4 | 3.6 |
| Total Extractables (mg/g) | 28.7 | 47.4 | 17.4 |
| Total Saturates (mg/g) | 1.1 | 2.0 | 0.7 |
| $CPI_{14-20}$ | 11.1 | 3.0 | 1.0 |
| $CPI_{20-32}$ | 3.9 | 2.6 | 5.0 |

total extractables were highest in July. Station 3 exhibited a maximum in October, possibly because outfall effluent particulates comprised the greatest proportion of the total riverine suspended matter during this period. (Note that this was not reflected in maximum concentrations of individual alkanes.) Gravimetric determinations of the saturate fractions were lowest in October at Stations 1 and 2B, yet highest at Station 3 during this period. Again the contribution of the outfall to the river in October may be responsible for the high values at Station 3. The negative correlation of individual alkanes with total saturates at Station 3 might indicate that the outfall is a more significant source of the unidentified or unresolved components in the "saturate" fraction than of the individual n-alkanes themselves.

The decrease in $CPI_{14-20}$ values from summer to winter at all stations reflected the decline of the algal production of $C_{15}$ and $C_{17}$. The $CPI_{20-32}$ values were highest in December indicating a winter dominance of the plant wax ensemble. Low values of this parameter were calculated from the October results at Stations 1 and 3. All stations exhibited increasing concentrations of pristane and phytane relative to $C_{17}$ from summer to winter, suggesting that these isoprenoids had a common source not associated with aquatic biological production.

## 6.3 MASS TRANSPORTS

In order to evaluate seasonal changes in hydrocarbon quantities, variations in river discharge and suspended matter concentrations must be taken into account. Table 16 is a summary of selected aliphatic hydrocarbon transports.

Nearly all the high-molecular-weight compounds measured at Stations 1, 2B, and 3 displayed transports in December that were an order of magnitude greater than values obtained at any other period. Only July transports of heptadecane were consistently greater than the December values, a consequence of summer algal growth. The higher winter values are again caused by increased river discharge and greater concentrations of suspended solids injected via runoff, riverbank erosion, and resuspension of bottom sediments. Heavier winter rainfall filtering through mats of decaying vegetation may have contributed significant quantities of hydrocarbons.

Table 16. A seasonal comparison of selected hydrocarbon transports at Stations 1, 2(B), and 3 on the Green River, 1978.

| STATION 1 | JULY | OCTOBER | DECEMBER |
|---|---|---|---|
| Discharge ($m^3$/sec) | 10.3 | 11.0 | 32.0 |
| TSM ($g/m^3$) | 2.6 | 1.4 | 3.2 |
| $C_{15}$ (μg/sec) | 34.6 | 41.9 | 86.0 |
| $C_{16}$ | 7.5 | 11.1 | 53.2 |
| $C_{17}$ | 351 | 223 | 153 |
| $C_{25}$ | 217 | 202 | 1080 |
| $C_{26}$ | 33.5 | 22.0 | 88.1 |
| $C_{27}$ | 416 | 259 | 1400 |
| $C_{28}$ | 35.1 | 28.8 | 78.8 |
| $C_{29}$ | 368 | 166 | 1630 |
| $C_{30}$ | 20.9 | 22.8 | 95.2 |
| $C_{31}$ | 313 | 114 | 1900 |
| $C_{32}$ | 22.2 | 18.8 | 74.8 |
| STATION 2(B) | | | |
| Discharge ($m^3$/sec) | 11.8 | 12.4 | 37.3 |
| TSM ($g/m^3$) | 5.1 | 2.2 | 5.1 |
| $C_{15}$ (μg/sec) | 468 | 163 | 291 |
| $C_{16}$ | 75.8 | 90.6 | 293 |
| $C_{17}$ | 2470 | 242 | 432 |
| $C_{25}$ | 283 | 148 | 1260 |
| $C_{26}$ | 49.9 | 19.4 | 118 |
| $C_{27}$ | 457 | 219 | 1580 |
| $C_{28}$ | 32.5 | 14.2 | 108 |
| $C_{29}$ | 363 | 183 | 1450 |
| $C_{30}$ | 34.3 | 24.0 | 124 |
| $C_{31}$ | 304 | 166 | 1280 |
| $C_{32}$ | 69.8 | 7.9 | 66.6 |

Table 16 (Continued)

| STATION 3 | JULY | OCTOBER | DECEMBER |
|---|---|---|---|
| Discharge ($m^3$/sec) | 13.3 | 13.4 | 42.0 |
| TSM ($g/m^3$) | 4.1 | 2.5 | 6.9 |
| $C_{15}$ (μg/sec) | 380 | 559 | 753 |
| $C_{16}$ | 90.0 | 156 | 794 |
| $C_{17}$ | 1760 | 382 | 959 |
| $C_{25}$ | 327 | 111 | 1780 |
| $C_{26}$ | 101 | 53.3 | 333 |
| $C_{27}$ | 383 | 185 | 1960 |
| $C_{28}$ | 66.0 | 54.9 | 354 |
| $C_{29}$ | 314 | 194 | 1950 |
| $C_{30}$ | 83.4 | 48.4 | 287 |
| $C_{31}$ | 221 | 118 | 1860 |
| $C_{32}$ | 33.8 | 34.0 | 185 |

The October data pose a unique case for interpretation. Transports of $C_{27}$, $C_{29}$, and $C_{31}$ at Station 1 were lowest in October. Stations 2B and 3 also exhibited reduced transports in the fall for most hydrocarbons, between $C_{25}$ and $C_{32}$. These results reflect the anomalous weather conditions experienced in October 1978. The rainfall (Table 1) in October was comparable to the low values measured in June. River discharges in July and October were similar (Table A-1) and the suspended load measured in October was less than that of July (Table A-2). A combination of these factors is responsible for the low transports observed at all stations in October.

## 6.4 SUMMARY

Some seasonal trends are shared by all stations. TSM concentrations are highest in December at all three stations. This corresponded to reduced concentrations of POC at Stations 2 and 3 (suggesting erosion of sediments downstream) and a POC maximum at Station 1. Most stations showed greatest concentrations of $C_{15}$ and $C_{17}$ in July and then dramatic dropoffs in these aquatic biological hydrocarbons by December. Consequently $CPI_{14-20}$ values are highest in July. The $CPI_{20-32}$ results at all stations are greatest in December when plant wax constituents were abundant. Although the lowest concentrations of hydrocarbons were obtained in December, the transports of all n-alkanes except $C_{17}$ were highest in winter. Transports of a number of compounds within the range from $C_{18}$ to $C_{32}$ were lowest in October. Low rainfall and subsequent low river discharge and TSM concentrations were probably responsible for these observations.

# 7.0 AROMATIC HYDROCARBONS

## 7.1 GENERAL DISCUSSION

As a part of the systematic survey of suspended hydrocarbons in the Green-Duwamish River system, aromatic hydrocarbons were extracted and separated from the paraffins as described in section 3.5. The chromatograms were exceedingly complex, showing major components eluting at regular retention indices. Because it was unlikely that these compounds were polynuclear aromatic hydrocarbons (PAH), the extracts obtained in October were further chromatographed on a column of Sephadex®. Whereas the complexity of the subsequent chromatograms was reduced, large component interference persisted and positive identification of some PAH remained ambiguous. In a final effort to determine whether any PAH were present, three samples were selected for detailed GC-MS analysis at the Institute of Geophysics and Planetary Physics at UCLA. The samples were Metro effluent filters, December Sample #2; October suspended matter, Station 3, Sephadex® cut; and December suspended matter, Station 3, first triplicate.

Initially the samples were scanned for the usual petroleum aromatics by parent ion. This gave no quantitative information but verified the presence of the following compounds, most of them in trace amounts:

p-, m-, o-xylenes
trimethyl benzenes
indan
naphthalene
methyl naphthalenes
tetramethylbenzene
biphenyl
acenaphthene
fluorene
cadalene
phenanthrene
benz (k) fluoranthene
benz (e) pyrene
benz (a) pyrene
methyl phenanthrenes
dimethyl phenanthrenes
fluoranthene
pyrene
retene
dibenzothiophenes
methyldibenzothiophenes
benz (g, h, i) fluoranthene
benz (a) anthracene
chrysene
binaphthyl
perylene
ananthrene
benz (g, h, i) perylene
coronene

Many of these aromatic compounds appeared to be eluting near the large peaks, although not as visible shoulders on the GC traces. The actual mass spectra of the major peaks comprising each of the three samples were obtained next. Compounds were identified by comparison with spectra in the <u>EPA/NIH Mass Spectral Data Base</u> (Heller and Milne, 1978). The predominant compounds were unambiguously methyl esters of even-carbon fatty acids (FAME). Fatty acids of higher plants and animals exhibit an even-carbon preference for carbon chains between 14 and 22 atoms long. Chain lengths of 16 and 18 carbon atoms predominate (Lehninger, 1975).

In the December sediment and Metro sample, two heavier compounds were tentatively identified as esters: 9-hexadecenoic acid, tetradecyl ester (HATE); and 9-hexadecenoic acid, hexadecyl ester (HAHE). Four other compounds were identified as possible esters: dodecanoic acid, tetradecyl ester (DATE); tetradecanoic acid, tetradecyl ester (TATE); tetradecanoic acid, hexadecyl ester (TAHE); and oleic acid, hexadecyl ester (OATE). For each of these compounds, the abundance of the major ion indicated in the data base was far greater than the abundance shown by the UCLA spectra. Nonetheless, these peaks have been assigned the abbreviations given above (Figures 18, 20, Table 18). Many of the unidentified major peaks in the three samples display spectral characteristics similar to these heavier compounds. Note that these heavy "esters" show an even-carbon preference for acids between 12 and 18 carbon atoms long.

The extraction technique employed here did not include saponification or methylation, thus, the recovery of the fatty acids was probably far from complete. Partial methylation of naturally occurring fatty acids apparently occurred inadvertently during the Soxhlet® extraction with methanol and methylene chloride. These compounds should have been partitioned during the separatory silica gel chromatography.

## 7.2 TOTAL "AROMATICS"

The concentrations of the "aromatic" fractions, which include a partial recovery of the fatty acids as methyl esters, are reported in Table 17. Analogous data for October are not available because these extracts were chromatographed on Sephadex® prior to gravimetry.

Total "aromatics" increased in July 1978, from 0.29 mg/g at Station 1 to 2.34 mg/g at Station 3. Values in December fell within the same range, however, the lowest concentration was measured at Station 2B (0.40 mg/g). The highest concentration in December was measured at Station 3 ($\bar{x}$ = 1.85 mg/g).

Concentrations of the total "aromatic" fractions in the Metro effluent sample should be viewed cautiously since recoveries were lower than usual. Values ranged from 30 mg/g to 60 mg/g, or approximately 10-100 times greater than those concentrations associated with riverine suspended matter.

Table 17. Concentrations of the total "aromatic" hydrocarbon fractions extracted from suspended matter collected from the Green River and Renton Metro effluent in 1978.

| | July (mg/g) | October (mg/g) | December (mg/g) |
|---|---|---|---|
| Station 1 | 0.29 | ---- | 0.69 |
| Station 2(B) | 0.45 | ---- | 0.40 |
| Station 3 | 2.34 | ---- | 1.59<br>2.12 |
| Metro Effluent | ---- | 28.2 | 35.5<br>42.9<br>61.8 |

## 7.3 INDIVIDUAL COMPONENTS

Figures 18, 19, and 20 show the chromatographic traces of the three samples sent to UCLA for GC-MS analysis. Major esters are identified as well as a few of the aromatic compounds common to crude oil and refined products. Brackets denote the approximate elution temperatures of the aromatics, some of which are coeluting with esters and other compounds.

In the hope that some knowledge may be gleaned from these samples, Table 18 lists the major compounds and their approximate concentrations. Some petroleumlike aromatics are included although they may be coeluting with other unidentified compounds. They nonetheless provide a rough estimate of the concentrations found on suspended matter in the Green River. The esters have been quantified roughly by adopting the response factor of the PAH in the aromatic standard (Table 6) which has a retention index closest to the ester of interest.

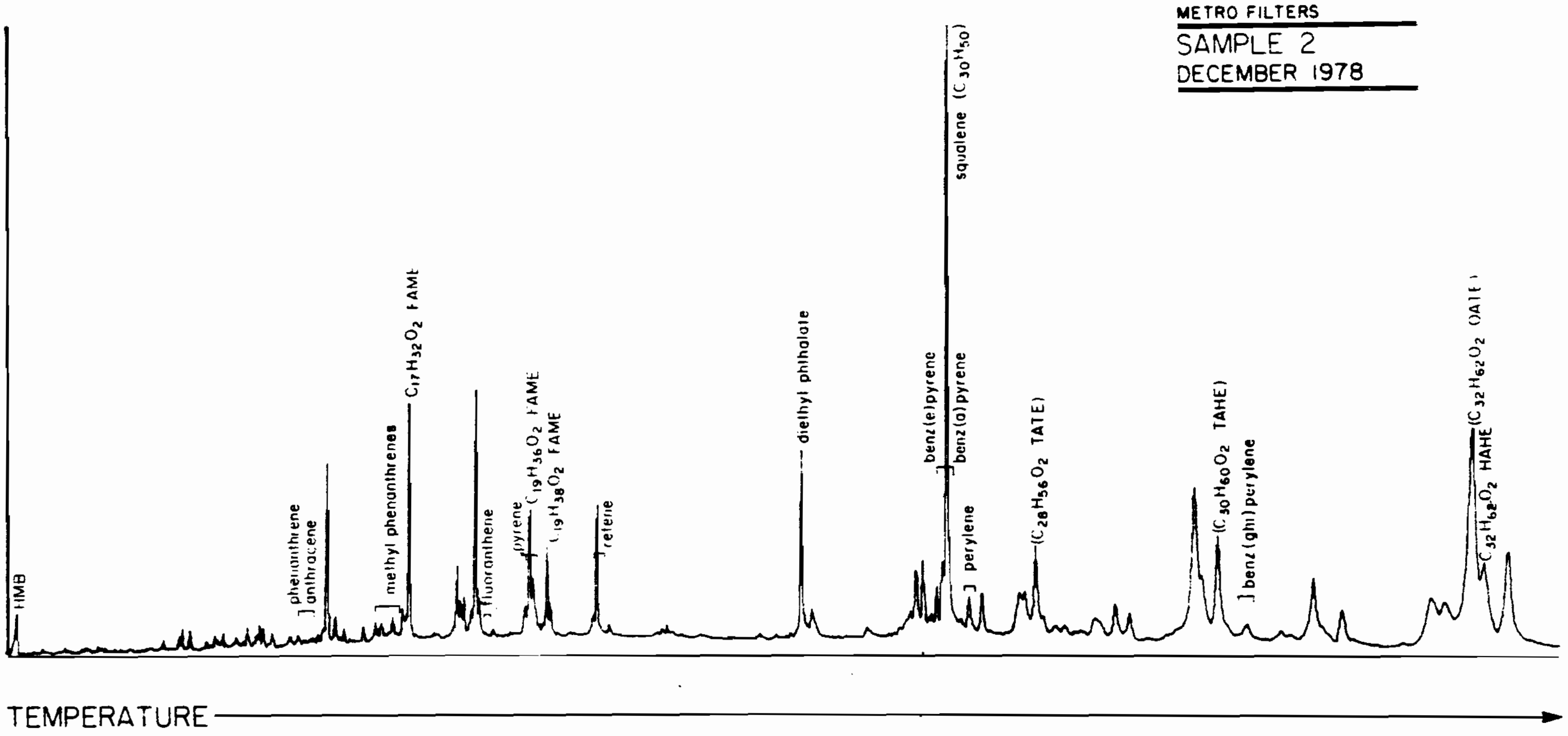

Figure 18. Gas chromatogram of the "aromatic" fraction associated with suspended solids in the Renton Metro effluent, Sample #2, December 1978. Compound abbreviations are defined in Section 7.3.

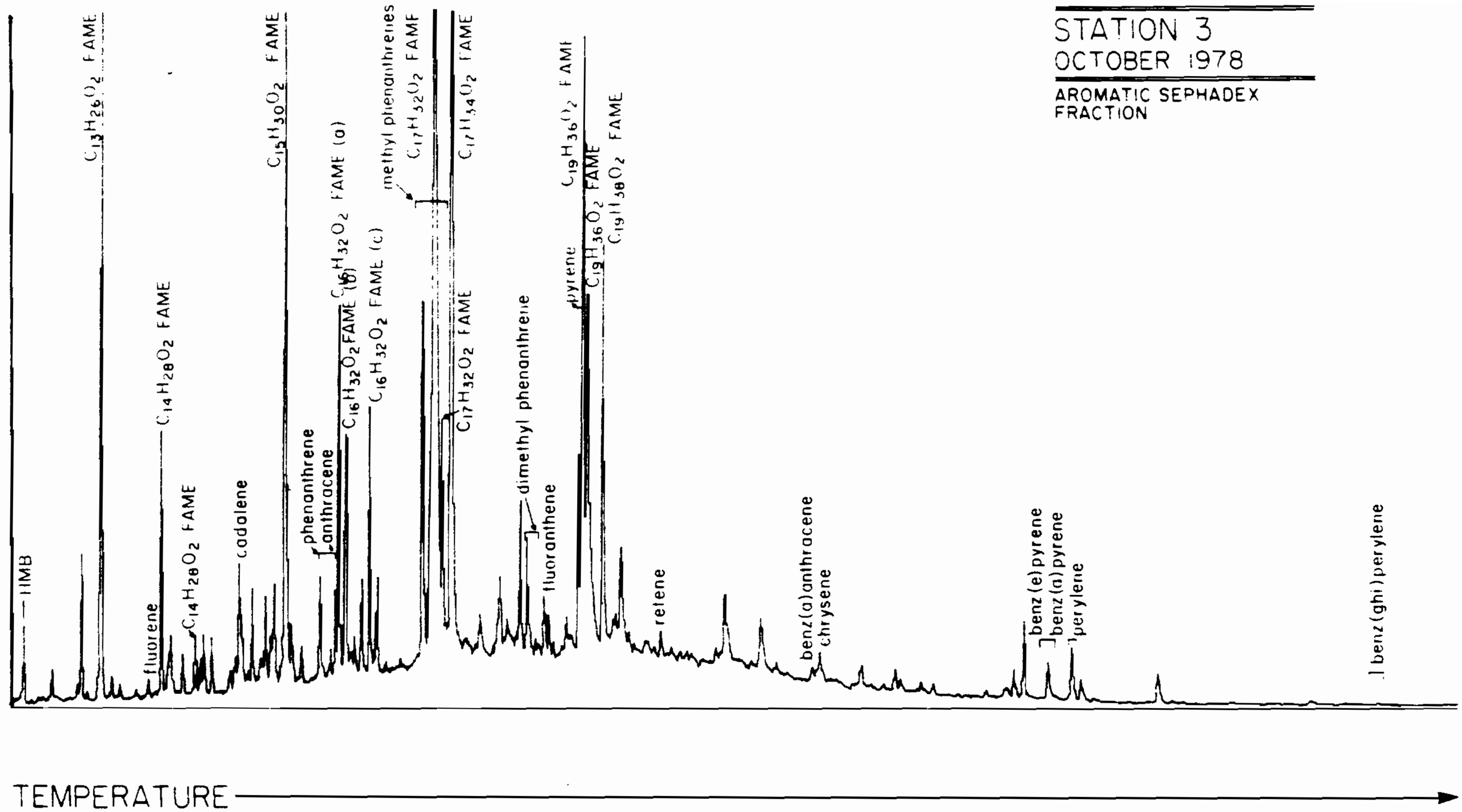

Figure 19. Gas chromatogram of the "aromatic" fraction extracted from suspended sediment retrieved at Station 3 in October 1978. Abbreviations of compounds are defined in Section 7.3.

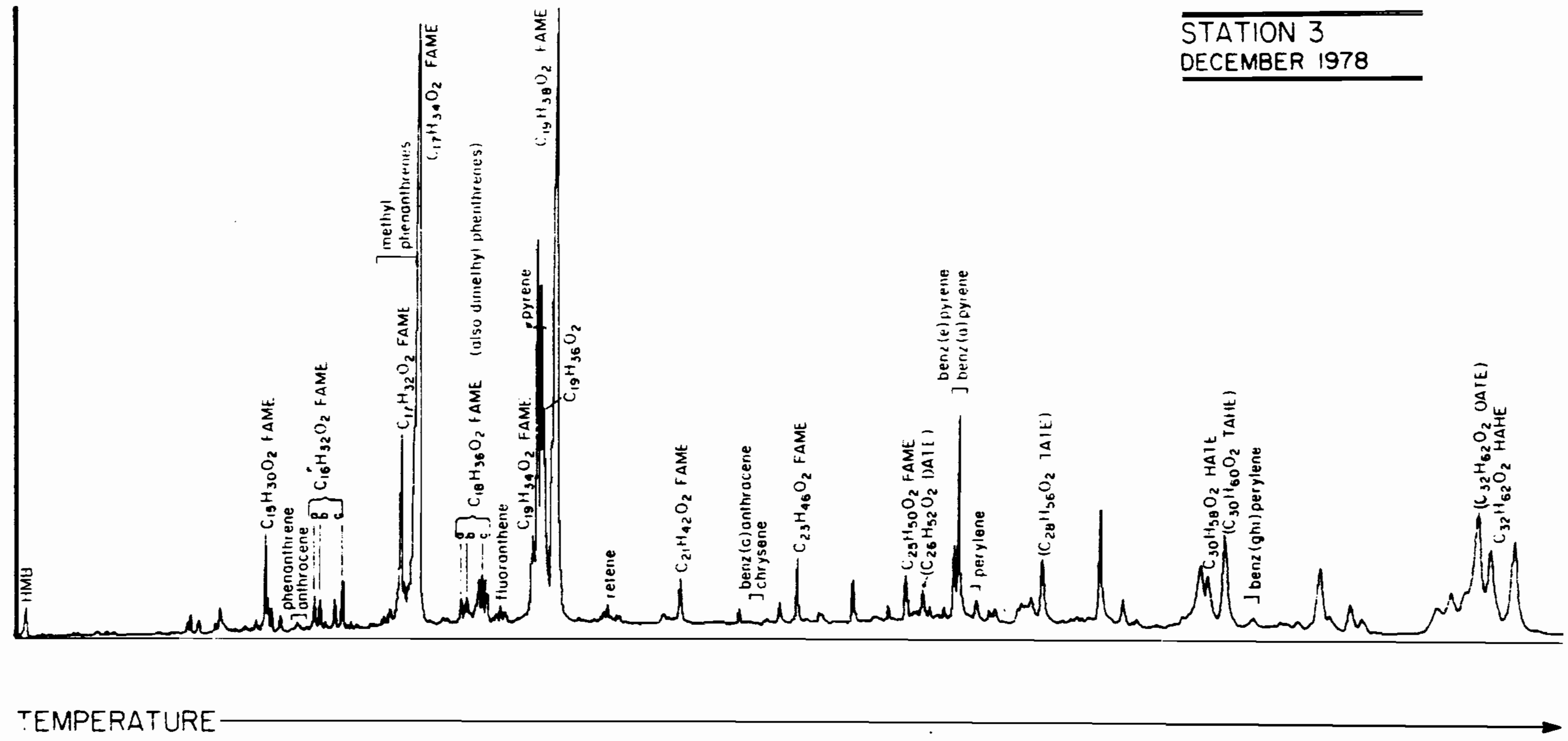

Figure 20. Gas chromatogram of the "aromatic" fraction extracted from suspended sediment retrieved at Station 3 in December 1978. Abbreviations of compounds are defined in Section 7.3.

Table 18. Approximate concentrations of the aromatics and fatty-acid esters extracted from suspended solids retrieved from the Green River and Renton Metro effluent, 1978.

| | Effluent Filters December Sample #2 (µg/g) | October Station 3 Sephadex® Cut (µg/g) | December Station 3 Triplicate 1 (µg/g) |
|---|---|---|---|
| $C_{13}H_{26}O_2$ FAME | ---- | 1.68 | ---- |
| fluorene | ---- | 0.02 | ---- |
| $C_{14}H_{28}O_2$ FAME (a) | ---- | 0.42 | ---- |
| $C_{14}H_{28}O_2$ FAME (b) | ---- | 0.12 | ---- |
| cadalene | ---- | 0.16 | ---- |
| $C_{15}H_{30}O_2$ FAME | ---- | 4.34 | 1.37 |
| $C_{16}H_{32}O_2$ FAME (a) | ---- | 0.73 | 0.41 |
| $C_{16}H_{32}O_2$ FAME (b) | ---- | 0.50 | 0.43 |
| $C_{16}H_{32}O_2$ FAME (c) | ---- | 0.56 | 0.76 |
| $C_{17}H_{32}O_2$ FAME (a)<br>methyl phenanthrene | 70.0 | 7.52 | 4.27 |
| $C_{17}H_{32}O_2$ FAME (b) | ---- | 0.49 | ---- |
| $C_{17}H_{34}O_2$ FAME | ---- | 6.29 | 28.1 |
| $C_{18}H_{36}O_2$ FAME (a) | ---- | ---- | 0.36 |
| $C_{18}H_{36}O_2$ FAME (b) | ---- | ---- | 0.50 |
| $C_{18}H_{36}O_2$ FAME (c) | ---- | ---- | 0.83 |
| fluoranthene | ---- | 0.15 | ---- |
| $C_{19}H_{34}O_2$ FAME | ---- | ---- | 1.61 |

Table 18 (continued)

| | | | |
|---|---|---|---|
| $C_{19}H_{36}O_2$ | 41.6 | 0.60 | 2.35 |
| pyrene | | | |
| $C_{19}H_{36}O_2$ FAME (b) | ---- | 0.25 | ---- |
| $C_{19}H_{38}O_2$ | 19.4 | 0.49 | 20.5 |
| retene | ---- | 0.08 | 0.52 |
| chrysene | ---- | 0.15 | ---- |
| $C_{21}H_{42}O_2$ FAME | ---- | ---- | 1.45 |
| $C_{23}H_{46}O_2$ FAME | ---- | ---- | 2.97 |
| $C_{25}H_{50}O_2$ FAME | ---- | ---- | 1.94 |
| ($C_{26}H_{52}O_2$ DATE) | ---- | ---- | 1.76 |
| squalene | 335 | ---- | ---- |
| benz(e)pyrene | ---- | 0.04 | 2.15 |
| benz(a)pyrene | ---- | 0.06 | ---- |
| perylene | (32.9) | 0.01 | 0.90 |
| ($C_{28}H_{56}O_2$ TATE) | 80.6 | ---- | 2.99 |
| $C_{30}H_{58}O_2$ HATE | ---- | ---- | 4.19 |
| ($C_{30}H_{60}O_2$ TAHE) | 148 | ---- | 7.11 |
| benz(g,h,i)perylene | 53.2 | ---- | 1.92 |
| ($C_{32}H_{62}O_2$ OATE) | 859 | ---- | 21.0 |
| $C_{32}H_{62}O_2$ HAHE | 187 | ---- | 9.38 |
| | | | |
| Sample size | 62.3 mg | 0.95 g | 1.70 g |

The Metro effluent filter, Sample #2, gave the highest aromatic and fatty-acid concentrations of the three samples. The GC-MS scan indicated a "trace" of perylene; the value, 33 μg/g, may be an overestimate. A relatively small amount of benz (g, h, i) perylene, 53 μg/g, is also reported. The methyl esters of only three fatty acids predominated: hexadecenoic acid (16:1), octadecenoic or oleic acid (18:1), and octadecanoic acid (18:0). The major fatty acids in waste water are usually 16:0, 18:0, and 18:1 (Farrington and Quinn, 1973, and references therein). Sources of these fatty acids include fecal matter and kitchen wastes (animal fats and vegetable oils). Concentrations of 16:0 in waste waters analyzed by Farrington and Quinn (1973) varied from 0.26 mg/l to 12.8 mg/l. Approximately 3.6 liters of effluent were filtered to obtain the solids for Sample #2 in December. Concentrations of the three fatty-acid methyl esters in this sample ranged from 0.3 μg/l to 1.2 μg/l; three orders of magnitude less than the values reported for 16:0 by Farrington and Quinn (1973). The methylation of fatty acids was obviously far from complete. Squalene, an isoprenoid of 30 carbon atoms and the precursor of sterols, was a dominant compound in the Renton Metro effluent. The heavier esters were approximately ten times more abundant than the methyl esters. Diethyl phthalate, a compound used in the manufacture of plastics, was a contaminant found in both the sample and the filter blank.

Although concentrations are given for the October sample at Station 3, the fatty acids were only partially recovered from the Sephadex® column. Note that fatty-acid methyl esters beyond $C_{19}$ have been eliminated and none of the heavy esters (TATE, etc.), present in the other samples, are evident here. The dominant fatty-acid methyl esters (Table 18) were 14:0 (4.34 μg/g), 16:1 (7.52 μg/g), and 16:0 (6.29 μg/g). Concentrations of a few aromatics are tentatively reported. Fluoranthene and cadalene (1, 6-dimethyl-4-isopropyl naphthalene) are present at concentrations of ~ 150 ng/g. Quantities of benz(a)pyrene and perylene (both known to be present, but identified here by retention time only) were approximately 60 ng/g and 10 ng/g, respectively. Benz(e)-pyrene and chrysene were identified by their mass spectra. Calculated concentrations were 40 ng/g and 150 ng/g, respectively.

The aromatic portion of the December sediment sample recovered at Station 3 is the most complex of the samples. Benz(a)pyrene is coeluting with a large unknown compound. The concentration of benz(e)pyrene is reported (2.15 μg/g) although the spectrum of the peak was not available for verification. Perylene and benz (g, h, i) perylene are reported at concentrations of 0.90 μg/g. Retene (7-isopropyl-1-methyl phenanthrene) was also present (0.52 μg/g). The methyl esters of two fatty acids, 16:0 (28.1 μg/g) and 18:0 (20.5 μg/g), were dominant compounds as was OATE (21.0 μg/g).

## 7.4 SUMMARY

The aromatic fraction extracted from suspended matter samples was complicated by the presence of fatty-acid esters. GC-MS identified many of these compounds unambiguously and confirmed the presence of petroleum aromatics from xylene through coronene. Gravimetric determinations of the total "aromatics" (which included the fatty-acid esters) varied from 0.3 mg/g to 2.3 mg/g in river samples with the highest concentrations measured at Station 3. Concentrations of total "aromatics" associated with Renton sewage effluent ranged from 28 to 62 mg/g.

Quantities of individual fatty acids were approximated using PAH response factors. The major methylated fatty acids in the effluent sample were 16:1, 18:1, and 18:0. Fatty acids from 14:0 to 18:0 were present in the October and December sediment samples at Station 3. Heavy compounds tentatively identified as tetradecyl and hexadecyl esters of the even-carbon fatty acids ($C_{12}$ - $C_{18}$) were also major compounds in the December effluent and sediment. The compound labelled oleic acid, tetradecyl ester (OATE) was most abundant.

The aromatic hydrocarbons retene, benz(e)pyrene, perylene, and benz (g, h, i) perylene were present in concentrations from 0.5 to 2.2 μg/g in the December sample and concentrations less than 0.08 μg/g in October. Concentrations of perylene and benz (g, h, i) perylene in the effluent sample were approximately 40 μg/g. Chrysene and fluoranthene were present in greatest amounts in the October sample (~0.15 μg/g).

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# APPENDIX A

This appendix contains data to further describe the Green River and the precision of the C-H-N method.

Tables A-1 and A-2 present discharge and suspended solid concentrations for the Green River in 1978. Tables A-3 and A-4 present analytical and sampling precisions of the C-H-N method.

Table A-1. Mean monthly discharge at two stations on the Green River, 1978 (USGS, 1978 and USGS, personal communication). See Figure 2 for a graphic presentation of this data.

|  | Near Auburn Kilometer 51.5 | At Tukwila Kilometer 20.0 |
|---|---|---|
| Month | $m^3$/sec | $m^3$/sec |
| January | 34.1 | 44.4 |
| February | 31.9 | 39.0 |
| March | 31.4 | 35.2 |
| April | 35.1 | 38.8 |
| May | 26.6 | 28.9 |
| June | 19.1 | 21.3 |
| July | 11.4 | 13.2 |
| August | 8.7 | 10.0 |
| September | 15.5 | 18.7 |
| October | 12.7 | 14.2 |
| November | 34.8 | 35.4 |
| December | 54.5 | 58.6 |

Table A-2. Concentrations of suspended solids in the Green River at Metro Stations A319, 311, and 3106 (Municipality of Metropolitan Seattle, 1978a) corresponding approximately to Stations 1, 2B, and 3, respectively, occupied in this study. Concentrations are in mg/l.

| Date | Station A319 | Station 311 | Station 3106 |
|---|---|---|---|
| 01/10/78 | - | 38.5 | 41.0 |
| 01/24/78 | 10.4 | 14.4 | 14.4 |
| 02/22/78 | 3.2 | 8.2 | 10.0 |
| 03/14/78 | 4.0 | 3.7 | 3.0 |
| 03/28/78 | - | 94.0 | 81.0 |
| 04/11/78 | 5.0 | 6.6 | 6.8 |
| 04/25/78 | 2.0 | 2.7 | 2.0 |
| 05/09/78 | 5.0 | 6.5 | 5.0 |
| 05/22/78 | 3.2 | 2.4 | 2.8 |
| 06/13/78 | 5.5 | 3.5 | 6.5 |
| 06/27/78 | 2.6 | 4.8 | 8.4 |
| 07/11/78 | 5.1 | 4.0 | 4.3 |
| 07/25/78 | 4.5 | 7.0 | 5.9 |
| 08/08/78 | 3.7 | 3.2 | 4.8 |
| 08/23/78 | 3.0 | 4.8 | 7.5 |
| 09/13/78 | - | 9.5 | 13.0 |
| 09/27/78 | 8.5 | 7.3 | 10.7 |
| 10/10/78 | 4.0 | 5.0 | 4.5 |
| 10/23/78 | - | 4.0 | 6.2 |
| 11/07/78 | 15.3 | 18.0 | 19.3 |
| 11/21/78 | 7.6 | 9.0 | 9.0 |
| 12/06/78 | 39.0 | 48.0 | 49.0 |
| 12/20/78 | - | 7.5 | 7.8 |

Table A-3. Analytical precision of the micro-Dumas method for determining TPC and TPN. Chromatographic response factors are based on combustion of known amounts of NBS acetanilide standard containing 10.36% N and 71.09% C by weight.

| Date of Standards | Weight of Standard | Nitrogen in Standard | Carbon in Standard | Nitrogen Response Factor | Carbon Response Factor |
|---|---|---|---|---|---|
| | (μg) | (μg) | (μg) | $[10^4$(mg/area)] | |
| July '78 | 33 | 3.4 | 23.4 | 1.60 | 5.16 |
| | 73 | 7.6 | 51.9 | 1.67 | 5.41 |
| | 126 | 13.0 | 89.6 | 1.58 | 5.23 |
| | 163 | 16.9 | 115.9 | 1.63 | 5.49 |
| | 200 | 20.7 | 142.2 | 1.51 | 5.27 |
| | 276 | 28.6 | 196.2 | 1.34 | 4.76 |
| | 567 | 58.7 | 403.1 | 1.57 | 5.56 |
| | | | Mean = | 1.56 ± 0.11 | 5.27 ± 0.27 |
| October '78 | 117 | 12.1 | 83.2 | 1.30 | 4.14 |
| | 132 | 13.7 | 93.8 | 1.33 | 4.14 |
| | 272 | 28.2 | 193.4 | 1.29 | 4.15 |
| | 282 | 29.2 | 200.5 | 1.38 | 4.40 |
| | 290 | 30.0 | 206.2 | 1.33 | 4.27 |
| | | | Mean = | 1.32 ± 0.03 | 4.22 ± 0.11 |
| December '78 | 44 | 4.6 | 31.3 | 1.99 | 5.75 |
| | 63 | 6.5 | 44.8 | 1.74 | 5.98 |
| | 67 | 6.9 | 47.6 | 1.12 | 3.80 |
| | 78 | 8.1 | 55.5 | 1.14 | 3.78 |
| | 86 | 8.9 | 61.1 | 1.13 | 3.81 |
| | 148 | 15.3 | 105.0 | 1.26 | 4.36 |
| | 149 | 15.4 | 106.0 | 1.13 | 3.98 |
| | 255 | 26.4 | 181.0 | 1.13 | 4.08 |
| | | | Mean = | 1.33 ± 0.34 | 4.45 ± 0.90 |
| Average relative standard deviations | | | | 12% | 9% |

Table A-4. Precision of replicate C-H-N analyses of suspended sediment from lower Cook Inlet, Alaska, employing the same method and instrument used in this study (Gary Massoth, Oceanographer, NOAA/PMEL, personal communication).

| Station/Cast | Sediment Type | No. of Replicates | Carbon | | | Nitrogen | | |
|---|---|---|---|---|---|---|---|---|
| | | | $\bar{X}$ (μg/l) | $\sigma$ | $\sigma/\bar{x}$ (%) | $\bar{X}$ (μg/l) | $\sigma$ | $\sigma/\bar{X}$ (%) |
| CB 9/4 | highly inorganic (1%C) | 5 | 253 | 34 | 14 | 27 | 2 | 9 |
| CB 9/16 | highly inorganic (1%C) | 5 | 188 | 29 | 15 | 19 | 1 | 9 |
| CB 7/20 | organic (10%C) | 6 | 278 | 2 | 1 | 52 | 2 | 3 |
| CB 7/27 | organic (10%C) | 4 | 229 | 59 | 26 | 45 | 8 | 19 |
| CB 1/1 | intermediate (3%C) | 6 | 137 | 45 | 33 | 10 | 2 | 16 |
| CB 1/3 | intermediate (3%C) | 6 | 82 | 24 | 30 | 8 | 2 | 21 |
| Mean relative standard deviation: | | | | | 20 | | | 15 |

# APPENDIX B

Concentrations of alkanes associated with suspended matter retrieved from the Green River and Renton Metro sewage effluent, 1978, are presented in this appendix. Concentrations are based on dry weight of sediment. Table B-1 shows paraffin concentrations based on suspended sediment recovered in July by both centrifugation and glass fiber filters. Hydrocarbon concentrations for centrifuge and filter samples obtained in October are presented in Tables B-2 and B-3. Table B-4 compares centrifuge and filter results for December samples. Alkane concentrations associated with suspended solids (obtained by filtration) in the Renton Metro effluent composites are shown in Table B-5.

Table B-1. Concentrations of alkanes associated with suspended matter in centrifuge and filter samples retrieved from the Green River in July 1978.

| | Centrifuge Samples | | | Filter Samples | |
|---|---|---|---|---|---|
| Hydrocarbon | Station 1 (ng/g) | Station 2 (ng/g) | Station 3 (ng/g) | Station 2 (ng/g) | Station 3 (ng/g) |
| 13 | 40 | 120 | 570 | 1110 | 1410 |
| 14 | 70 | 340 | 850 | 1290 | 1230 |
| 15 | 1290 | 7780 | 6960 | 6050 | 1030 |
| 16 | 280 | 1260 | 1650 | 1900 | 3120 |
| 17 | 13100 | 41000 | 32300 | 32100 | 43170 |
| Pr | 320 | 950 | 3120 | 1750 | 6170 |
| 18 | 410 | 840 | 1120 | 1090 | 2410 |
| Phy | 180 | 490 | 2510 | 570 | 3740 |
| 19 | 600 | 840 | 750 | 660 | 2270 |
| 20 | 210 | 490 | 770 | 504 | 1850 |
| 21 | 630 | 980 | 900 | 1140 | 2340 |
| 22 | 330 | 550 | 620 | 560 | 1600 |
| 23 | 2360 | 2370 | 1990 | 2340 | 4180 |
| 24 | 600 | 560 | 790 | 370 | 1570 |
| 25 | 8120 | 4700 | 5990 | 4400 | 10200 |
| 26 | 1250 | 830 | 1850 | 470 | 2310 |
| 27 | 15540 | 7600 | 7030 | 6740 | 9460 |
| 28 | 1310 | 540 | 1210 | 70 | 3070 |
| 29 | 13730 | 6030 | 5750 | 5250 | 9430 |
| 30 | 780 | 570 | 1530 | 290 | 1430 |
| 31 | 11670 | 5050 | 4060 | 6780 | 7580 |
| 32 | 830 | 1160 | 620 | 1410 | 1670 |

Table B-2. Concentrations of alkanes associated with suspended matter retrieved by centrifugation from the Green River in October 1978.

| Hydrocarbon | Station 1 (ng/g) | Station 2B (ng/g) | Station 3 (ng/g) | Station 3R (ng/g) |
|---|---|---|---|---|
| 13 | 520 | 2270 | 3240 | 5420 |
| 14 | 330 | 4000 | 4660 | 6860 |
| 15 | 2720 | 5960 | 14200 | 19200 |
| 16 | 720 | 3320 | 3710 | 5620 |
| 17 | 14500 | 8870 | 10300 | 12500 |
| Pr | 570 | 1540 | 2890 | 3540 |
| 18 | 580 | 920 | 1480 | 2710 |
| Phy | 260 | 540 | 2300 | 2180 |
| 19 | 620 | 750 | 1340 | 2050 |
| 20 | 320 | 460 | 1410 | 1860 |
| 21 | 780 | 830 | 1280 | 1150 |
| 22 | 520 | 570 | 960 | 1300 |
| 23 | 2720 | 1830 | 1690 | 1570 |
| 24 | 850 | 580 | 1010 | 1060 |
| 25 | 13100 | 5430 | 3320 | 3290 |
| 26 | 1430 | 710 | 1390 | 1790 |
| 27 | 16800 | 8010 | 5420 | 5610 |
| 28 | 1870 | 520 | 1350 | 1930 |
| 29 | 10800 | 6720 | 5490 | 6120 |
| 30 | 1480 | 880 | 1170 | 1720 |
| 31 | 7420 | 6100 | 3440 | 3610 |
| 32 | 1220 | 290 | 940 | 1090 |

Table B-3. Concentrations of alkanes associated with suspended matter retrieved by filtration from the Green River in October 1978. Concentrations of the compounds where N.D. (not detected) appears were below the limits of detection when corrected for blanks.

| Hydrocarbon | Station 1 (ng/g) | Station 2B (ng/g) | Station 3 (ng/g) | Station 3R (ng/g) |
|---|---|---|---|---|
| 13 | 1000 | 3280 | 2050 | 5580 |
| 14 | 4570 | 4700 | 5080 | 12710 |
| 15 | 3250 | 6980 | 22730 | 33250 |
| 16 | 790 | 4240 | 5310 | 16170 |
| 17 | 14390 | 8450 | 20790 | 31880 |
| Pr | 1060 | 1710 | 6450 | 17450 |
| 18 | 670 | 2110 | 3440 | 13510 |
| Phy | 80 | 780 | 4450 | 10340 |
| 19 | N.D. | 690 | 3010 | 11500 |
| 20 | 60 | 1180 | 3030 | 12250 |
| 21 | N.D. | 1080 | 2600 | 10340 |
| 22 | N.D. | 1910 | 2490 | 10540 |
| 23 | 2090 | 2770 | 3120 | 7950 |
| 24 | N.D. | 150 | 1530 | 5530 |
| 25 | 11930 | 7080 | 16120 | 12880 |
| 26 | N.D. | 70 | 2390 | 7540 |
| 27 | 16580 | 11500 | 10650 | 19380 |
| 28 | N.D. | N.D. | N.D. | 2630 |
| 29 | 9470 | 9620 | 12400 | 19960 |
| 30 | N.D. | N.D. | 410 | 2680 |
| 31 | 5440 | 8840 | 10280 | 15660 |
| 32 | N.D. | N.D. | 3010 | 6910 |

Table B-4. Concentrations of alkanes associated with suspended matter in centrifuge and filter samples retrieved from the Green River in December 1978. Concentrations of the compounds where N.D. (not detected) appears were below the limits of detection when corrected for blanks.

| | Centrifuge Samples | | | Filter Samples | |
|---|---|---|---|---|---|
| Hydrocarbon | Station 1 (ng/g) | Station 2B (ng/g) | Station 3* (ng/g) | Station 2B (ng/g) | Station 3 (ng/g) |
| 13 | 190 | 390 | 1230 | N.D. | 910 |
| 14 | 200 | 710 | 1520 | 40 | 1870 |
| 15 | 870 | 1530 | 2600 | 1190 | 3100 |
| 16 | 520 | 1540 | 2740 | 1210 | 2160 |
| 17 | 1490 | 2270 | 3310 | 2350 | 2570 |
| Pr | 750 | 1370 | 2250 | 1630 | 1940 |
| 18 | 540 | 1020 | 2030 | 1520 | 1800 |
| Phy | 690 | 910 | 1250 | 650 | 1010 |
| 19 | 1190 | 1280 | 1200 | 580 | 430 |
| 20 | 520 | 450 | 1040 | 1100 | 1030 |
| 21 | 830 | 510 | 760 | 1360 | 1370 |
| 22 | 500 | 320 | 610 | 160 | 20 |
| 23 | 1820 | 1320 | 1380 | 250 | 3000 |
| 24 | 620 | 480 | 800 | 980 | 1660 |
| 25 | 10500 | 6630 | 6150 | 1250 | 11570 |
| 26 | 860 | 620 | 1150 | 1070 | 1870 |
| 27 | 13700 | 8290 | 6780 | 17270 | 15700 |
| 28 | 770 | 570 | 1220 | N.D. | N.D. |
| 29 | 15900 | 7610 | 6740 | 16400 | 16730 |
| 30 | 930 | 650 | 990 | N.D. | 410 |
| 31 | 18600 | 6740 | 6430 | 15660 | 16900 |
| 32 | 730 | 350 | 640 | 400 | 1060 |

*Mean values of triplicates

Table B-5. Concentrations of alkanes associated with suspended solids recovered via filtration from Renton Metro effluent.

| | OCTOBER | DECEMBER | | |
|---|---|---|---|---|
| | | 1 | 2 | 3 |
| Hydrocarbon | 10/19-20/78 0730-0730 (µg/g) | 12/18-20/78 1800-0600 (µg/g) | 12/20-21/78 1000-0800 (µg/g) | 12/21-22/78 1300-1100 (µg/g) |
| 13 | 17 | 13 | 15 | 10 |
| 14 | 23 | 17 | 15 | 12 |
| 15 | 58 | 19 | 19 | 14 |
| 16 | 16 | 12 | 13 | 10 |
| 17 | 42 | 15 | 14 | 11 |
| Pr | 18 | 17 | 26 | 20 |
| 18 | 14 | 13 | 16 | 13 |
| Phy | 14 | 14 | 22 | 17 |
| 19 | 15 | 11 | 14 | 8 |
| 20 | 16 | 16 | 15 | 8 |
| 21 | 18 | 9 | 12 | 6 |
| 22 | 22 | 12 | 11 | 7 |
| 23 | 23 | 17 | 21 | 7 |
| 24 | 30 | 32 | 24 | 8 |
| 25 | 37 | 48 | 47 | 10 |
| 26 | 54 | 50 | 41 | 13 |
| 27 | 72 | 50 | 112 | 15 |
| 28 | 80 | 47 | 52 | 16 |
| 29 | 105 | 44 | 91 | 21 |
| 30 | 99 | 29 | 36 | 13 |
| 31 | 130 | 34 | 95 | 18 |
| 32 | 102 | 19 | 30 | 8 |
| Volume Filtered (l) | 3.43 | 3.61 | 3.17 | 3.15 |
| Effluent S.S. Concentrations (mg/l) | 8.31 | 17.25 | 12.73 | 12.75 |

# APPENDIX C

## FILTRATION VERSUS CENTRIFUGATION FOR RETRIEVAL OF SUSPENDED HYDROCARBONS

### C.1 GENERAL STATEMENTS

Most studies of interactions between lipids and suspended solids have employed glass fiber filters for the recovery of suspended matter (Van Vleet and Quinn, 1977; Schultz and Quinn, 1977). This study is the first to engage a continuous-flow centrifuge in addition to glass fiber filters for the recovery of suspended hydrocarbons. By comparing the results obtained from these two methods, the variability and the relative bias inherent in each procedure might be determined.

Samples taken during the follow-up field trip in October 1980 showed that Gelman filters recovered 80% of the suspended matter retained by a 0.4μm Nuclepore® filter at Station 1 (Oct. 27, 1980 at 1420) and 56% at Station 3 (Oct. 30, 1980 at 0900). Centrifuge influent and effluent were also passed through glass fiber filters at the latter station. Results showed the centrifuge to be 90% efficient at recovering material retained by a 47 mm Gelman type A-E filter with a nominal mesh size of 0.4μm. The efficiency of the Gelman filter varies greatly. Discharge at Station 1 is relatively constant, but at Station 3 tidal pumping perturbs river flow. Concentration of the suspended load and the size of the particulates fluctuate with these changes in discharge. In addition, any fluctuation in quantity and/or size of particulates expelled in METRO effluent affects recovery efficiency at Station 3.

### C.2 FILTER BLANKS

Contamination is perhaps the most difficult problem to contend with when using glass fiber filters for the collection of suspended hydrocarbons. A description of the methods used to clean the filters, and the magnitudes of the filter blanks are reported in this section. Filters used in July were combusted for 4 hours in a muffle furnace at 400°C. In the field these filters were enclosed in plastic holders (hexane-washed) and suspended material was collected by pressure filtration (14-20 psi) directly from the manifold. Filters for the October and December samplings were cleaned by Soxhlet extraction for 72 hours in 65% $CH_2Cl_2$/35% $CH_3OH$ with a solvent change every 24 hours. Although a filter blank was not run concurrently with the October samples, a combination of the October solvent blank values (unusually high) and the averages of the July, December, and Metro filter blanks were applied to the October data. Suspended matter was collected by vacuum filtration through a glass system during the October and December field excursions.

The average relative contributions of the n-alkanes in the filter blanks to these compounds in filter samples for each station and season are given below. The table includes average percentages for all the n-alkanes ($\overline{\text{Total}}$; $C_{13}$-$C_{32}$), the odd-carbon compounds ($\overline{\text{Odds}}$), and the even-carbon compounds ($\overline{\text{Evens}}$).

| | | $\overline{\text{TOTAL}}$ (%) | $\overline{\text{ODDS}}$ (%) | $\overline{\text{EVENS}}$ (%) |
|---|---|---|---|---|
| July | Station 2 | 40 | 23 | 58 |
| | Station 3 | 33 | 22 | 45 |
| October | Station 1 | 92 | 42 | 142 |
| | Station 2B | 58 | 33 | 83 |
| | Station 3 | 41 | 27 | 56 |
| | Station 3R | 21 | 16 | 27 |
| December | Station 2B | 62 | 39 | 85 |
| | Station 3 | 52 | 33 | 70 |

Contamination from the filters comprised an average of 21% to 92% of each of the n-alkane components. Blanks contributed the greatest proportions of the samples taken at Station 1 for all three seasons. Values decreased monatonically with distance down river. This systematic bias in the contributions of blanks from Stations 1 to 3 reflects the increased amounts of normal alkanes recovered by filtration. Due to the overwhelming predominance of the algal hydrocarbons ($C_{15}$ and $C_{17}$) and the plant wax constituents (odd hydrocarbons, $C_{25}$-$C_{31}$), the blank contributed an average of only 42% (Station 1, October) to 16% (Station 3R, October) of the odd-carbon compounds in each sample. The average value for the even-carbon compounds ranged from 142% (Station 1, October) to 27% (Station 3R, October). The filter blank itself showed little odd- or even-hydrocarbon preference, but was enriched in the n-alkanes, $C_{25}$ through $C_{31}$.

A significant error is associated with a small value that is obtained by subtracting two large numbers of questionable certainty. In addition, the filter results are based on relatively small amounts of suspended matter. The average mass of suspended solids retrieved by three or four filters was 0.076 g, versus an average centrifuge sample size of 1.58 g. Alkane concentrations and intrinsic parameters for both filter and centrifuge samples are compared in the following sections for major disparities.

## C.3 THE NORMAL PARAFFINS

Tables B-1 through B-4 list the concentrations of the individual n-alkanes determined from both filter and centrifuge suspended sediment samples. Concentrations of n-alkanes did not follow a definitive trend favoring either filter or centrifuge samples. At Station 2 in July, filter and centrifuge concentrations were comparable, while filter concentrations at Station 3 were generally greater than the centrifuge quantities. In October, the centrifuge paraffin concentrations at Stations 1 and 2B were similar to the the filter concentrations. Filter concentrations at Station 3 and 3R were at least two times greater than centrifuge quantities. Similar concentrations of volatile components were found at Stations 2B and 3 in December. Filter samples exhibited twice the concentrations of the plant wax hydrocarbons that were measured in the centrifuge samples.

A variety of factors may be responsible for the observed filter to centrifuge disparities. The river is highly variable in time and space, especially the lower river. The relative contributions of surface runoff and outfall discharge change constantly. In addition, tidal excursions caused anomalies at Station 3, and perhaps more subtle change at Station 2B. Figure C-1 shows the tidal cycle superimposed over the sampling itinerary at Stations 2B and 3 for October and December. (Figure 13 is a similar illustration for July.) Samples collected by continuous centrifugation integrate these variations over the sampling period whereas filter samples only represent instantaneous concentrations. Representation of average river conditions by point samples in time is equivocal and should be tested.

## C.4 COMPOSITIONAL CHARACTERISTICS

Table C-1 compares three parameters calculated from centrifuge and filter samples collected concurrently. In most cases the $CPI_{14-20}$ results obtained from centrifuge samples are higher than those obtained from filters. The disparity is greatest in July at both stations and in October at Station 1. Comparing concentrations of individual n-alkanes in these samples, it is apparent that the filters have retained relatively greater amounts of $C_{14}$ and $C_{16}$. Possibly, the odd- and even-carbon compounds of the volatile and heavy fractions arise from different sources; they may be associated with particles of different sizes or densities. In July, for instance, the volatile even-carbon compounds may be associated with a lighter, colloidal or dissolved phase that is readily scavenged by the filters, but not the centrifuge. Such a light colloidal phase would clog filters faster than a heavier particulate phase, further skewing results.

The $CPI_{20-32}$ values on the other hand, are generally higher for the filter samples than for the centrifuge sediment. This bias is mainly a result of the near negligible concentrations of heavy even alkanes in the filter samples after the blank had been subtracted. Again, perhaps the plant wax constituents were associated with finer particulates more easily retained by the filter mesh.

The $\sum_{13}^{31}$ odd/ $\sum_{14}^{32}$ even ratios in July (and less dramatically at Station 3R in October) were significantly higher for the centrifuge sediments

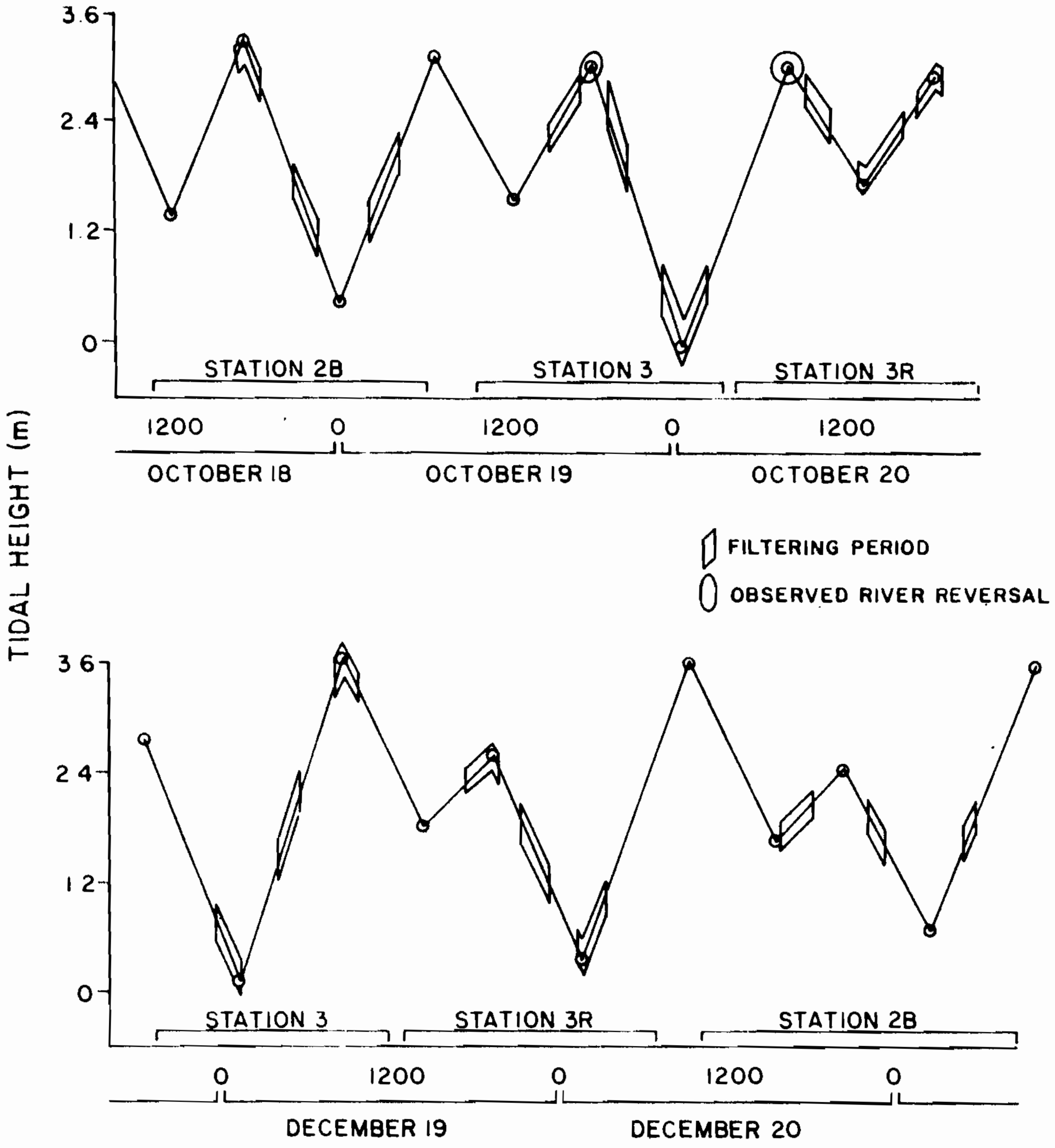

Figure C-1. Tidal amplitudes at Elliott Bay (U.S. Dept. of Commerce, 1978) and the schedules of suspended matter sampling on the Green River in October and December 1978. Observed reversals in river discharge are noted.

than for the filter samples. When coupled with the higher $CPI_{14-20}$ values and the lower $CPI_{20-32}$ results derived for the July centrifuge sediment, it is evident that the odd-carbon preference resides predominantly in the volatile fraction of these summer samples. At all other stations the odd/even ratios for the filters were greater than those obtained from the centrifuge sediment. This may be a reflection of seasonal variations in particulate size and simultaneously, a seasonal change in the hydrocarbons associated with these particulates. However, in light of the variabilities calculated for the duplicate samples obtained in October (averaging 25% for the individual alkanes but ranging from 2% to 59%), the differences noted here may not be significant.

## C.5 SUMMARY

Filter blanks comprised an overall average of 50% of each individual n-alkane measured in the filter samples. The blanks contributed an average of 29% of the odd-carbon compounds and 71% of the even alkanes reflecting the greater abundance of algal and plant wax constituents measured at most sites. In all cases, alkanes associated with the filter blanks contributed relatively less toward hydrocarbon quantities as one proceeded downriver due to the increased suspended hydrocarbon concentrations.

Concentrations of the individual n-alkanes determined from the filter samples were usually greater than or equal to the concentrations measured in the centrifuge samples. Discrepancies are attributed to variations in surface runoff, outfall discharge, and tidal pumping, each of which varies on a scale of less than a day. Changes in the factors mentioned above influence the size and densities of the particles available for scavenging by each method. Samples collected by centrifugation represent a time-averaged condition, whereas filtration represents instantaneous concentrations.

Generally the $CPI_{14-20}$ results were higher for the centrifuge samples than for filters, reflecting the preferential retrieval of $C_{14}$ and $C_{16}$ by the filters. The $CPI_{20-32}$ values, however, were usually greater for the filter samples than for the centrifuge sediment. The small concentrations of the heavy even alkanes in the filter samples were swamped by the magnitude of the filter blanks, producing (in part)

Table C-1. A comparison of compositional parameters derived for suspended hydrocarbons retrieved by centrifugation and filtration. The standard deviations are based on triplicate analyses of the homogenized centrifuge sample collected at Station 3 in December 1978.

| | $CPI_{14-20}$ | $CPI_{20-32}$ | $\sum_{13}^{31}$ odd/ $\sum_{14}^{32}$ even |
|---|---|---|---|
| <u>JULY</u> | | | |
| Station 2 | | | |
| Centrifuge | 19.8 ± 0.7 | 7.0 ± 0.4 | 10.7 ± 0.2 |
| Filter | 10.1 | 8.6 | 8.4 |
| Station 3 | | | |
| Centrifuge | 11.1 ± 0.4 | 3.9 ± 0.2 | 6.0 ± 0.1 |
| Filter | 7.9 | 3.7 | 5.0 |
| <u>OCTOBER</u> | | | |
| Station 1 | | | |
| Centrifuge | 11.1 ± 0.4 | 7.5 ± 0.4 | 7.5 ± 0.2 |
| Filter | 7.3 | (808) | 10.5 |
| Station 2B | | | |
| Centrifuge | 2.6 ± 0.1 | 8.0 ± 0.4 | 3.8 ± 0.1 |
| Filter | 1.8 | 15.8 | 4.2 |
| Station 3 | | | |
| Centrifuge | 3.3 ± 0.1 | 2.9 ± 0.2 | 2.8 ± 0.1 |
| Filter | 3.7 | 5.6 | 3.9 |
| Station 3R | | | |
| Centrifuge | 2.8 ± 0.1 | 2.3 ± 0.1 | 2.3 ± 0.1 |
| Filter | 1.8 | 2.3 | 1.9 |
| <u>DECEMBER</u> | | | |
| Station 2B | | | |
| Centrifuge | 1.6 ± 0.1 | 10.2 ± 0.6 | 5.5 ± 0.1 |
| Filter | 1.3 | 17.9 | 8.7 |
| Station 3 | | | |
| Centrifuge | 0.99 ± 0.03 | 5.0 ± 0.3 | 2.3 ± 0.1 |
| Filter | 1.1 | 6.6 | 6.1 |

the bias in this ratio. The $\sum_{13}^{31}$ odd/ $\sum_{14}^{32}$ even ratios are higher for centrifuge sediments in the summer. The differences in alkane concentrations, and subsequently, the calculated parameters, may not be significant considering the ambiguity in sampling variability.

In light of the problems associated with filtration for organic analyses, namely:

1) the POC versus DOC debate (Section 5.1.3)
2) the instantaneous versus integrated sample argument
3) the magnitude of the filter blanks (50% of sample)
4) the small sample size associated with filters,

the centrifuge appears to be a more acceptable method for retrieval of suspended hydrocarbons.