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16. Abstract Trace organics were surveyed using gas chromatography coupled to mass spectrometry for highway runoff samples from two Seattle sites. The characterization of the organics exhibited concentrations of aliphatic, aromatic and complex oxygenated compounds. Vehicles, including exhaust emissions, were concluded to be the source of many of the organics.			
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INTRODUCTION AND OBJECTIVES

Stormwater runoff from impervious surfaces such as highways and rural streets contain organic materials, nutrients, and other pollutants which frequently impact aquatic systems and water uses. Certain organic compounds are toxic at very low concentrations, and small structural differences in compounds may cause greater differences in their toxicity. Identification of trace organics in highway runoff is essential to evaluate the potential adverse effects.

Little research has been done on the systematic classification of organic pollutants in highway runoff waters, although there are studies on pesticides and polychlorinated biphenyls (PCBs).

During the past few years, stormwater runoff has been monitored at highway runoff sites (Asplund, 1980) on Interstate-5, north of Seattle, and on SR 520 near the University of Washington, providing data on suspended solids, metals, chemical oxygen demand, grease-oils and other pollutants. The lack of industrial sources of organics near these sites make them ideal for a study to characterize the types of organic compounds present in highway runoff waters. To accomplish this the following specific goals were set.

1. To examine the major classes of organic compounds using mass spectrometry coupled to gas chromatography.
2. To relate the trace organic data to traditional water quality analyses such as VSS, grease-oils, TOC and COD and make comparisons with the storm parameters and traffic data.
3. To assess probable sources and potential adverse health effects of the trace organics present in highway runoff.

OCCURRENCE AND SOURCES

Much of the literature on trace organics focuses on hydrocarbons, especially aliphatic, polycyclic aromatic, and chlorinated hydrocarbons. There has been a rapid increase of information about certain toxic compounds, especially the priority pollutants as defined by U.S. Environmental Protection Agency.

Organic and inorganic contaminants are deposited on highway surfaces. These substances result from motor vehicle traffic, atmospheric fallout and direct spillage on or near the highway surface (Shaheen, 1975). Pollutant mass on the highway surface may also be strongly influenced by local land use and highway maintenance practices (Moc, et al., 1980; Little and Wiffen, 1978; Gupta, et al., 1978a, b). Inorganic constituents that have potential adverse effects include nutrients (phosphates and nitrogens) and toxic metals such as lead (Laxen and Harrison, 1977). Zinc, copper, iron, nickel, and chromium may also be deposited on the roadway as a result of automobile corrosion and product additives. Organic material present in highway runoff may result from tire wear, exhaust emissions, lubricants, asphalt surfacing, and gasoline and crankcase drippings.

Many contaminants are largely associated with the particulate matter on the highway surface (Howell, 1978; Hedley and Lockley, 1975). For example, metal concentrations in highway runoff follow the particulate concentrations (Clark, 1980). Studies on the organic contaminants in runoff waters indicate that between 80 to 95 percent are associated with the particulates (MacKenzie and Hunter, 1979).

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Recent studies have investigated the presence of petroleum derived hydrocarbons in urban and highway storm runoff (Hunter, et al., 1979; Wakeham, 1975; Hallhagen, 1973). Analyses by gas chromatography of runoff extracts and crankcase oil are very similar, especially the corresponding sulphur profiles indicating similar compounds in each (MacKenzie and Hunter, 1979).

Runoff from highways and heavily traffic areas has increased concentrations of hydrocarbons, typically an order of magnitude greater than runoff from other nearby urban areas. A Swedish study determined an average hydrocarbon concentration of 10 mg/L in highway runoff, whereas runoff draining from a nearby apartment dwelling contained an average 9.9 mg/L. Wakeham (1975) obtained similar results in the Seattle area with aliphatic hydrocarbon concentrations in highway runoff ranging from 6 to 24 mg/L while concentrations range of 0.2 to 7.5 mg/L was determined in runoff from nearby urban areas.

Chlorinated hydrocarbons have been measured in runoff waters in a few studies. Envirex (1978) surveyed eight highway sites across the United States and found an overall average concentration of 0.33 g/liter of polychlorinated biphenyls (PCB's) in runoff. Sartor, et al. (1974) found in a study of road surface contaminates in twelve cities that the average PCB concentration (weighted in favor of large cities) was 0.3 g/curb-kilometer, 0.77 $\mu\text{g/g}$ dry solids. Pesticides were also present on the road surfaces of one or more of these cities. Halogenated hydrocarbons are widely dispersed and transported throughout the environment by natural mechanisms, such as wind, rain, and atmospheric fallout. They may also be present in exhaust emissions.

The probable sources of organics in highway runoff include rubber, crankcase oil, fuel, combustion byproducts, pesticides, asphalt pavement, plant material and debris. Compositions of street surface contaminants have been examined by Shaheen (1975). Contributions of exhaust emissions are not reflected in Table 1.

Definitive contributions from unburned fuels, exhaust emissions, and crankcase oils are difficult to estimate due to the large variability in these sources. There is also considerable variability in refined gasoline produced by various processes.

Exhaust emissions which may be deposited consist primarily of lead bearing material, carbon as soot, unburned fuel, and minor amounts of organics released due to incomplete combustion. Airborne particulate matter contains oxygenates, aromatics and aliphatics with the oxygenated fraction as the principal component (Neligan, et al, 1961, Seizinger and Dimetriades, 1972; Sawicki, 1967). For a variety of sites in California the range of these organics in particulate matter were 2-30 percent aromatics, 8-46 percent aliphatics, and 33-92 percent oxygenates (Appel, et al., 1973), with about 20 percent organic acids and a minor fraction of cyclohexane insoluble constituents.

The oxygenated compounds identified in exhaust emissions from automobiles include aromatic and aliphatic alcohols, ketones, ethers, aliphatic esters, phenols, nitro alkanes, heterocyclic aza compounds, and carboxylic acids. The presence of many of these compounds in highway runoff may be anticipated because of adsorption onto exhaust particulates which are then deposited onto the roadway.

Table 1. Analysis of possible street surface contaminants (Shaheen, 1975).

Material	Tot. Vol. Solids (mg/g)	BOD (mg/g)	COD (mg/l)	Grease (mg/l)	Petroleum (mg/l)	n-Paraffins (mg/g)
Gasoline	1000	150	680	1.3	1.3	1.3
Lubricating Grease	970	140	-	750	670	570
Motor Oil	1000	140	220	990	940	850
Transmission Fluid	1000	100	200	990	940	880
Antifreeze	990	38	1100	140	70	6.1
Undercoating	1000	90	310	960	180	120
Asphalt Pavement	64	1.2	86	21	15	9
Concrete	71	1.4	64	2.7	1.3	1
Rubber	990	27	2000	190	100	56
Diesel Fuel	1000	80	400	390	310	210
Brake Lining	290	17	420	31	8.3	7.6
Brake Fluid	1000	26	2400	880	33	19
Cigarettes	860	85	780	30	21	2.7
Salt	75	-	-	0	0	0
Cinders	0.0	-	59	1.3	1.2	1.2

Polynuclear aromatic hydrocarbons (PAH) are formed during combustion processes. Any pyrolysis of carbonaceous material at high temperatures is a suspected source of PAH. In addition to automotive contributions they also result from coal (gas and oil) space heating, incineration, and outdoor burning. The percentage contributions of PAH from automobiles in airborne particulates are estimated to be higher in suburban than urban areas. Polynuclear carbonyl compounds are also present in auto exhaust, furnace effluents, and effluents from open burning.

Organic nitrogen compounds are also expected in highway runoff. Identification of such compounds has been made in automobile emissions (Schuchmann and Laidler, 1972) and amino compounds are used as gasoline additives, in lubricants and in antioxidant in tires.

Effects of Organic Pollutants

Organic pollution of the aquatic environment can cause deterioration of the ecological system, resulting in depletion of dissolved oxygen, an enrichment of heterotrophic fauna, a decrease in diversity, and grease and oil slicks. In addition, many organic contaminants have toxicity, so living organisms including fish, benthic invertebrates, algae and bacteria may be subject to acute or chronic effects. At lower concentrations the organisms may be affected through bioaccumulation at lower trophic levels. Finally, organic contaminants can have adverse health effects on man through contaminated drinking water supplies and bioaccumulation in the food chain.

Portele (1981) has conducted a study of the aquatic toxicity of highway runoff waters. Otherwise little is known about the combined effects on receiving waters although there is extensive literature on oil pollution, heavy metals and chlorinated hydrocarbon. The persistence of organic compounds in the environment may allow widespread contamination and concentration in the food chain (Blumer, 1979). Bioaccumulation can cause reduced resistance to disease, interference in reproduction or migration and transfer of toxic effects to organisms higher in a food chain.

There have been many studies of effects of atmospheric vehicle emissions on animals but few that can be related to exposure via runoff. The standardized bacterial test for mutagenicity (Ames test) has shown correlation to carcinogenicity for some compounds. Used crankcase oils (Payne and Martin, 1978) and diesel exhaust particulates (Chan, et al., 1981) have both shown mutagenicity by the Ames test.

Many aromatic compounds are carcinogens or co-carcinogens, especially the polynuclear aromatic hydrocarbons (PAH). Among the most potent is 3,4-benzopyrene (Sittig, 1980), which has been identified in automobile exhaust (8.5 g/m^3 , Colucci and Begeman, 1965). Approximately 22 percent of the total benzopyrene is associated with particulates of diameter greater than $7.0 \text{ }\mu\text{m}$ which would tend to settle out rapidly (Katz and Pierce, 1976). Benzopyrene constitutes about 5 percent of the emitted, identified PAH from motor vehicles. It should be emphasized that benzopyrene and PAH emitted from motor vehicles is a minor source compared to others, including coal burning and cigarette smoking.

Oxygenated organic compounds also may be carcinogenic but generally with much lower activity than for PAHs. Some of the oxygenated compounds are alkylating agents, and many alkylating compounds, such as epoxides, lactones and peroxy compounds, have carcinogenic activity (Van Durren, et al., 1965; Kotin and Falk, 1963).

Toxicity studies with fuel oils have conflicting results. Bingham and Barkely (1979) found Texas and asphaltic crude oils produced neither benign or malignant tumors, while a sample of industrial fuel oils was a very active carcinogen. Holland, et al. (1979) tested the carcinogenicity of a natural crude composite and several syncrudes on mouse skin. All of the syncrudes tested produced squamous carcinomas while the blended natural crude did not. Simmers (1965) demonstrated that asphalt and its fractions were carcinogenic to mice.

Many kinds of organic pollutants are deposited on roadways and enter the runoff waters. Predominant among the classes are the hydrocarbons, evidently originating from petroleum products. Sulphur compounds, possibly from crankcase oil, have been determined in runoff water, and widespread but low levels of pesticides and PCB's have been found on both roadways and in runoff. Oxygenates and organic-nitrogen compounds may also contribute to the pollutant loading on highways.

Motor vehicles are the primary source of pollutants on the road surface, with minor sources including wind borne particulates, debris, spills, and precipitation. Many of the pollutants in runoff waters are toxic in aquatic system and some may be carcinogenic. There is little data on concentrations of compound or classes of compounds in runoff and even less information on the potential adverse effects. There is

legislative control over release and concentrations of some toxic organic compounds, but not particularly over ones expected in runoff.

DESCRIPTION OF STUDY AREA

Interstate-5 Site Description

The Interstate-5 station is located in an urban setting ten miles north of the industrial area of metropolitan Seattle near Northeast 158th Street (Figure 1). Highway runoff is collected from a drainage area of 1.22 acres (4937 m²) consisting of four 12-ft wide x 780-ft long northbound lanes and 10-ft wide median and shoulder strips. The freeway lanes are paved with Portland cement concrete and the shoulder and median of asphalt pavement. Average daily traffic is about 50,000 vehicles.

The sample collection system consists of a calibrated H-flume, flowsplitter, and sample storage tank (Clark, 1980). The H-flume and flowsplitter have fiber glass surfaces and the holding tank (49 ft³ or 1.39 m³) is constructed of concrete with a polyethylene liner. Runoff waters flow from the highway surface, along the curb to a collection box and then through a culvert into the H-flume. Contamination and losses due to the plastic in the system were assumed negligible because of the large runoff volume to surface area and frequent collection. Samples were collected in amber glass bottles.

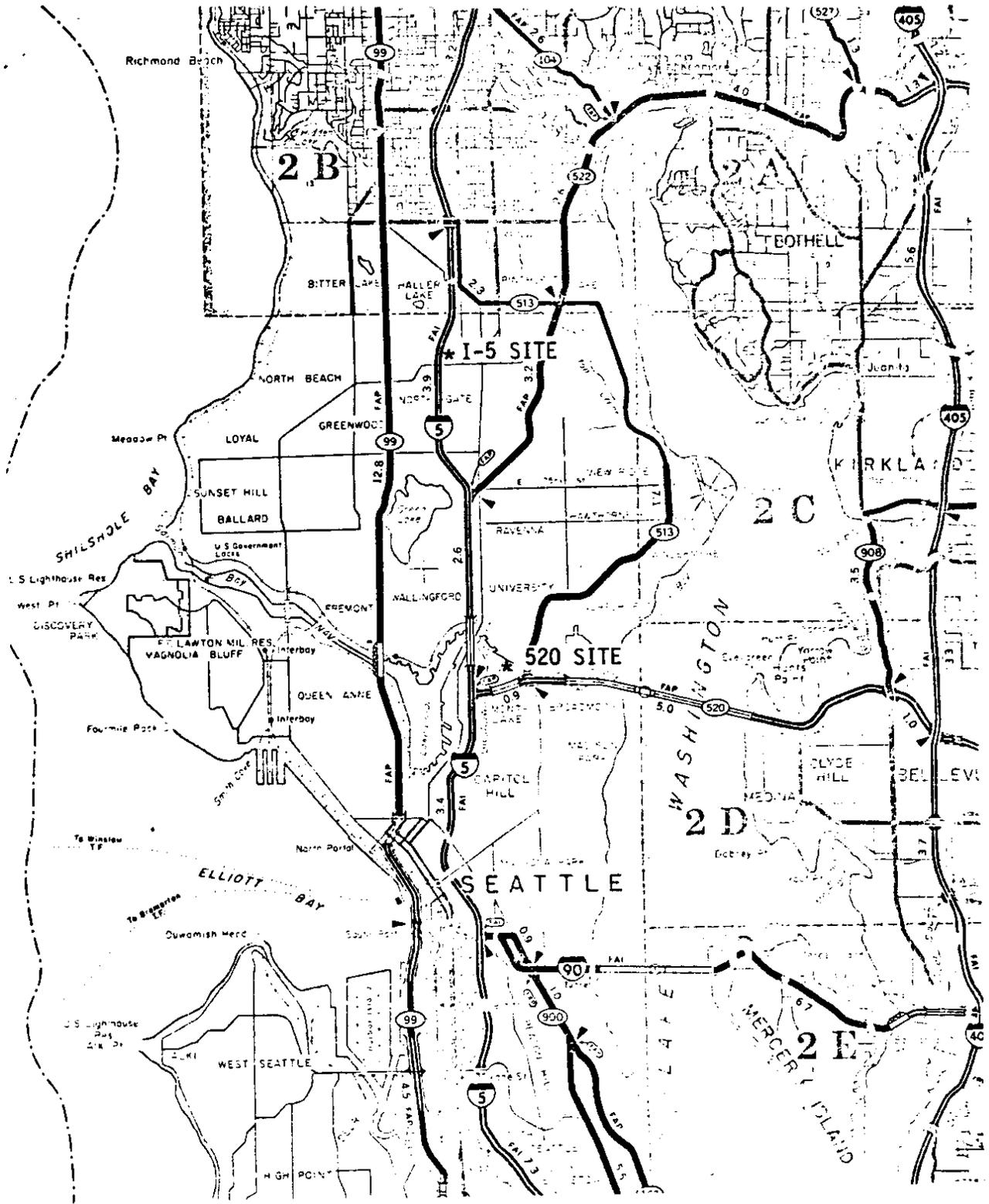


Figure 1. Map of sampling site locations in Seattle.

State Road 520 Site Description

The State Road 520 (SR-520) sampling station is located in an urban area approximately 7 miles northeast of the industrial areas of metropolitan Seattle (Figure 1). Highway runoff is collected from a drainage area of 0.099 acres (401 m²) consisting of two 12-ft wide x 150-ft long westbound lanes from a bridge section with a 2% grade and including a portion of an on-ramp. The freeway lanes, New Jersey type barrier (1-ft wide), and shoulder strip (2-ft wide) are Portland cement concrete. Average daily traffic is approximately 42,000 vehicles.

The sample collection system consists of a zinc plated steel pipe, a modified flowsplitter, and a 55-gallon storage drum (Tseng, 1979). The metal drum has a disposable polyethylene liner. Location of the SR-520 site and the I-5 site have minimal organic contributions from the surroundings. The New Jersey type barrier and side railing at the SR-520 site effectively traps the particulate matter, and consequently the runoff contains greater concentrations of suspended solids than the I-5 site.

Climatology

The climate in the Seattle area is mild with considerable amounts of low intensity precipitation, usually less than 0.1 inches per hour (.25 cm/hr). The average annual precipitation is 39 inches with 75 percent of the rainfall occurring from October through March, the sampling period of this investigation. Snowfall rarely occurs since the average winter temperatures is 40°F (5°C). The prevailing wind direction is from the southwest. Storm precipitation data was obtained from

a recording bucket rain gauge at the I-5 site and from the N.O.A.A. weather station adjacent to the SR-520 site.

SAMPLING AND ANALYSIS

The study sites are located in Seattle on the northbound lanes of I-5 in north Seattle near N. 158th Street and on the westbound lanes of SR-520 near 23rd Avenue. Both sites are equipped with flowsplitters, that collect composite samples. They are described by Clark (1980), and results of sampling for conventional pollutants are reported by Tseng (1979), and Asplund (1980).

All samples were collected in one-gallon capacity, amber glass bottles with teflon lined caps. Approximately four liters of storm water was collected directly from a well-mixed holding tank of the compositing sampler, and transported immediately to the laboratory for analysis. Water samples were stored in a dark cold room at 4°C until extraction which was carried out as soon as possible.

Analysis for total and volatile suspended solids (TSS and VSS), chemical oxygen demand (COD), total organic carbon (TOC), grease and oils, pH, and conductivity were performed in accordance with Standard Methods for the Examination of Water and Wastewater (14th Edition, 1975; except as noted by Asplund et al (1981). TOC was measured on a Beckman IR Carbon Analyzer.

Samples for Organics

The extraction and isolation of hydrocarbons generally follows the procedure delineated by Farrington, et al. (1972), and Giger and Schaffner (1978).

Water samples were mixed, and 1,000 ml measured in a graduated cylinder. The particulate and aqueous phases were separated by filtration through pre-extracted, pre-weighed Gelman glass fiber filters, Type A-E.

The soluble organics were extracted three times with methylene chloride in separatory funnels. The combined extracts were reduced to 2-3 ml by a rotary evaporator under vacuum pressure in a water bath at 15°C and then adjusted to a known volume. The total weight of the extractable organics was obtained by weighing small aliquots (10-50 μ l) on a Cahn 4100 electrobalance after a constant weight was reached by cautious air drying on a hotplate.

The particulates were air dried at 40°C for 24 hours. Extraction of the organics from the dried particulate fraction was carried out in a Soxhlet apparatus with pre-extracted paper thimbles using a methanol:methylene chloride azeotrope (1:9) for a 24-hour period or until new solvent in contact with the sample remained colorless.

Elemental sulphur is often found in environmental samples and may interfere with the gas chromatography hydrocarbon analysis. To remove this sulphur, the organic extracts were percolated through a column of activated copper (Blumer, 1957). Eluates were directly analyzed by gas chromatography/mass spectrometry.

Gas Chromatography/Mass Spectrometry Analysis

The GC/MS work was performed in the Department of Environmental Health laboratories on samples extracted in our laboratories. The mass spectrometer used was a Finnigan (Model 4023) quadrupole instrument combined with an on-line computer utilizing an INCOS data system to control instrument parameters, data acquisition and data analysis. A Hewlett Packard gas chromatograph (Model 5840A) was directly coupled to the mass spectrometer for separation of the organics prior to mass spectrometric analysis. Detailed methods are described by Zawlocki (1981).

Trace Organic Analysis

Replicate samples were filtered and extracted for trace organic analysis. Reproducibility in filtration of the particulates was usually within 5 percent. The total organic extracts replicates were generally within 20 percent, indicating good precision.

System blanks were included throughout the entire procedure and showed no appreciable background contamination. Analysis by gas chromatography indicated that the blanks contained less than 5 percent by weight of the compounds identified in the samples.

Sample recovery was checked by the addition of standards which were analysed by GC/MS. The response for compounds identified by mass spectrometry varies and can give an error as much as \pm 50 percent, which results in inaccurate calculations of sample recoveries. A standard with a variety of compounds was analyzed by GC/MS to check the relative sensitivities of the types of compounds identified. The

numerical results for specific compounds and for classes of compounds must be considered to be imprecise.

The mass spectra data are analyzed through comparison with spectra in a computer-stored library of spectra. A spectra match is selected by the computerized search through fit and purity criteria. Compound identifications were rejected in this study if either the fit or purity criteria values were low or if the concentrations were less than about 0.1 ng/ μ l.

Limited chromatographic resolution was achieved due to the complex nature of the samples. The constituents have been arranged as classes of compounds rather than individual compounds for these reasons. The reliability of identification in different compound classes is summarized in Table 2.

Individual mass spectra were analyzed for questionable compound identifies. For example, the large abundance of brominated compounds identified in two samples (I5-131P and 520-43P) was questionable. Evaluation of the individual mass spectra in these samples showed that many were misidentified hydrocarbons. Individual mass spectra were subsequently examined for each of the halogenated compounds identified by the data system.

Compounds identified were combined into classes, and concentrations in extract samples were calculated by comparing the mass spectrometer response to that of an internal standard. The concentrations then, for the original runoff samples were obtained by correcting for the dilution factor in the sample preparation. Finally the storm loadings (lb/acre) for the organics were computed by incorporating the

Table 2. Reliability of identification and concentration for individual compound categories.

CLASS OF COMPOUND	RELIABILITY	COMMENT
Alcohols	High	Evident in samples; exact name/structure confused.
Aliphatic Hydrocarbons	High	Clearly evident; frequent confusion in exact name/structure.
Aromatic Compounds	High	Evident; isomers confused
Halogenated Organics	Limited	Evident; frequently misidentified hydrocarbons requiring inspection of individual mass spectra for halogen determination.
Ketones and Aldehydes	Limited	Evident; highly substituted, polar compounds likely to be in error.
Organosulfur Compounds	Limited	Thiophenes and thiazoles evident; possible error in thiocyanate identities, further confirmation needed
Oxygenates	Limited	Unlikely abundance of highly oxygenated compounds and acids; likely errors in structure identity; further confirmation needed.
Nitrogen Containing	Limited	Evident; questionable identification of cyanates and amino acids, confirmation needed.
Phenols	High	Evident; isomers confused.

volume collected by the sampler, the sampler flowsplitting fraction, and the area of the site.

RESULTS

Runoff samples from storm events were obtained with a range of rainfall, rainfall intensity, preceding dry days and traffic amounts (Table 3). The variations that were obtained include a long, dry period, for example, storm I5-78 had 36 preceding dry days and therefore a high traffic volume preceding the storm.

Data obtained by Asplund (1981) for the concentrations of pollutants in the eight storm samples are presented in Table 4. The values for suspended solids, COD and TOC are in the range for other samples from the sites. The factors influencing the concentrations include, but are not limited to, the climatic and traffic parameters in Table 3. For instance, both storm events 520-11 and 520-43 had similar amounts of traffic during the storm and similar dry periods, but the intensity of the 520-11 event was approximately double that of the 520-43 event. Mass spectrometry-gas chromatography (GC/MS) analysis was performed on the runoff from the storm event on May 28 at both sites; (520-43 and I5-131).

The amount of organic matter in the samples should be directly correlated to the TOC, which is the carbon contained in the organic, the COD, which is the amount of organics measured by their oxidation, and VSS, which is the amount of particulate material (organic) which can be combusted. TSS is also included since it has shown promise of being

Table 3. Rainfall, runoff, and traffic data of storm events.

Storm Event	Date	Rainfall (In)	Duration (hr)	Average Intensity (In/hr)	Vehicles During Storm	Vehicles Preceding Storm	Runoff Volume (ft ³)	Runoff Coefficient	Dry ⁵ Days
15-78 ¹	10-14-79	0.25	7	.036	5,980	2,022,980	903	0.82	36
15-79 ¹	10-20-79	0.74	18	.041	38,540	142,690	1287	0.39	6
15-93 ¹	12-18-79	1.34	22	.061	46,300	46,300	4301	0.93	1
520-11 ¹	12-02-79	1.39	17	.082	26,610	224,200	350 ³	0.75 ⁴	5
520-16 ¹	12-19-80	0.70	19	.037	35,800	62,650	176 ³	0.75 ⁴	1
520-43 ²	05-28-80	0.80	18	.044	23,400	187,200	201 ³	0.75 ⁴	6
15-131 ²	05-28-80	0.86	20	.043	46,980	298,120	3059	0.80	6
15-87 ²	12-2-79	1.20	18	.067	58,830	294,570	2862	0.71	5

Notes: 1. Organic data for this storm are for conventional pollutants and organic extracts only.

2. Organic data for this storm include conventional pollutants, organic extracts and GC/MS analysis.

3. Measured values are low due to leakage through expansion joints.

4. Estimated (Asplund, 1980).

5. Dry days preceding storm event.

Table 4. Conventional pollutant analyses.

PARAMETER	I-5-78	I-5-79	I-5-93	520-11	520-16	520-43	I-5-131	I-5-87
pH	5.4	5.9	5.3	4.8	5.5	6.3	5.8	4.3
TSS(mg/l)	97.0	32.0	118.0	335.0	144.0	408.0	57.0	72.0
VSS(mg/l)	26.0	12.0	26.0	115.0	53.0	74.0	19.0	10.0
COD(mg/l)	61.0	61.0	52.0	271.0	130.0	280.0	166.0	59.0
TOC(mg/l)	21.8	18.4	28.3	36.8	25.8	355.8	97.5	12.5
Oil/Grease (mg/l)	38.7*	38.7*	30.7	30.7	48.8	480.0	93.5	14.6

*Storms combined for analysis

an excellent surrogate parameter to correlate with other pollutant concentrations. Grease/oils should represent the extractable organics (measured as carbons) and be comparable to the value for total organics extracted. Further analysis of these data along with the organic compound data did not support any strong conclusion. It is believed that experimental uncertainty and the small number of samples observed patterns that should be observable.

The data obtained in preparatory and extraction of the samples for total organics extract (TOE), the storm loadings for the TOE, and the ratio of the TOE to the TSS are presented in Table 5.

The organic concentrations were variable especially for the soluble fraction. However since the majority of the extracts were from the particulate fractions, the total concentrations ranged only from 12.4 to 31.4 mg/l. The ratio of particulate TOE to TSS was variable over about the same range from 0.074 to 0.317 mg/mg. Such a ratio may prove useful in estimating possible organic concentrations at other highway locations.

The grease/oil values (Table 4) and the total TOE values (Table 5) do not show the expected high degrees of correlation. There were problems in analysis for grease/oils that are described by Asplund (1981); the total TOE values are believed to be much more accurate.

The organic compounds are classified and combined into nine categories: alcohols, aliphatic hydrocarbons, aromatic compounds, halogenated organics, ketones and aldehydes, organosulphur compounds, oxygenates, nitrogen containing compounds and phenols. The oxygenate category includes ethers, esters, carboxylic acids, and epoxides; alcohols,

Table 5. Extractable organic concentration and pollutant loadings of particulate and soluble fractions.

PARAMETER	STORM 1-5-78			STORM 1-5-79			STORM 1-5-93			STORM 520-11		
	Parti- culate	Soluble	Total*									
TOTAL ORGANIC EXTRACT (mg/l)	15.6	7.8	23.4	7.3	5.1	12.4	9.5	3.0	12.5	30.8	0.62	31.4
STORM MASS LOAD- ING FOR TOE (lb/acre)	0.72	0.36	1.08	0.48	0.33	0.81	2.1	0.66	2.76	6.8	0.14	6.94
TOTAL ORGANIC EXTRACT TO TOTAL SUSPENDED SOLIDS RATIO	0.165	-	-	0.317	-	-	0.074	-	-	0.076	-	-
=====												
PARAMETER	STORM 520-16			STORM 520-43			STORM 1-5-131			STORM 1-5-87		
	Parti- culate	Soluble	Total*									
TOTAL ORGANIC EXTRACT (mg/l)	19.1	2.7	21.8	17.6	4.6	22.2	13.4	9.3	22.7	13.5	1.1	14.6
STORM MASS LOAD- ING FOR TOE (lb/acre)	2.1	0.3	2.4	2.2	0.6	2.8	2.1	1.4	3.5	2.7	1.2	2.9
TOTAL EXTRACT (mg/mg)	0.130	-	-	0.049	-	-	0.109	-	-	0.214	-	-

*Measurements were performed on the particulate and soluble fractions; the total is the sum of the two measurements.

phenols, and aldehydes and ketones were classified separately. Since some compounds have functional groups of several types there is overlap among several of the categories. Considering the uncertainties in compound identification, the compounds were classed according to functional group because the functional groups were determined with more certainty than the specific compound identities.

The categorization results for the three samples are presented in Table 6 by concentration in particulate and soluble fraction and in Table 7 by percentage distribution. The distributions are calculated in two ways: the fraction of a class (e.g. aliphatics) that is particulate; and the percentage that class is (e.g., aliphatics) of the total chromatographed organics.

The major features of the categorizations are the large portions associated with the particulates and the predominance of oxygenated compounds and aliphatic hydrocarbons, which together constituted 60 to 80 percent of the total. Other important fractions are aromatic compounds, alcohols, nitrogen compounds, and in single samples organosulphur compounds and phenols.

Aliphatic Hydrocarbons

Figure 2 shows the total concentration of unsubstituted aliphatic hydrocarbons which include paraffin, olefin and alicyclic hydrocarbons. The chromatogram for aliphatics (Figure 3) contained a homologous series of normal alkanes with an equal distribution of odd and even carbon chain lengths. This distribution implies that hydrocarbons were from petroleum rather than recent biological origin (Wakeham, 1976).

Table 6. Extractable organics classified into nine categories.

CLASS OF COMPOUNDS	STORM 1-5-87		STORM 1-5-131		STORM 520-43		Total (g/l)
	Particulate (g/l)	Soluble (g/l)	Particulate (g/l)	Soluble (g/l)	Particulate (g/l)	Soluble (g/l)	
Alcohols	T	160	478	155	327	126	453
Aliphatic Hydrocarbons	3710	3220	1850	636	913	20	933
Aromatic Compounds including Heterocyclics	2050	148	297	96	596	128	724
Halogenated Organics	T	T	173	9	114	T	114
Ketones and Aldehydes	1130	T	87	39	385	128	513
Organosulphur Compounds	1200	62	T	5.3	4.9	T	4.9
Oxygenates excluding alcohols, phenolics, ketones/-aldehydes.	3170	410	3510	228	2440	126	2570
Nitrogen Containing Compounds	1420	62	87	28	325	135	460
Phenolics	2830	80	T	2.9	T	T	T
Total Chromatographed	10236	6803	6308	1204	4083	320	4403

Table 7. Percentage distribution into the particulate phase among all categories.

PARAMETER	STORM I-5-87			STORM I-5-131			STORM 520-43		
	% Particulate of Category	% in Category of Total	% Particulate of Category	% Particulate of Category	% in Category of Total	% Particulate of Category	% Particulate of Category	% in Category of Total	
Alcohol	T	0.9	75.5	8.4	72.2	10.3			
Aliphatic Hydrocarbons	53.5	40.7	74.4	33.1	97.9	21.2			
Aromatic Compounds	93.2	12.9	75.6	5.2	82.3	16.4			
Halogenated Compounds	T	T	89.0	1.1	99.9	2.6			
Ketones/Aldehydes	99.9	6.6	69.1	1.7	75.0	11.6			
Organosulphur	95.1	7.4	T	0.07	99.9	0.11			
Oxygenates, excluding alcohols, phenols, ketones and aldehydes	88.6	21.0	93.9	49.8	95.0	58.4			
Nitrogen Compounds	95.8	8.7	75.7	1.5	70.7	10.4			
Phenols	97.3	17.1	T	0.04	T	T			
TOTAL*	60.1	100.	84.0	100.	92.7	100.			

*The sum of percentages may be greater than (or less than) 100 because an individual compound may be represented in several categories.

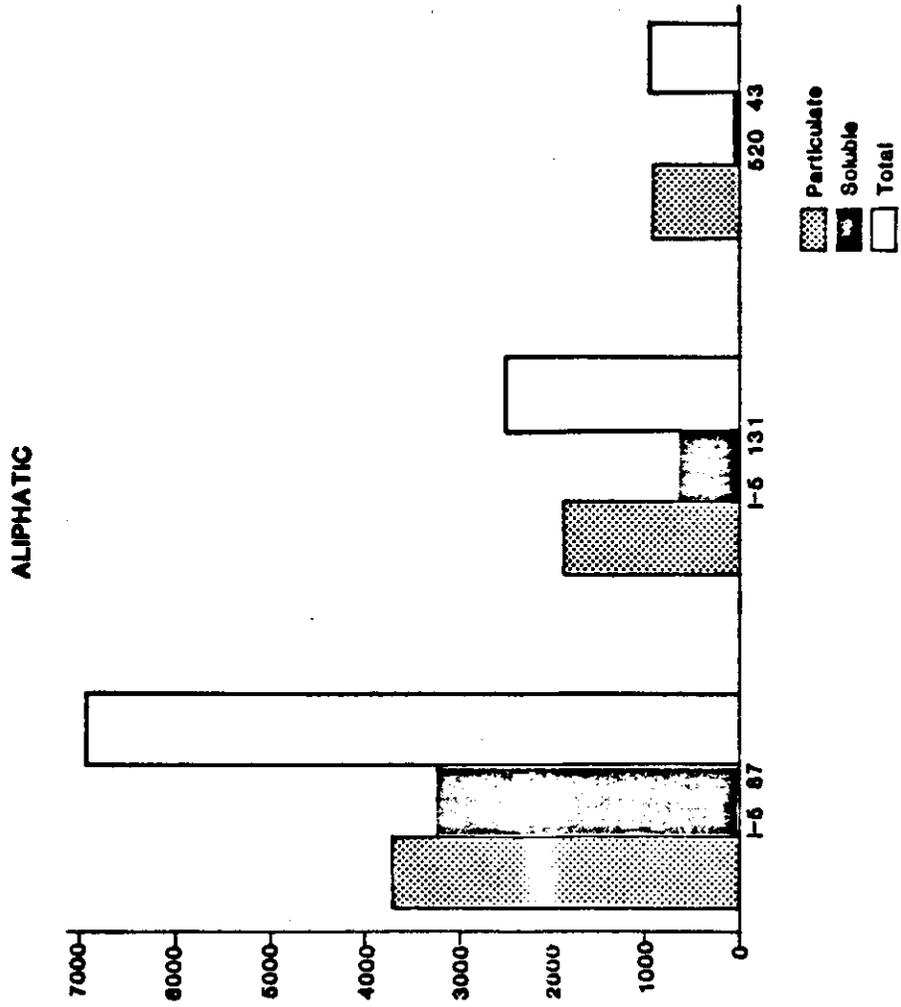


Figure 2. Distribution of aliphatic hydrocarbons.

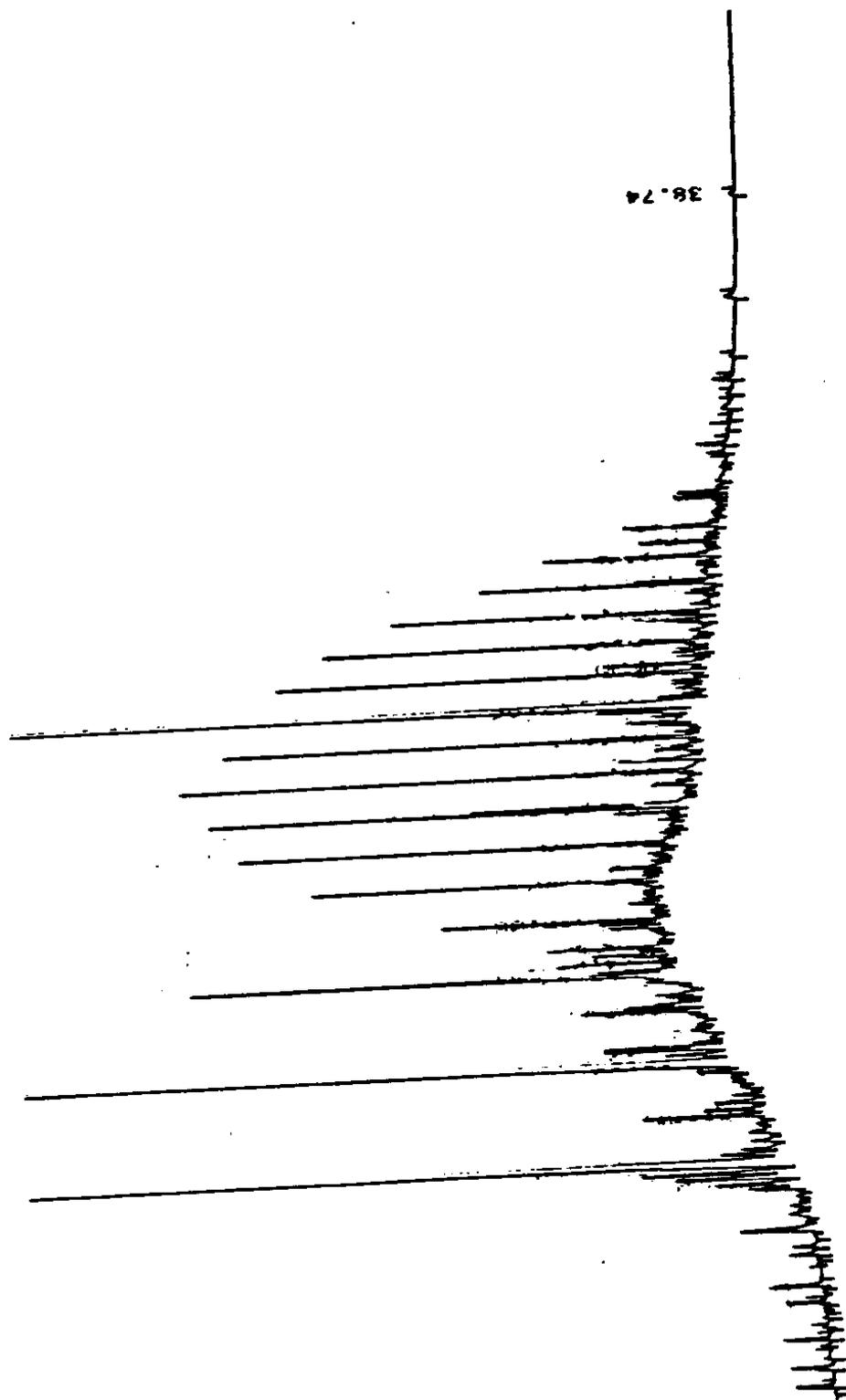


Figure 3. Chromatogram: Sample I5-87, aqueous phase; homologous series of n-alkanes.

The particulate fraction chromatograms were more complex with many poorly resolved peaks. The identifications and the chromatogram indicate motor vehicles are the predominant source of this predominant class of organics. Presumably unburned fuel, lubricants, and combustion byproducts are the principal sources of aliphatics.

Oxygenated Hydrocarbons

The distribution of the other large category of organic compounds is shown in Figure 4. Phenols, alcohols, ketones and aldehydes are classified separately for discussion purposes, leaving ethers, esters, epoxides, oxidized aromatics, and mono and dibasic carboxylic acids to be summed together as oxygenates. Many of the compounds contain several oxygen functional groups.

Some of the oxygenates are emitted in automobile exhaust, and some may result from carbonyl and ether formation via autooxidation of reactive unsaturated hydrocarbons (Kawahara, 1969). Oxygenated compounds may also preferentially be concentrated, relative to other organic constituents, in the runoff samples. Volatile hydrocarbons are lost as a result of evaporation, and some other compounds may be partially biodegraded by microorganisms to form oxygenated organic compounds.

Approximately 90 percent of the oxygenated hydrocarbons were associated with the particulate matter in the runoff samples. Interstate-5 samples contained more oxygenates than those from SR-520, which is in agreement with the general traffic level.

OXYGENATES

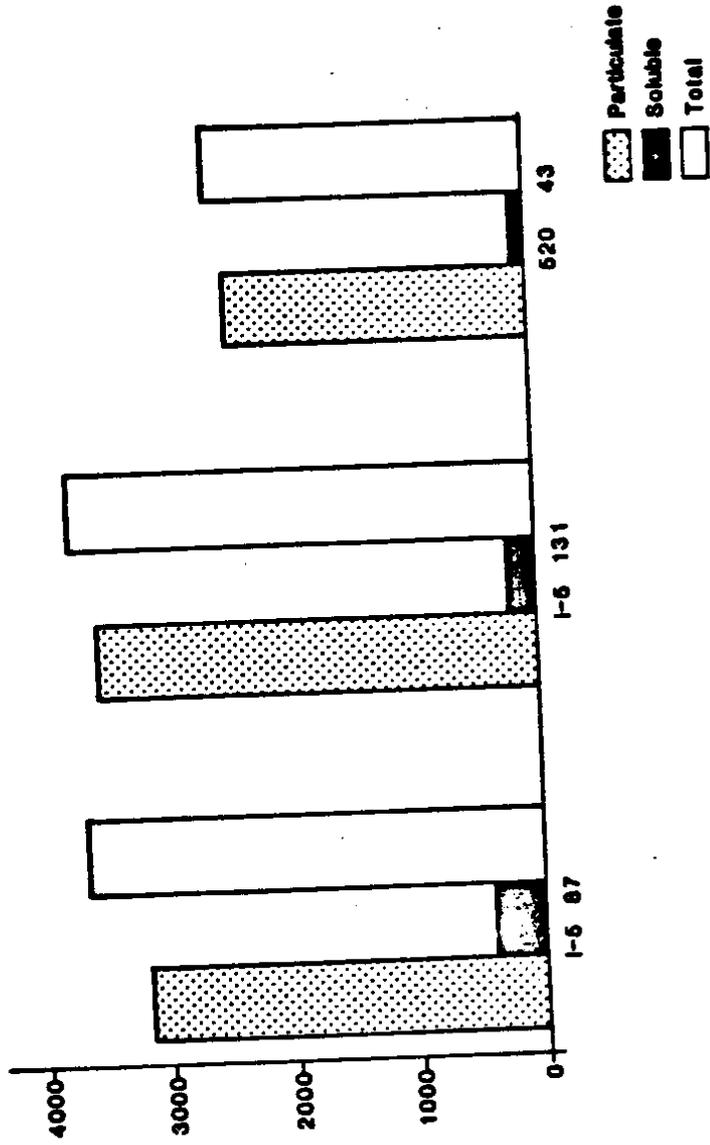


Figure 4. Distribution of oxygenated compounds.

Aromatic Compounds

This category includes substituted, heterocyclic, and mono and polycyclic aromatic hydrocarbons. The majority, 75 to 93 percent, of the aromatic compounds were associated with the particulate matter (Table 7), however, the soluble concentrations were nearly constant in these samples.

Aromatic compounds constituted a relatively large portion of the organic matter present in the samples, especially in the 520 site sample and included oxidized aromatics such as benzoic acid, phenyl acetic acid and higher homologs. The ratio of aromatic compounds to hydrocarbons in runoff is higher than in oils and gasoline, suggesting that some compounds were formed by oxidation. Exhaust aerosols from automobiles apparently contribute to the aromatic content of runoff waters.

Comparison of the aromatic concentration between the I-5 and SR 520 sites for the same storm event shows 520 with an aromatic concentration twice that of I-5 and a 30 percent greater mass loading at the 520 site (Table 6).

Alcohols and Phenols

Many of the alcohols and phenols in the samples contained several hydroxyl groups and alkyl groups. The soluble phase contained greater than 20 percent of the alcohols, but a greater portion of phenols was associated with the particulate phase.

Gasoline, gasoline additives and lubricants contain alcohols and phenols such as 2, 6-d₁-tertiary-butyl, 4-methyl phenol; substituted phenols are also identified in automobile exhaust (Seizinger and Dimi-

triades, 1972). However, many other sources are also possible, so the origin of the compound in runoff is not certain.

Nitrogen Containing Compounds

The majority of the organic nitrogen compounds observed in the samples were aromatic, heterocyclic compounds. Although nitro-olefins have been found as combustion products of hydrocarbons in laboratory studies (Wasserberger, et al., 1970), they were not observed in these samples. Typically, indole, indene, thiazole, pyridinyl and imidazole ring formations were present. Amino compounds were also relatively abundant in the samples, and compounds with this functional group are known to be used as additives in gasoline and lubricating oils. Novakov, et al. (1972) has reported substantial concentrations of pyridinyl and amino compounds in airborne particulate matter. Amino acids were rarely observed, with the exception of small amounts in the 520-43 sample, indicating the probable absence of biological sources. Heterocyclic compounds such as quinolines were observed, and these compounds have been found in automobile exhaust and effluents from coal and incinerator burning (Sawicki, et al., 1975).

Organosulfur Compounds

The majority of organosulfur compounds were substituted benzothiazoles and thiocyanate compounds. The cyanates were found, but the identification is questionable. Thiazoles are widely used in rubber compounding; concentrations in passenger tires are 1.0 to 3.0 percent. Substantial concentrations of organosulfur compounds were found only in

the 15-87 storm event runoff sample, and these were almost entirely associated with the particulate matter (95 percent, Table 7).

Keotones and Aldehydes

Mass fragments believed to be from ketones and aldehydes occurred in all samples. They represent a small portion (approximately 1.0 to 13.0 percent) of the total sample chromatographed (Table 7). The majority of these compounds (97 percent or greater) were found in the particulate phase and were also substituted with hydroxy or nitrogen constituents.

Halogenated Compounds

Brominated and chlorinated hydrocarbons were observed in all samples with brominated species predominant. The presence of these compounds, typically 1,2 dibromo-dodecane, in runoff waters may be attributed to combustion products and drippings from gasoline. Metal deactivators are added to gasoline, such as TEL from Ethyl Corporation, which contain 17.9 percent ethylene dibromide and 18.8 percent ethylene dichloride by weight (the halogens are approximately equal in concentration). Perhaps during combustion and condensation formation of stable brominated hydrocarbons occurs as well as the formation of lead salts.

There is little evidence of polychlorinated biphenyls (PCB) and chlorinated aromatic hydrocarbons in the runoff waters from the highway sites studied. These compounds were rarely observed in the mass spectra data and then in only very trace amounts. Further research is

needed by specific extraction and chromatography to quantify these constituents.

However, chromatograms using the electron capture electron indicate the presence of halogens in both particulate and aqueous fraction. Mass-spectrometry analysis was not able to resolve and identify many of these peaks, so the values reported in Table 6 are a low estimate of the total halogenated organics.

Loading Estimation and Concentration

The data in this investigation is not sufficient to show relation between storm, traffic and runoff characteristics. The data support Tseng's (1979) conjecture that the traffic volume during the storm has a greater effect on the pollutant loadings than the rainfall. However, comparison of several storm events (Tables 3 and 8) indicates that traffic flow alone is not sufficient to predict the pollutant loading. The loadings calculated for the individual storm are too limited to form the basis for long term prediction for the specific sites studied, let alone for other locations.

Comparison Between Sites

In general, the SR-520 station had much more particulate matter in the runoff water than the I-5 station for similar quantities of rainfall but did not have much greater organic concentrations. Comparison between the two stations, I-5 and SR-520, for the same storm event (520-43 and I5-131) shows that pollutant mass loadings from the particulate matter were very similar even though the SR-520 site had three

Table 8. Pollutant mass loadings and concentrations.

PARAMETER	STORM 520-16		STORM 520-43		STORM 1-5-131		STORM 1-5-87		STORM 1-5-79		STORM 1-5-79		STORM 1-5-93		STORM 520-11	
	mg/l	lb/acre	mg/l	lb/acre	mg/l	lb/acre	mg/l	lb/acre	mg/l	lb/acre	mg/l	lb/acre	mg/l	lb/acre	mg/l	lb/acre
Particulate	147	16.3	362	45.8	123	19.2	63	12.	95	4.4	23	1.5	128	28.1	404	89.0
TSS	144	15.9	408	51.6	57	8.9	72	14.	97	4.5	32	2.1	118	25.9	435	95.8
VSS	53	5.9	74	9.4	19	2.97	10	2.0	26	1.2	12	0.79	26	5.7	115	25.3
CO ₂	130	14.4	280	35.4	166	25.9	59	12	61	2.8	61	4.0	52	11.4	271	59.7
Pb	0.5	0.05	0.9	0.1	0.7	0.11	0.3	0.06	0.8	0.04	0.1	0.007	0.8	0.2	0.8	0.2
Particulate Extract	19.1	2.1	17.6	2.2	13.4	2.1	13.5	2.66	15.6	0.72	7.3	0.48	0.5	2.1	30.8	6.79
Aqueous Extract	2.7	0.4	4.6	0.6	9.3	1.4	1.1	0.22	7.8	0.36	5.1	0.33	3.0	0.66	0.62	0.14
Alcohols	0.453	0.057	0.057	0.057	0.633	0.099	0.16	0.032								
Aliphatic	0.933	0.118	2.49	0.389	6.93	1.37										
Aromatic	0.724	0.092	0.393	0.061	2.20	0.43										
Halogens	0.114	0.014	0.082	0.013	T	T										
Ketones/Aldehydes	0.513	0.065	0.126	0.020	1.13	0.22										
Organo Sulfur	0.005	0.0006	0.005	0.001	1.26	0.25										
Oxygenates	2.57	0.325	3.74	0.586	3.58	0.71										
Phenols	T	T	0.003	0.0005	2.91	0.57										
Nitrogen	0.46	0.058	0.115	0.018	1.148	0.29										

Table 8. Pollutant mass loadings and concentrations.

PARAMETER	STORM 520-16		STORM 520-43		STORM 1-5-131		STORM 1-5-87		STORM 1-5-79		STORM 1-5-93		STORM 520-11		
	mg/l	lb/acre	mg/l	lb/acre	mg/l	lb/acre	mg/l	lb/acre	mg/l	lb/acre	mg/l	lb/acre	mg/l	lb/acre	
Particulate	147	16.3	362	45.8	123	19.2	63	12.	95	4.4	23	128	28.1	404	89.0
TSS	144	15.9	408	51.6	57	8.9	72	14.	97	4.5	32	118	25.9	435	95.8
VSS	53	5.9	74	9.4	19	2.97	10	2.0	26	1.2	12	26	5.7	115	25.3
COO	130	14.4	280	35.4	166	25.9	59	12	61	2.8	61	52	11.4	271	59.7
Pb	0.5	0.05	0.9	0.1	0.7	0.11	0.3	0.06	0.8	0.04	0.1	0.8	0.2	0.8	0.2
Particulate Extract	19.1	2.1	17.6	2.2	13.4	2.1	13.5	2.66	15.6	0.72	7.3	0.5	2.1	30.8	6.79
Aqueous Extract	2.7	0.4	4.6	0.6	9.3	1.4	1.1	0.22	7.8	0.36	5.1	3.0	0.66	0.62	0.14
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Nitrogen	0.46	0.058	0.115	0.018	1.148	0.29									

times the amount of particulate matter and I-5 had twice the amount of traffic during the rainfall (Figure 5).

At both I-5 and SR-520, the distribution of the various classes of organic compounds in the runoff samples for the same storm event was similar which would indicate similar sources and mechanisms.

SUMMARY AND CONCLUSIONS

A survey of trace organics occurring in highway runoff from the I-5 and SR 520 sites was completed, examining 8 storms. Composite samples were collected and analyzed for both trace organic pollutants and conventional pollutants.

The samples contained low concentrations of a large number of complex organic compounds. Several hundred compounds were tentatively identified utilizing a computerized search system and the NBS library of organic compounds (35,000 spectra). The identities of specific compounds are not highly reliable for a variety of reasons, including low GC and mass spectral resolution caused by limited sample fractionation and cleanup.

These considerations led to a primary emphasis on behavior of categories of compounds, where total concentration in the categories are less uncertain than specific identities. Compounds with concentrations ranging from about 1 to 100 $\mu\text{g/L}$ were grouped into nine categories: alcohols, aliphatic hydrocarbons, aromatics, halogenated, ketones/aldehydes, organosulfur, oxygenates, nitrogen containing compounds, and phenols.

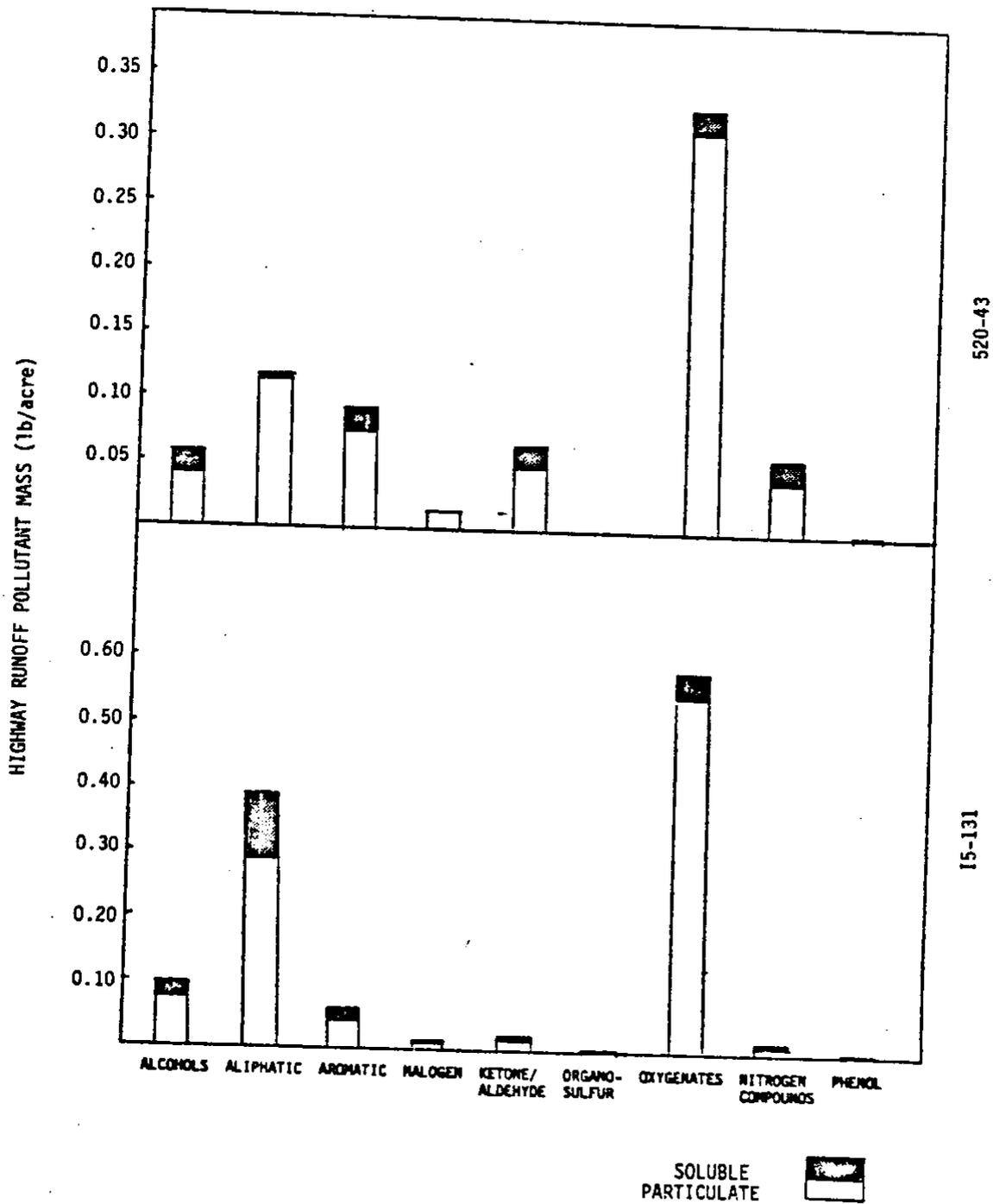


Figure 5. Comparison of category pollutant mass for the May 28th storm event at I-5 and 520 sites.

Traditional water quality parameters were measured for all of the storms sampled. These analyses included total suspended solids (TSS) and estimations of organic content by volatile suspended solids (VSS), chemical oxygen demand (COD), total organic carbon (TOC) and the grease-oil analysis. Although the grease-oil and TOC analyses were in agreement with each other no strong correlation was seen with either the organic extract analysis or the VSS, both of which were indicative of the amount of organics present in the samples. In general, both COD and VSS showed a weak proportionality to the organic extract analyses.

The major classes of organic compounds in the runoff samples were oxygenates, aliphatic hydrocarbons and aromatic compounds. Aliphatic hydrocarbon concentrations ranged from 5.0 to 25.0 mg/L and total organic extract concentrations ranged from 12.0 to 31.0 mg/L. In general, aliphatic hydrocarbons were more abundant than aromatic compounds in both particulate and aqueous phases. Aliphatic hydrocarbons and oxygenated compounds showed a considerable degree of unsaturation and included many branched compounds. The particulate solids had larger amounts of organic matter than the aqueous phase.

The specific conclusions are:

1. Extraction and GC/MS/DS analysis indicated that on the average, 80 percent of the aromatic compounds were associated with the particulate matter in the highway runoff waters. The entire range for organics concentrated on the particulates was between 59 and 98 percent of the total organics present in the sample. Extractable organics associated with the particulate solids ranged from 5 to 20 percent of the particulate mass.

2. Oxygenated compounds and aliphatic hydrocarbons were the predominant classes of compounds. Aromatic compounds were also relatively abundant.
3. The proportions of the various classes of compounds and the types of oxygenated compounds found resemble combustion byproducts such as auto exhaust and organics found in airborne particulate matter. The major sources of organic pollutants were from a petroleum origin including lubricating oils, fuels, combustion emissions and rubber or plastics.
4. Biological compounds are not predominant in the samples as shown by absence of even chain length predominance in the normal alkanes and the absence of amino acids.
5. Brominated organic compounds constitute the largest fraction of halogenated compounds present in several samples. The halogenated organics represent approximately one to two percent of the compounds identified.
6. Among the particularly hazardous compounds, polynuclear aromatics and nitrogen heterocyclics were found in runoff. However, polychlorinated biphenyls and other chlorinated aromatics were not detected.
7. Insufficient data were obtained to establish if correlations exist between traffic and the organic pollutant loadings. Traditional water quality analyses were not accurate indicators of the kinds and concentrations of organics in these runoff samples.

8. The relatively large fraction of extractable organics in the TSS and the large number of unidentified compounds indicate that more research on runoff trace organics may be useful.

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