

# HYDROCARBONS IN URBAN RUNOFF

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**ABSTRACT:** Runoff from 15 watersheds in the San Francisco Bay area are sampled over a 2-yr period and analyzed for hydrocarbons. Both gravimetric analyses and high-resolution gas capillary chromatography are performed. It is found that land uses with high commercial/industrial activity have much greater aliphatic hydrocarbon emissions than non-commercial areas. A relationship between commercial land use and the anthropogenic aliphatic hydrocarbon fraction is found. The ratio of total extractable organics to total organic carbons is found to vary with land use, with a ratio of six or more indicating significant commercial/industrial activity. Aromatic hydrocarbons, including polynuclear aromatics are also found, but in smaller concentrations than aliphatics.

## INTRODUCTION

Urban runoff contributes unknown but significant quantities of hydrocarbons to coastal waters. The National Academy of Sciences (16) has estimated the hydrocarbon contribution of urban runoff to the oceans is 15–90% of the emissions from industrial and municipal wastewaters. The estimates are widely disputed since they are based upon conventional oil and grease measurements (18), as opposed to hydrocarbon measurements. Hoffman, et al. (12) have refined these estimates, but reported very similar values. Furthermore, there is some dispute as to the best way of measuring hydrocarbons. The conventional oil and grease analysis measures polar compounds as well as hydrocarbons and does not distinguish between anthropogenic and biogenic hydrocarbons.

The extent of environmental damage of hydrocarbons on coastal waters and fisheries is also disputed, but most investigators agree that anthropogenic hydrocarbons have a much greater impact than biogenic hydrocarbons. In an effort to control hydrocarbon emissions, and particularly anthropogenic hydrocarbons, previous investigators have concluded that a relationship exists between land use and hydrocarbon load. Eganhouse, et al. (6,7) characterized many of the organic compounds found in the Los Angeles River during one storm event. Hoffman, et al. (10,11) found a relationship between land use and hydrocarbon loads. Matsumoto (13,14) showed that polluted Tokyo river waters have different ratios of hydrocarbons, extractable organics, and total organic carbon (TOC) compared with runoff from the unpolluted Ogasawara Islands. Stenstrom, et al. (21) showed that controlling high hydrocarbon-producing areas (e.g., parking areas), even if they comprise a small fraction of the total area, can produce significant reductions in total mass emissions.

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**TABLE 1. Sampling-Site Drainage Land Use**

Station (1)	Land Use			Area (Km <sup>2</sup> ) (5)	Arterials <sup>a</sup> (Km) (6)	Sampling Data						
	Residential (%) (2)	Commercial/ industrial (%) (3)	Undeveloped (%) (4)			4/85 (7)	7/84 (8)	10/84 (9)	11/84 (10)	Hourly monitor (11)	2/85 (12)	3/85 (13)
	Richmond	73	22			5	6.47	0.32	y	y	y	y
Sleepy Hollow	26	0	74	8.03	0.0	y	y	y	y	y	y	n
Sonoma	2	0	98	157.	0.0	y	y	y	y	n	y	n
Napa	10	3	87	43.8	0.0	y	y	y	y	n	y	n
Temescal	53	13	34	15.3	12.9	y	y	y	y	n	y	y
Glen Echo	51	14	35	2.22	0.0	y	n	y	y	n	y	n
Arroyo Viejo	40	12	48	16.3	2.25	y	y	y	y	n	n	y
Elmhurst	58	34	8	7.77	0.0	y	y	y	y	y	n	y
Pine-Gallinda	23	5	72	68.4	0.0	y	n	y	y	n	n	y
Castro Valley	56	12	32	11.65	5.31	y	y	y	y	n	y	n
Crandall	44	15	41	3.11	2.41	y	n	y	y	n	y	n
Guadalupe	22	4	74	155.	12.4	y	y	y	y	n	y	n
Calabazas	56	14	30	37.6	14.6	y	y	y	y	n	y	n
Matadero	5	2	93	7.51	1.93	y	y	y	y	n	y	n
Colma	38	21	41	25.4	12.0	y	y	y	y	n	y	y

<sup>a</sup>Freeways and expressways.

Note: y = sampled; n = not sampled.

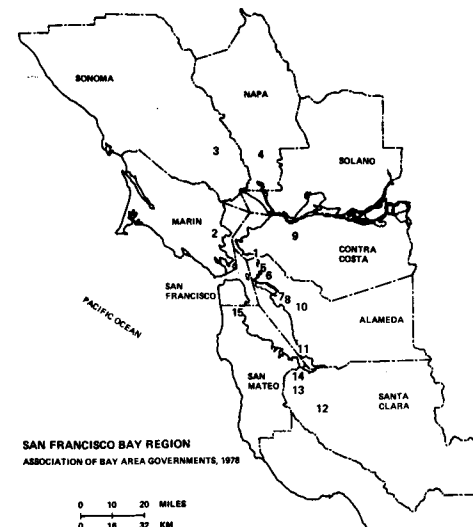
It is the intent of the work presented here to synthesize the aforementioned approaches of studying organic pollutants in urban runoff. We had four specific objectives: (1) To study the relationship between the concentrations of total extractable organics (TEO), hydrocarbons, polar compounds, TOC, and land use; (2) to investigate the change in concentrations of the various types of organics with time for a given storm in a given watershed; (3) to compare the chemical composition of the extracts from different land use areas; and (4) to assess the anthropogenic contribution to total emissions. Results from two earlier studies (19,20) were also incorporated into the findings reported here.

**METHODS**

**Study Area.** Fifteen sampling stations representing 15 watersheds in the San Francisco Bay and Oakland, California, areas were chosen for study. Each watershed was evaluated in terms of land use and area. Boundaries for each watershed were determined using maps supplied by local water agencies and the United States Geological Survey (USGS). After defining watershed boundaries, areas within each watershed were determined by planimetry.

Land use was determined largely on the basis of 1980 census data compiled by the Association of Bay Area Governments (ABAG). Land use data were categorized into three types: residential, commercial/industrial, and undeveloped. Streets and highways were not included as a separate land use, but were calculated as linear distance.

The land use and area of the sampling sites are shown in Table 1. Fig. 1 shows sampling locations. The five stations that were eventually selected for molecular characterization of the extractable organics were Elmhurst Creek, Colma Creek, Temescal Creek, Sleepy Hollow Creek, and Matadero Creek. Extracts from Guadalupe, Calabazas, and Crandall Creeks



**FIG. 1. Sampling Locations**

were fractionated once in the early part of the study. Table 1 also shows the dates and sites of sampling. Not all stations were sampled during each sampling period due to travel difficulties and the lack of runoff during the dry weather sampling in July.

**Sampling Procedures.** Sampling was done by inserting 4-L glass bottles into the free-falling streams whenever possible. If the flow was too low to allow for this method, bailing with a stainless steel bucket was used to fill the bottles. The samples were acidified to pH 2 with HCl and stored at 2-4°C until the time of extraction (usually within seven days). Samples were also collected in 1-L plastic bottles for pH, conductivity, turbidity, TSS, TDS, and TOC analysis.

**Laboratory Analysis.** All chemicals used were analytical grade or better. All solvents were distilled before use and salts were baked at 550°C for at least four hours. Unless otherwise noted, *Standard Methods* (18) procedures were used.

The collected samples were first filtered through a 0.45-µm Whatmann glass fiber filter. Particulates were extracted with methylene chloride using a Soxhlet extractor for 12 hr. The filtrate was extracted using liquid/liquid extraction. The particulate and soluble fractions were treated identically after extraction.

Liquid/liquid extractions of the filtered 4-L water samples were performed using three successive 250 ml portions of methylene chloride. Twenty grams of NaCl were added to break emulsions in order to improve extraction efficiency. Each of the three methylene chloride portions was shaken and stirred with the water sample for 10 min using the extraction apparatus shown in Fig. 2.

Extracts for both particulate and soluble fractions were concentrated to a small volume (10-15 ml) by rotary evaporation at 32°C, and the concentrated solution was further dried with anhydrous sodium sulfate.

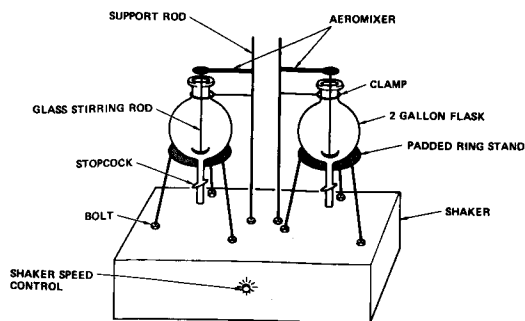


FIG. 2. Extraction Apparatus

The resultant water-free methylene chloride extract was then transferred to a tared 25-ml flask and dried by rotary evaporation with final drying under a gentle stream of nitrogen gas for approximately 10 min at 37°C. Gravimetric analysis for total extractable organics was performed using an electrobalance for total extractable organics (TEO).

The automated shaker/stirrer system improved extraction precision by allowing the use of large sample volumes. Normally it is difficult to handle samples as large as 4 L, but samples as large as 8 L can easily be managed with the apparatus shown in Fig. 2. The large sample volume increased the quantity of extracted organics, which improved gravimetric precision and accuracy. It was also observed that greater extraction times (>10 min) did not result in increased extraction efficiency.

The extracted organics were separated into an aliphatic hydrocarbon fraction, an aromatic hydrocarbon fraction, and two polar fractions by liquid chromatography. Deactivated silica gel (40–140) was used as the adsorbent in a 1.9-m diameter column. It was necessary to clean the silica gel by extracting with methylene chloride for 12 hr since significant quantities of extractable contaminants were present. Aliphatic hydrocarbons were eluted with 1.5–2 column lengths of hexane; 1.5–2 column lengths of benzene were used to elute aromatic hydrocarbons; 1.5–2 column lengths of 1:1 chloroform-methanol eluted the first polar fraction, and 3.0 column lengths of methanol eluted the second polar fraction. In some of the analyses, the two hydrocarbon fractions and two polar fractions were combined. We found that the second polar fraction yielded few gas chromatographable compounds, and in later analyses we decided to collect the two polar fractions together. Nonelutable organics retained on the silica gel were quantified by the difference in total extract weight obtained in the previous step and extract weights of the eluted fractions. A 14-cm silica gel column was sufficient to separate 30 mg of extractable organics.

The four fractions were examined on high resolution fused silica columns using a Varian Vista 6000 gas chromatograph equipped with a splitless injector and hydrogen flame ionization detector. An SP 2100 column (22 m × 0.25 mm id) was used to analyze the hydrocarbon fractions. Temperature was programmed from 50–280°C at 4°C/min for the aliphatic fraction. The initial temperature for the aromatic fraction was

100°C with a 4-min initial hold. Helium carrier gas pressure was 141 kPa (20.5 psig). A 30-m Carbowax 20M column (0.25 mm id) was used to analyze the polar fraction (fractions 3 and 4 combined). Temperature was programmed from 70–205°C at 4°C/min with a 4-min-initial hold. Helium carrier gas pressure was 152 kPa (22 psig). Compound identification was made by GC retention time matches with known standards using a 0.05 min window. Peak areas were determined by a Hewlett Packard integrator.

TSS and TDS determinations were performed in duplicate. TOC determinations were made in triplicate using an Ionics 1270 analyzer.

## RESULTS

**Statistical Results.** Since the study area was quite large, rainfall over all 15 stations was not consistent. Therefore, to quantify rainfall events, the hydrograph was divided in three phases (storm phase): active rainfall, immediately following rainfall, and the day after cessation of rainfall. The dry season samples were collected during the summer (the Bay Area usually does not receive rainfall from spring to early winter).

Table 2 shows the mean values of the conventional water quality parameters as a function of storm phase. SAS (19) was used for all statistical calculations. The means were compared using an analysis of variance using station as a class, testing for differences over storm phases. They are significantly different in the statistical sense at the 95% level of significance or better, with the exception of soluble TEO, which is only significant at 91%. These results are in contrast to previous work by the writers (21) where little difference was found among storm phases and rainfall rates. In the previous study samples were collected hourly; the implication of the differences in our findings is that water quality parameters do vary during the storm event, but not over short periods. This is unfortunate since many of the control techniques for oil and grease runoff take advantage of varying water quality during the storm (17).

TABLE 2. Mean Value of Water Quality Parameters

Parameter (1)	Mean Values for Each Storm Phase			
	Active rainfall (2)	Following rainfall (3)	Day after rainfall (4)	Dry season (5)
Turbidity	39.7	35.2	25.3	6
pH	6.92	7.26	7.53	7.7
TSS	540	103	45.7	11.0
TDS	192	516	514	738
TEO	9.42	7.75	4.07	3.03
Soluble TEO	2.71	3.66	2.43	1.34
Particulate TEO	6.71	4.09	1.64	1.69
Conductivity	130	421	428	754
TOC	8.52	9.18	9.5	-

Note: All values in mg/L except pH, turbidity (NTU), and conductivity ( $\mu\text{mho/cm}$ ); approximately 80 observations for each parameter except TOC, for which there were 20.

TABLE 3. Fractionation Results

Station (1)	Particulate				Soluble			
	Aliphatic (2)	Aromatic (3)	Polar (4)	Nonelutable (5)	Aliphatic (6)	Aromatic (7)	Polar (8)	Nonelutable (9)
Calabazas	1.910	1.49	1.760	1.39	0.615	0.90	4.540	1.360
Colma	6.500	0.39	0.630	-0.06	1.870	0.38	1.530	0.200
Colma	1.290	0.40	0.290	0.00	0.390	0.29	0.650	0.030
Colma	0.250	0.18	0.130	-0.03	0.240	0.27	0.810	-0.140
Colma	0.560	0.38	0.630	-0.01	0.310	0.11	1.130	-0.050
Crandall	0.580	0.36	1.545	0.72	0.220	0.17	5.400	2.120
Elmhurst	2.900	0.88	1.070	0.58	0.250	0.23	0.795	0.325
Elmhurst	3.220	0.61	0.560	0.73	0.330	0.13	2.070	0.050
Elmhurst	2.750	0.48	1.010	0.38	1.780	0.52	1.720	0.300
Guadalupe	2.410	1.09	3.700	0.00	1.030	2.44	5.630	1.440
Matadero	0.500	0.25	0.300	0.00	0.250	0.15	0.270	0.000
Matadero	0.535	1.59	0.717	1.38	0.410	0.75	1.740	0.440
Matadero	0.220	0.38	0.220	0.00	0.100	0.26	0.280	0.000
Matadero	0.190	0.19	0.200	0.00	0.090	0.22	1.180	0.260
Sleepy Hollow	0.18	0.40	0.22	-0.01	0.150	0.290	0.68	0.095
Sleepy Hollow	0.38	0.28	0.58	0.02	0.280	0.170	0.24	0.000
Sleepy Hollow	0.45	0.66	0.86	-0.10	0.100	0.150	0.15	0.060
Sleepy Hollow	0.60	0.24	0.91	0.23	0.110	0.160	0.82	0.550
Temescal	0.41	0.55	0.73	0.00	0.215	0.215	0.88	-0.020
Temescal	28.83	2.10	9.81	2.98	0.870	0.420	1.99	-0.090
Temescal	4.85	0.41	0.97	0.07	0.440	0.210	1.92	0.100
Temescal	0.87	0.28	0.71	-0.01	0.310	0.150	1.49	0.000

Note: All values in mg/L.

Table 3 shows the fractionation results. Since the nonelutable fraction must be determined by mass balance, small negative values are possible. Analysis of variance was also conducted to test the hypothesis that the hydrocarbon fraction changed as a function of storm phase. Significant differences (at 95%) generally were not found among the extracted hydrocarbon fractions for different storm phases in terms of either concentration or percentage of TEO. The concentration of hydrocarbons changed during storm phases but the relative contributions of the four fractions did not.

The effect of land use on TEO emissions was evaluated in several ways. An analysis of variance testing for differences among land uses was made over five stations selected for fractionation. A statistically significant relationship (99%) was found between commercial/industrial land use and particulate TEO. Commercial/industrial land use had the highest emissions. Soluble TEO was not significantly different among land uses.

No significantly different relationships among TEO fractions and land use could be found. However, since we strongly suspected a relationship, we investigated additional correlations. The ratio of aliphatic to aromatic hydrocarbons was tested. Table 4 shows the mean of the ratio of aliphatic to aromatic hydrocarbon concentrations. Highly commercial stations have a much greater aliphatic to aromatic hydrocarbon concentration ratio. An analysis of variance showed that the differences in the ratios were significant at the 98% level of confidence. Sleepy Hollow and Matadero, both noncommercial stations, had ratios close to 1:1. Elmhurst, the most

TABLE 4. Ratio of Aliphatic to Aromatic Hydrocarbons

Station (1)	Percent commercial (2)	Mean ratio (3)	Number of observations (4)	Minimum value (5)	Maximum value (6)
Colma	21	4.8	5	1.1	10.9
Elmhurst	34	9.9	4	2.8	27.5
Matadero	5	1.1	5	0.4	2.2
Sleepy Hollow	0	1.1	4	0.5	1.8
Temescal	13	6.5	6	0.8	12.3

commercial station had a ratio of 9.9:1, with Colma and Temescal having intermediate ratios. These results indicate that commercial activity, such as vehicular activity, produces aliphatic hydrocarbons. We extracted used motor oil and found the composition to be 97% aliphatics. Others have implicated motor oil with hydrocarbon emissions from commercial areas.

Another interesting finding was the ratio of TEO to TOC concentrations. Both humic acids and TEO contribute to TOC, but only hydrocarbon and oil and grease compounds contribute to TEO. If urbanization produces an increase in extractable organics, or a decrease in humic materials, a relationship would exist between commercial land use and this ratio. The higher the ratio, the greater the contribution of humic and presumably biogenic materials. An analysis of variance was made to test this hypothesis, and significant relationships were found for the particulate TEO as well as TEO.

The final tool used to test the relationship between commercial land and hydrocarbon emissions was the distribution of odd-numbered hydrocarbon fractions beginning at C<sub>25</sub>. Eganhouse, et al. (6) reported that biogenic sources contribute the odd-numbered hydrocarbons in runoff beginning at C<sub>25</sub>, and Hoffman, et al. (12) have confirmed this relationship. Even-numbered and lower-numbered hydrocarbons are primarily anthropogenic. To test this hypothesis, the chromatogram areas of the aliphatic fraction for the odd-numbered peaks, beginning at C<sub>25</sub>, were totaled and compared to the remaining peak areas. This was done for both soluble and particulate hydrocarbon fractions. The percentage in the biogenic fraction (>C<sub>25</sub>) ranged from a high of 44% for the Matadero soluble fraction collected in November 1984, to a low of 0.2 for the Temescal particulate fraction collected in the same sampling. Statistically significant differences were found for all three classes of land use for particulate, soluble, and total extractable organics. The differences were among the most significant (>99.99%) found in this study. Fig. 3 shows the C<sub>25</sub> fraction and above-peak areas as a percentage of total area versus land use.

## CHROMATOGRAPHY RESULTS

**Aliphatic Hydrocarbons.** It is interesting to note that different sampling stations have different hydrocarbon distributions and that the same sampling station has shown different looking chromatograms during the seven months of sampling. Eganhouse, et al. (6) demonstrated that the same sampling station may even show different hydrocarbon patterns during a single storm event.

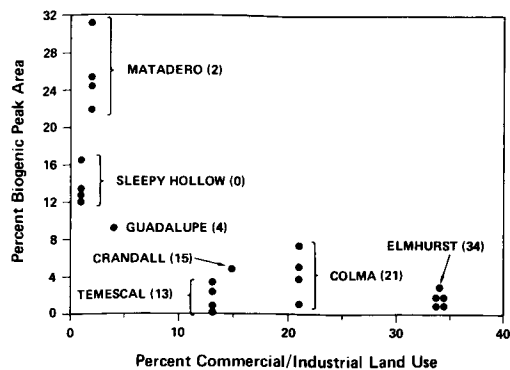


FIG. 3. Biogenic Peak Area as Function of Land Use

We were able to observe and identify three major contributing sources of aliphatic hydrocarbons in the runoff waters. Overall five hydrocarbon patterns were observed but the three identified patterns appeared in 68 of the 69 chromatograms. The three identified sources of aliphatic hydrocarbons are automobile motor oil [Fig. 4(a)], diesel fuel [Figs. 4(b,c)] and plant/microbial waxes [Fig. 4(d)]. The two unidentified patterns were *n*-alkane series centered at  $C_{27}$  and an *n*-alkane series centered at  $C_{23}$ .

Temescal Creek (Fig. 5) has consistently shown a chromatographic pattern that closely resembles diesel fuel. Freshly extracted diesel fuel shows an abundance of *n*-alkanes ranging from 10–25 carbons [Fig. 4(b)]. However, if a few drops of diesel fuel are aerated for 24 hr in 2 L of water, many of the 10–15 carbon *n*-alkanes are lost, and the resultant chromatographic pattern [Fig. 4(c)] is nearly identical to the aliphatic fraction in Temescal Creek. The 24-hr aeration experiment was meant to simulate natural losses due to evaporation.

The sampling station for Temescal Creek is located in an industrial park area. It was suspected that the diesel fuel contamination may be from a nearby bus repair yard or other diesel fuel-using facilities in the area. A sample was collected upstream of the commercial activity, which showed that 14% of the integrated peak area can be attributed to diesel fuel. The usual Temescal Creek chromatogram was comprised of primarily (90%) diesel fuel.

Sleepy Hollow and Matadero Creeks, located in predominantly noncommercial areas, showed essentially the same chromatographic patterns (Figs. 6–7). Most frequently, one observes contamination by diesel fuel or motor oil, along with a heavy *n*-alkane series. The heavy *n*-alkane series is most likely attributable to plant leaf waxes or microbial secretions and usually accounts for 10–40% of the observed aliphatic hydrocarbons. The heavier petroleum fractions, transmission fluid, and motor oil are composed of a complex mixture of aliphatics and do not have a predominant *n*-alkane series (5). The heavy *n*-alkane series was usually centered at  $C_{29}$  and showed low amounts of even-numbered paraffins ( $C_{26}$ ,  $C_{28}$ ,  $C_{30}$ ,  $C_{32}$ ). Such a predominance of odd-numbered *n*-alkanes over the even-numbered paraffins has been reported by Eglinton (8), Castillo (3), and Bottari (1) in

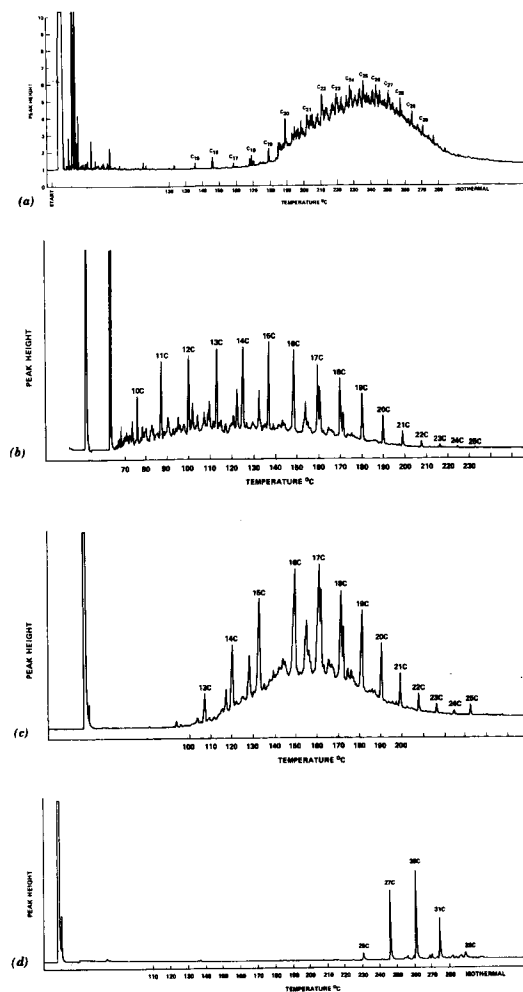


FIG. 4. Chromatogram for: (a) Used Motor Oil (Allphatic Fraction); (b) Fresh Diesel Fuel (Allphatic Fraction); (c) Weathered Diesel Fuel (Allphatic Fraction); (d) Plant Waxes (Allphatic Fraction)

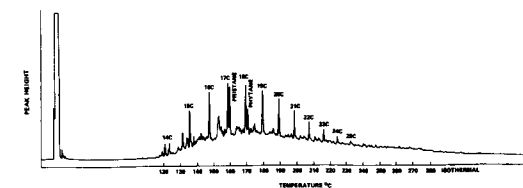


FIG. 5. Chromatogram for Temescal Creek (Allphatic Fraction)

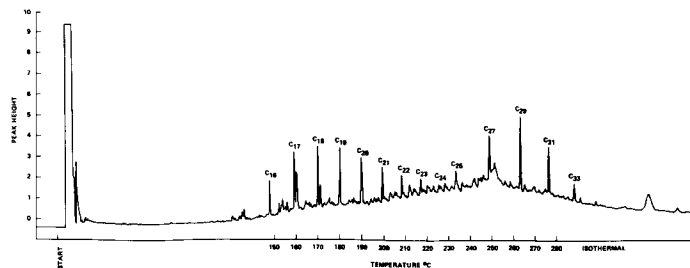


FIG. 6. Chromatogram for Sleepy Hollow Creek (Aliphatic Fraction)

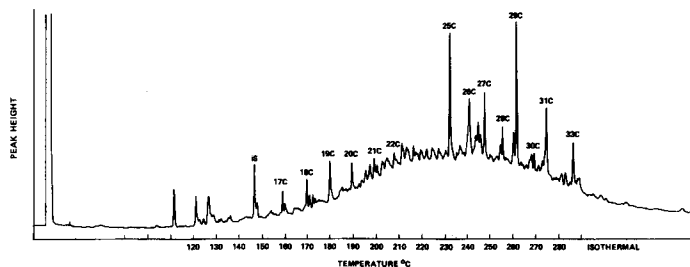


FIG. 7. Chromatogram for Matadero Creek (Aliphatic Fraction)

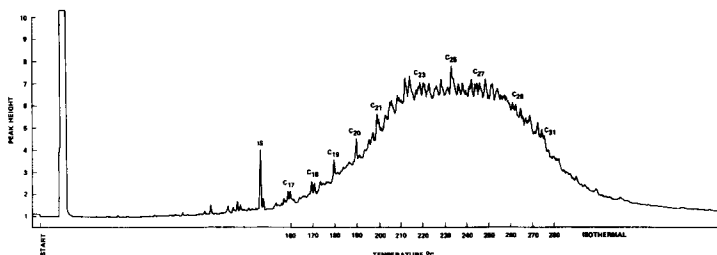


FIG. 8. Chromatogram for Elmhurst Creek Showing Unresolved Complex Mixture Typical of Used Motor Oil (Aliphatic Fraction)

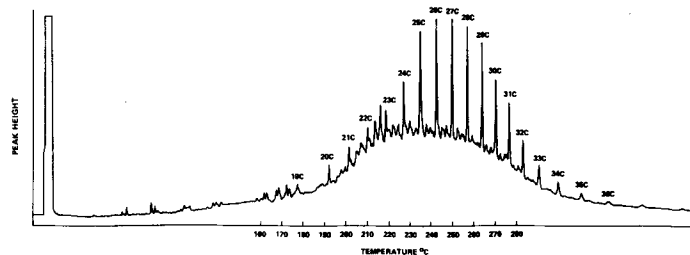


FIG. 9. Chromatogram for Elmhurst Creek Showing Biogenic Heavy Hydrocarbons and Probable Diesel Fuel Contamination in Addition to Unresolved Complex Mixture (Aliphatic Fraction)

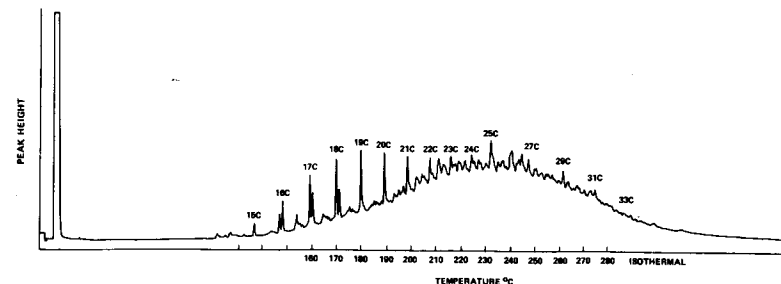


FIG. 10. Chromatogram for Colma Creek (Aliphatic Fraction)

higher plants. Casadevall (2) observed a similar pattern with the hydrocarbon rich alga *Botryococcus brauni*. Our observations, as well as those of others (6,12,20), indicate that C<sub>29</sub> and C<sub>31</sub> are the most abundant biogenic *n*-alkanes. Matadero Creek, however, on two occasions showed large C<sub>26</sub> and C<sub>28</sub> peaks. This observation may indicate seasonal growth variations since the hydrocarbon distribution in a plant varies significantly with plant age (8).

It is noteworthy that more than 70% of the observed aliphatics in both Sleepy Hollow and Matadero Creeks are attributable to anthropogenic sources despite the low levels of urbanization in the watersheds (7% in Matadero and 26% in Sleepy Hollow).

The Elmhurst Creek station, collecting the runoff from a heavily industrial area, has consistently shown the same chromatographic pattern. Ten of 11 chromatograms (Fig. 8) look nearly identical with the aliphatic fraction of motor oil. The only extract that deviated from this pattern, containing a heavy *n*-alkane series, is shown in Fig. 9 and it still contained the "fingerprint motor oil hump." Hoffman, et al. (10) observed a similar alkane series, which they attributed to industrial fuel oils.

The aliphatic hydrocarbons in Colma Creek show a compilation of the previously mentioned trends (Fig. 10). The motor oil hump is evident along with the biogenic heavy hydrocarbons (C<sub>27</sub>, C<sub>29</sub>, C<sub>31</sub>, C<sub>33</sub>) as well as the diesel fuel contamination (C<sub>15</sub>-C<sub>23</sub>).

**Hourly Monitored Storms.** Hourly samples were collected for a single storm event from Elmhurst Creek as well as Sleepy Hollow Creek. It was our intent to investigate the hydrocarbon distribution as a function of time during the storm event. Eganhouse (6) observed a shift in the hydrocarbon distribution from unimodal centered at C<sub>23</sub> during the early storm to a bimodal distribution during the latter storm hours. He also observed more heavy hydrocarbons associated with the particulate fraction than with the soluble fraction.

We did not observe any significant changes in the chromatograms of the hourly monitored Sleepy Hollow storm event. In addition, the soluble and particulate fractions looked very similar. The only observed difference in the hourly monitored Elmhurst storm was the heavy hydrocarbon load in the 13:30 pm soluble fraction (Fig. 9). Only traces of the *n*-alkane series shown in Fig. 9 were routinely found. In 22 of our 34 observations, the soluble fraction contained more biogenic hydrocarbons than the particu-

late fraction. Although the biogenic hydrocarbons are of high molecular weight and consequently very water insoluble, unlike motor oil, they are not flushed from roads and parking lots with particulates and thus are not preadsorbed. In contrast, the biogenic hydrocarbons must be desorbed from plant material into the runoff waters. This may explain the fact that the soluble fractions seem to contain greater percentages (not amounts) of biogenic hydrocarbons than the particulate fractions. The soluble and particulate TEO concentrations declined as the storm progressed.

**Aromatic Hydrocarbons.** The benzene elutable fractions have been termed the aromatic fraction because it is the fraction in which polynuclear aromatic hydrocarbons will elute. Numerous other compounds (alkyl benzenes, cyclic hydrocarbons > 20 carbons and heavy polyunsaturated hydrocarbons) will also be collected in this fraction, and the majority of these compounds were not identified. Our intent in examining this fraction was to test for the presence of polynuclear aromatic hydrocarbons and to compare the fingerprint appearance of various land use fractions.

Many of the second fractions examined showed a large complex eluting at 250°C (Fig. 11). Some showed a complex eluting at 160°C, of which anthracene was a constituent (Fig. 12). The most commonly identified PNA hydrocarbons were anthracene, fluoranthene, indenol pyrene, and benzo-perylene. Chrysene was detected on two occasions. The other polynuclear aromatic hydrocarbons for which we tested, but did not detect, were naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, pyrene, benzo (a) anthracene, benzo (b) fluoranthene, benzo (k) fluorane, benzo pyrene, and dibenz (ah) anthracene. Since these identifications were made only by retention time, they are considered tentative.

There were no clear-cut observable differences in the chromatograms of different land use areas, except that Elmhurst Creek frequently (7 of 8) did not show the 250°C complex (Fig. 12). This late eluting complex was present in all of the Sleepy Hollow and Matadero chromatograms and most of the Colma and Temescal second fraction chromatograms.

Since this late eluting complex seems to be associated with low urbanization, it may be inferred that it represents a biogenic source. Further support for this assertion comes from the work of Bottari, et al. (1) who isolated several 25–30°C plant terpenes as a silica gel benzene elute (their first fraction was collected with petroleum ether). The retention time of our 250°C mixture is comparable to C<sub>26–28</sub> n-alkane retention times. This complex showed some carry-over (up to 25%) in the aliphatic fraction but was primarily elutable by benzene. This may indicate that it is a cyclic aliphatic with some unsaturation (possibly plant terpenes). Without mass spectral or GC retention time matches, this suggestion must be regarded as tentative.

**Polar Fraction.** The chloroform/methanol elute is the fraction that gives the extractable oil and grease its noted yellowy brown color. It contains any organic compound with a polar functional group such as alcohols, carboxylic acids, phenolics, and ketones. We used 65 reference polar compounds for identification. Our standards included alcohols, acids, ketones, and phenols.

Polar compounds are notably difficult to analyze because of their poor resolution by GC. It is common practice to silylate (6), acetylate (4), or react the compounds with diazomethane (9,15) to render a nonpolar

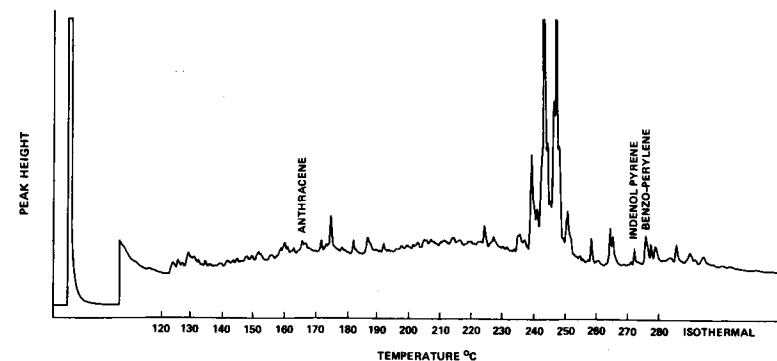


FIG. 11. Chromatogram for Sleepy Hollow Creek (Aromatic Fraction)

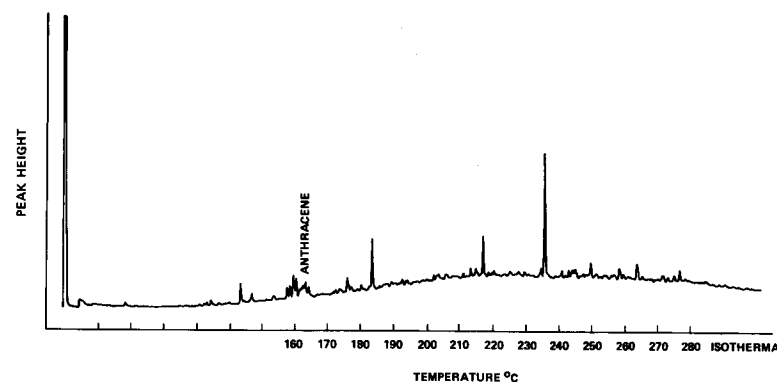


FIG. 12. Chromatogram for Elmhurst Creek (Aromatic Fraction)

derivative that is more amenable to gas chromatography. We chose to use the polar Carbowax column without derivatization because of the difficulty of treating the large number of samples used in the analysis. In addition, the Carbowax column showed excellent resolution for alcohols and phenols although acids were still not well resolved. We regularly identified straight chain alcohols such as octanol, nonanol, tridecanol, and tetradecanol as well as substituted phenols such as 3,5 xyleneol, 3,4 xyleneol, ethyl phenol, and 2,3,5 trimethyl phenol. Elmhurst Creek on several occasions showed large concentrations of unidentified polar compounds. None of the other less urbanized sampling stations contained such high-magnitude GC peaks.

Overall, the polar chromatograms show somewhat consistent patterns for a given station, but a varied appearance among the five stations. The lack of any positive identification of compounds leaves us unable to make any conclusions about the origins of these polar organics. The dissimilarity of the chromatograms, however, may indicate that polar compounds could potentially be used as an indicator of land use in the same manner as hydrocarbon distribution patterns.

## SUMMARY AND CONCLUSIONS

Several urban pollution indicators were observed in this study. The aliphatic fractions of the different land use areas showed different hydrocarbon distribution patterns. The percent *n*-alkanes > C<sub>25</sub> correlated well with percent undeveloped areas, indicating that these hydrocarbons are of biogenic origins. Motor oil and diesel fuel were the major anthropogenic sources of hydrocarbons.

The lack of significant correlation between TEO fractions and land use may be partly attributable to our sampling program. Samples were collected during different times of a given storm at the various stations. The lack of significant correlation is also possibly due to the disproportionately large contribution of anthropogenic inputs even in low commercial land use areas. The Sleepy Hollow sampling station has no commercial areas and is 76% undeveloped; however, nearly 85% of the aliphatic hydrocarbons are attributable to motor oil and diesel fuel pollution. The Matadero Creek watershed is 93% undeveloped, yet nearly 75% of the aliphatics are attributable to anthropogenic sources. It seems that the slightest urbanization will significantly increase organic pollution. Therefore, it might be difficult to find truly unpolluted land where a difference in hydrocarbon fractions could be found.

Aliphatic hydrocarbons are generally considered to be biodegradable and only become toxic to marine life at elevated concentrations. Therefore, elevated mass emissions are more critical than the mere presence of the aliphatics at low concentrations. Polynuclear aromatics, however, are more toxic than aliphatic hydrocarbons and tend to accumulate in food chains (22). Hoffman, et al. (11) have shown that urban runoff is a major contributor to PNA emission loads and that industrial areas have a greater contribution than residential areas.

In agreement with the findings of Hoffman et al. (11), we found no significant qualitative chromatographic differences between the PNAs present in the extracts of the various land use extraction. It seems that even modest urbanization contributes some PNAs to urban runoff since we observed anthracene and other PNAs in Sleepy Hollow and Matadero Creeks (mostly undeveloped watersheds). Due to the elution of the large biogenic complex with the PNAs, it was not possible to gravimetrically distinguish the PNA loads among the various land uses. A more stringent fractionation scheme would be required to elute the PNAs separately. A larger volume of water may also be required.

The ratio of TOC/soluble organic extract emerges as a significant parameter related to land use. Both the biogenic humic substances and the extractable organics contribute to TOC. Urbanization decreases the relative humic input and increases the extractable organics. This easily determined TOC ratio is a promising parameter for monitoring the extent of urban pollution. Although further work is required to assess a ratio that would be indicative of urban pollution, our studies suggest that a ratio of 6:1 indicates moderate urbanization.

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