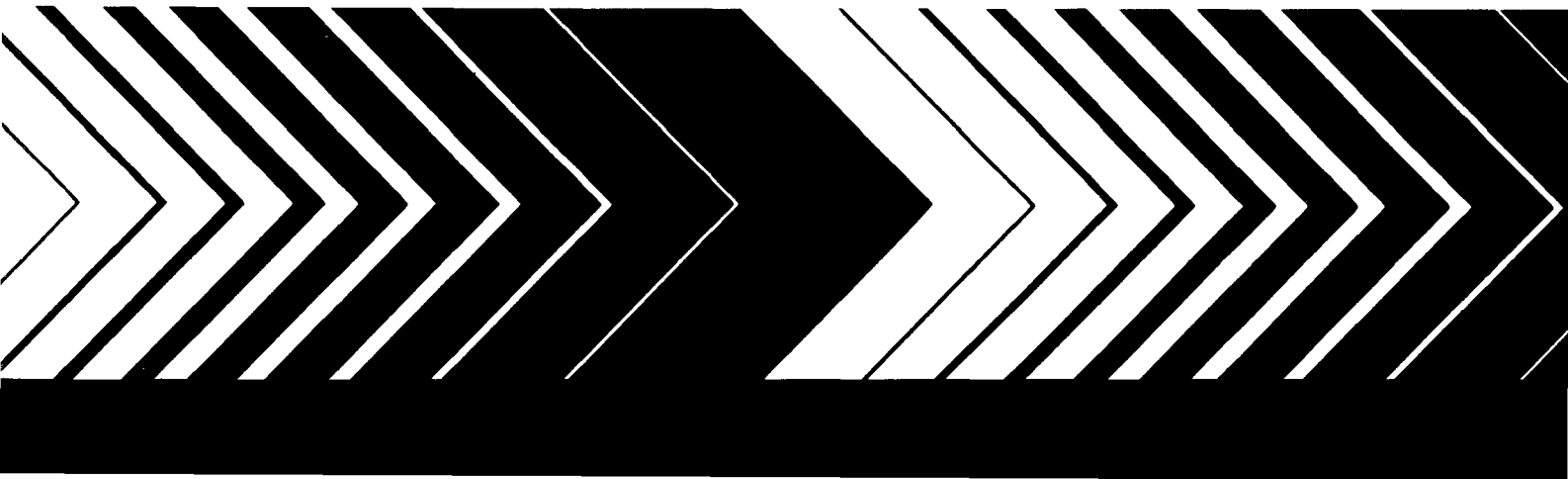




# Regional Air Pollution Study

## Point and Area Source Organic Emission Inventory



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EPA-600/4-78-028  
June 1978

REGIONAL AIR POLLUTION STUDY  
Point and Area Source Organic Emission Inventory

by

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Task Order 108I

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## ABSTRACT

An inventory of organic emissions from stationary and mobile sources has been assembled for the St. Louis Air Quality Control Region. The inventory covers point and area sources for process, combustion and evaporative emissions.

A breakdown into five categories has been assigned to each source type. The categories are (1) paraffins, (2) olefins, (3) aromatics, (4) aldehydes, and (5) non-reactives. The breakdown was made part of the RAPS Emission Inventory System, which is stored on the EPA's Univac computer at Research Triangle Park, N.C.

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## 1.0 INTRODUCTION

The Regional Air Pollution Study (RAPS) has as its first goal the validation of atmospheric dispersion models. Emissions data, generally supplied in the form of an emission inventory, are a major constituent of a dispersion model. The RAPS Point and Area Source Hydrocarbon Inventory was designed to provide emission data for the evaluations of photochemical reaction models. Since organics participate in photochemical reactions leading to "smog", the inventory includes all available organic emission data. As the reactivity of organics varies widely, it is important to determine not only the amount emitted, but also the composition.

Chemical kinetic mechanisms present in air quality simulation models require some form of hydrocarbon classification in order to treat the reaction processes and rates associated with their structural make-up. One such classification scheme required in using a lumped chemical kinetic reaction mechanism approach distributes hydrocarbons in the atmosphere structurally into paraffin, olefin, aromatic, aldehyde, and non-reactive classes. This report describes how this classification has been determined for hydrocarbon emissions in the St. Louis AQCR and provides sufficient reference data to derive alternative schemes as required.

## 2.0 TOTAL HYDROCARBON INVENTORY

The basic RAPS Hydrocarbon Inventory is composed of several separate inventories which have been described in various reports.

The hydrocarbon inventory for stationary point sources was developed by Rockwell under Contract No. 68-02-2093, T0108F, and provides an up-to-date listing of hydrocarbon emissions from stationary point sources in the St. Louis AQCR, with a breakdown into methane and non-methane hydrocarbons. The inventory includes all industrial hydrocarbon emission sources which emit more than one ton per year of hydrocarbons. Point sources in the St. Louis Air Quality Control Region (AQCR-70) emit approximately 47,600 tons per year, or 22.6 percent of the hydrocarbon emissions in the AQCR. The report also describes an analytical technique, based on gas chromatography, which is suitable for analysis of hydrocarbons in the concentration range of 1 to  $10^6$  ppm and is linear with respect to both carbon number and hydrocarbon concentration.

Area source evaporative hydrocarbon emissions from dry cleaning plants, surface coating, and gasoline marketing are included in the "Residential and Commercial Area Sources Emission Inventory" (EPA 450/2-75-078), which provides information on hydrocarbon emissions on a grid square basis. Spatial allocations were based on population and land use densities. Temporal apportioning was based on an 8 AM to 5 PM workday or the diurnal traffic cycle in St. Louis.

Hydrocarbon emissions from small industrial sources are included in the report on "Stationary Industrial Area Sources" (EPA No. 68-02-2093, T0108D). This category contributes only about 110 tons annually, or about 0.05 percent of the total hydrocarbon emissions.

Emissions from mobile sources are the subject of several inventories: The Highway Vehicle Emission Inventory described in EPA 450/3-76-035 and

EPA 450/3-77-019 defines emissions from motor vehicles on a grid square or line basis. Emissions from river vessels are described in "River Towboat Air Pollution in St. Louis" (DOT-TSC-OST-75-42). The "Airport Emission Inventory" (EPA 450/3-75-048) deals with emissions from aircraft. A report on rail operations (EPA 450/3-77-025) describes the methodology and resultant inventory. Emissions from off-highway sources are described in "Off-Highway Mobile Source Emission Inventory" (EPA Contract No. 68-02-2093, T0108E).

A summary of hydrocarbon emissions is shown in Table 1.

TABLE 1. TOTAL HYDROCARBON EMISSION INVENTORY

SOURCE CATEGORY	ANNUAL EMISSIONS, TONS
<u>Point Sources</u>	
Fuel Combustion	2,717
Chemical Manufacturing	6,702
Primary Metals - Coke Ovens	2,339
Refinery Operations	7,161
Surface Coatings	21,072
Petroleum Storage and Marketing	7,457
Solid Waste Disposal	136
Miscellaneous	24
TOTAL	47,610
<u>Area Sources</u>	
Industrial Area Sources	110
Residential and Commercial	22,610
Vehicles, Line Sources	100,440
Vehicles, Area Sources	12,565
Railroads	4,220
River Vessels	940
Airports	1,460
Off-Highway Mobile	16,280
Gasoline Marketing	13,650
Dry Cleaning	645
Surface Coating	3,757
TOTAL	176,677
TOTAL, ALL SOURCES	224,287

## 2.1 POINT SOURCES

Point sources are those individually identified industrial sources which

release emissions through a stack, such as a boiler, or a vent, as in the case of a petroleum storage tank. (Exceptions to this are leaks in refineries from valves, seals, flanges, etc., which are included as point sources under the appropriate SCC numbers.) Point sources in the St. Louis Air Quality Control Region (AQCR) emit approximately 47,600 tons per year total hydrocarbons, or 22.6 percent of the hydrocarbon emissions in the AQCR. The lower cut-off used to define point sources is one ton per year hydrocarbons.

The point source inventory is comprised of data for individual sources in the AQCR for which emissions have been obtained in the course of the RAPS study. Each source is classified by its identification code, called the Source Classification Code (SCC). The SCC is an identification system developed for the National Emissions Data System (NEDS), upon which the point source hierarchy is structured. The SCC system is being used for the RAPS point source data handling system. All data are stored and retrieved by use of the SCC. A process which emits one or more of the criteria air pollutants can be represented by one or several SCC numbers. Table 2 shows a typical sample of SCC numbers. The SCC numbers consist of four groupings. For example, in SCC 4-03-001-02:

- Group I - a single digit (4) - designates "Point Source, Evaporative"
- Group II - two digits (03) - designates "Petroleum Storage"
- Group III - three digits (001) - designates "Fixed Roof"
- Group IV - two digits (02) - designates "Breathing-Crude"

In addition, the base unit upon which the emission factors are based is given; in this case, "1000 gallons storage capacity".

The starting point of an emission inventory is data collection. Inventory data such as process, consumption or storage data are gathered. Modeling information is also collected in the form of location and stack parameters. From the inventory data, the appropriate emission factors are obtained and stored in the data file. These factors are based upon the best available information, generally gathered from source tests. The inventory data gathered and emission factors are applied to generate emission figures for total hydrocarbons, as well as other criteria pollutants. Table 3 shows a typical sample of emission factors and the associated SCC numbers.

TABLE 2. SAMPLE OF THE NATIONAL EMISSIONS DATA SYSTEM (NEDS)  
SOURCE CLASSIFICATION CODE (SCC) REPORT

SCC 10 *****				SCC CATEGORY NAMES *****				UNITS	
I	II	III	IV	I	II	III	IV		
3	90	001	99	INDUSTRIAL PROCESS/INPROCESS FUEL	1	ANTHRACITE COAL	10THER/NOT CLASIFD	ITONS BURNED	
3	90	002	01	INDUSTRIAL PROCESS/INPROCESS FUEL	1	BITUMINOUS COAL	1CEMENT KILN	ITONS BURNED	
3	90	002	06	INDUSTRIAL PROCESS/INPROCESS FUEL	1	BITUMINOUS COAL	1BICK KILN/DRY	ITONS BURNED	
3	90	002	07	INDUSTRIAL PROCESS/INPROCESS FUEL	1	BITUMINOUS COAL	1GYPSUM KILN/ETC	ITONS BURNED	
3	90	002	08	INDUSTRIAL PROCESS/INPROCESS FUEL	1	BITUMINOUS COAL	1COAL DRYERS	ITONS BURNED	
3	90	002	99	INDUSTRIAL PROCESS/INPROCESS FUEL	1	BITUMINOUS COAL	1OTHER/NOT CLASIFD	ITONS BURNED	
3	90	004	01	INDUSTRIAL PROCESS/INPROCESS FUEL	1	RESIDUAL OIL	1ASPHALT DRYER	11000 GALLONS BURNED	
3	90	004	02	INDUSTRIAL PROCESS/INPROCESS FUEL	1	RESIDUAL OIL	1CEMENT KILN	11000 GALLONS BURNED	
3	90	004	03	INDUSTRIAL PROCESS/INPROCESS FUEL	1	RESIDUAL OIL	1LIME KILN	11000 GALLONS BURNED	
3	90	004	04	INDUSTRIAL PROCESS/INPROCESS FUEL	1	RESIDUAL OIL	1KAOLIN KILN	11000 GALLONS BURNED	
3	90	004	05	INDUSTRIAL PROCESS/INPROCESS FUEL	1	RESIDUAL OIL	1METAL MELTING	11000 GALLONS BURNED	
3	90	004	06	INDUSTRIAL PROCESS/INPROCESS FUEL	1	RESIDUAL OIL	1BRICK KILN/DRY	11000 GALLONS BURNED	
3	90	004	07	INDUSTRIAL PROCESS/INPROCESS FUEL	1	RESIDUAL OIL	1GYPSUM KILN/ETC	11000 GALLONS BURNED	
3	90	004	99	INDUSTRIAL PROCESS/INPROCESS FUEL	1	RESIDUAL OIL	1OTHER/NOT CLASIFD	11000 GALLONS BURNED	
3	90	005	01	INDUSTRIAL PROCESS/INPROCESS FUEL	1	DISTILLATE OIL	1ASPHALT DRYER	11000 GALLONS BURNED	
3	90	005	02	INDUSTRIAL PROCESS/INPROCESS FUEL	1	DISTILLATE OIL	1CEMENT KILN	11000 GALLONS BURNED	
3	90	005	03	INDUSTRIAL PROCESS/INPROCESS FUEL	1	DISTILLATE OIL	1LIME KILN	11000 GALLONS BURNED	
3	90	005	04	INDUSTRIAL PROCESS/INPROCESS FUEL	1	DISTILLATE OIL	1KAOLIN KILN	11000 GALLONS BURNED	
3	90	005	05	INDUSTRIAL PROCESS/INPROCESS FUEL	1	DISTILLATE OIL	1METAL MELTING	11000 GALLONS BURNED	
3	90	005	06	INDUSTRIAL PROCESS/INPROCESS FUEL	1	DISTILLATE OIL	1BICK KILN/DRY	11000 GALLONS BURNED	
3	90	005	07	INDUSTRIAL PROCESS/INPROCESS FUEL	1	DISTILLATE OIL	1GYPSUM KILN/ETC	11000 GALLONS BURNED	
3	90	005	99	INDUSTRIAL PROCESS/INPROCESS FUEL	1	DISTILLATE OIL	1OTHER/NOT CLASIFD	11000 GALLONS BURNED	
3	90	006	01	INDUSTRIAL PROCESS/INPROCESS FUEL	1	NATURAL GAS	1ASPHALT DRYER	1MILLION CUBIC FEET BURNED	
3	90	006	02	INDUSTRIAL PROCESS/INPROCESS FUEL	1	NATURAL GAS	1CEMENT KILN	1MILLION CUBIC FEET BURNED	
3	90	006	03	INDUSTRIAL PROCESS/INPROCESS FUEL	1	NATURAL GAS	1LIME KILN	1MILLION CUBIC FEET BURNED	
3	90	006	04	INDUSTRIAL PROCESS/INPROCESS FUEL	1	NATURAL GAS	1KAOLIN KILN	1MILLION CUBIC FEET BURNED	
3	90	006	05	INDUSTRIAL PROCESS/INPROCESS FUEL	1	NATURAL GAS	1METAL MELTING	1MILLION CUBIC FEET BURNED	
3	90	006	06	INDUSTRIAL PROCESS/INPROCESS FUEL	1	NATURAL GAS	1BICK KILN/DRY	1MILLION CUBIC FEET BURNED	
3	90	006	07	INDUSTRIAL PROCESS/INPROCESS FUEL	1	NATURAL GAS	1GYPSUM KILN ETC	1MILLION CUBIC FEET BURNED	
3	90	006	99	INDUSTRIAL PROCESS/INPROCESS FUEL	1	NATURAL GAS	1OTHER/NOT CLASIFD	1MILLION CUBIC FEET BURNED	
3	90	007	99	INDUSTRIAL PROCESS/INPROCESS FUEL	1	PROCESS GAS	1OTHER/NOT CLASIFD	1MILLION CUBIC FEET BURNED	
3	90	008	99	INDUSTRIAL PROCESS/INPROCESS FUEL	1	COKE	1OTHER/NOT CLASIFD	ITONS	
3	90	009	99	INDUSTRIAL PROCESS/INPROCESS FUEL	1	WOOD	1OTHER/NOT CLASIFD	ITONS BURNED	
3	90	999	97	INDUSTRIAL PROCESS/INPROCESS FUEL	1	OTHER/NOT CLASIFD	SPECIFY IN REMARK	1MILLION CUBIC FEET BURNED	
3	90	999	98	INDUSTRIAL PROCESS/INPROCESS FUEL	1	OTHER/NOT CLASIFD	SPECIFY IN REMARK	1000 GALLONS BURNED	
3	90	999	99	INDUSTRIAL PROCESS/INPROCESS FUEL	1	OTHER/NOT CLASIFD	SPECIFY IN REMARK	ITONS BURNED	
3	90	999	99	INDUSTRIAL PROCESS/INPROCESS FUEL	1	OTHER/NOT CLASIFD	SPECIFY IN REMARK	ITONS PROCESSED	
4	01	001	01	POINT SC EVAP	1	CLEANING SOLVENT	1HYDROCLEANING	1PERCHLOMETHYLENE	ITONS CLOTHES CLEANED
4	01	001	02	POINT SC EVAP	1	CLEANING SOLVENT	1HYDROCLEANING	1STANDARD	ITONS CLOTHES CLEANED
4	01	002	01	POINT SC EVAP	1	CLEANING SOLVENT	1DEGREASING	1STANDARD	ITONS SOLVENT USED
4	01	002	99	POINT SC EVAP	1	CLEANING SOLVENT	1DEGREASING	1OTHER/NOT CLASIFD	ITONS SOLVENT USED
4	01	999	99	POINT SC EVAP	1	CLEANING SOLVENT	1OTHER/NOT CLASIFD	SPECIFY IN REMARK	ITONS SOLVENT USED
4	02	001	01	POINT SC EVAP	1	SURFACE COATING	1PAINT	1GENERAL	ITONS COATING
4	02	003	01	POINT SC EVAP	1	SURFACE COATING	1VARNISH/SHELLAC	1GENERAL	ITONS COATING
4	02	004	01	POINT SC EVAP	1	SURFACE COATING	1LACQUER	1GENERAL	ITONS COATING
4	02	005	01	POINT SC EVAP	1	SURFACE COATING	1ENAMEL	1GENERAL	ITONS COATING
4	02	006	01	POINT SC EVAP	1	SURFACE COATING	1WHITEN	1GENERAL	ITONS COATING
4	02	999	99	POINT SC EVAP	1	SURFACE COATING	1OTHER/NOT CLASIFD	SPECIFY IN REMARK	ITONS COATING
4	03	001	01	POINT SC EVAP	1	PETROLEUM STG	1FIXED ROOF	1BREATHING-PHUGUCT	11000 GALLONS STORAGE CAPACITY
4	03	001	02	POINT SC EVAP	1	PETROLEUM STG	1FIXED ROOF	1BREATHING CHUUE	11000 GALLONS STORAGE CAPACITY

TABLE 3. SAMPLE OF EMISSION FACTORS

POINT SC EVAP - SURFACE COATING (CONTINUED)		POUNDS EMITTED PER UNIT					UNITS	
*****	*****	PART	SOX	NOX	HC	CO		
VARNISH/SMELLAC								
4-02-003-01	GENERAL	.			1.000.		TONS	COATING
LAQUER		.						
4-02-004-01	GENERAL				1.540.		TONS	COATING
ENAMEL								
4-02-005-01	GENERAL	0.	0.	0	840.	0.	TONS	COATING
PRIMER								
4-02-006-01	GENERAL				1.320.		TONS	COATING
COATING JVEN								
4-02-008-01	GENERAL						TONS	COATING
SOLVENT								
4-02-009-01	GENERAL						TONS	COATING
OTHER/NOT CLASIFO								
4-02-999-99	SPECIFY IN REMARK						TONS	COATING
POINT SC EVAP - PETROL PROD STG								
*****	*****							
FIXED HOUF								
4-03-001-01	BREATH-GASOLIN	0.	0.	0.	80.3	0.	1000 GALLONS	STORAGE CAPACITY
4-03-001-02	BREATH-CRUDE	0.	0.	0.	94.8	0.	1000 GALLONS	STORAGE CAPACITY
4-03-001-03	WORKING-GASOLINE	0.	0.	0.	9.00	0.	1000 GALLONS	THROUGHPUT
4-03-001-04	WORKING-CRUDE	0.	0.	0.	7.30	0.	1000 GALLONS	THROUGHPUT
4-03-001-05	BREATH-JET FUEL	0.	0.	0.	25.2	0.	1000 GALLONS	STORAGE CAPACITY
4-03-001-06	BREATH-KEROSENE	0.	0.	0.	13.1	0.	1000 GALLONS	STORAGE CAPACITY
4-03-001-07	BREATH-DIST FUEL	0.	0.	0.	13.1	0.	1000 GALLONS	STORAGE CAPACITY
4-03-001-08	BREATH-BENZENE	0.	0.	0.	18.3	0.	1000 GALLONS	STORAGE CAPACITY
4-03-001-09	BREATH-CYCLOHEX	0.	0.	0.	20.8	0.	1000 GALLONS	STORAGE CAPACITY
4-03-001-10	BREATH-CYCLOPENT	0.	0.	0.	58.4	0.	1000 GALLONS	STORAGE CAPACITY
4-03-001-11	BREATH-HEPTANE	0.	0.	0.	11.3	0.	1000 GALLONS	STORAGE CAPACITY
4-03-001-12	BREATH-HEXANE	0.	0.	0.	32.1	0.	1000 GALLONS	STORAGE CAPACITY
4-03-001-13	BREATH-ISOCETANE	0.	0.	0.	13.9	0.	1000 GALLONS	STORAGE CAPACITY
4-03-001-14	BREATH-ISOPENTANE	0.	0.	0.	142.	0.	1000 GALLONS	STORAGE CAPACITY
4-03-001-15	BREATH-PENTANE	0.	0.	0.	94.9	0.	1000 GALLONS	STORAGE CAPACITY
4-03-001-16	BREATH-TOLUENE	0.	0.	0.	5.84	0.	1000 GALLONS	STORAGE CAPACITY
4-03-001-17	WORKING-JET FUEL	0.	0.	0.	2.40	0.	1000 GALLONS	THROUGHPUT
4-03-001-18	WORKING-KEROSENE	0.	0.	0.	1.00	0.	1000 GALLONS	THROUGHPUT
4-03-001-19	WORKING-DIST FUEL	0.	0.	0.	1.00	0.	1000 GALLONS	THROUGHPUT
4-03-001-20	WORKING-BENZENE	0.	0.	0.	2.00	0.	1000 GALLONS	THROUGHPUT
4-03-001-21	WORKING-CYCLOHEX	0.	0.	0.	2.30	0.	1000 GALLONS	THROUGHPUT
4-03-001-22	WORKING-CYCLOPENT	0.	0.	0.	6.40	0.	1000 GALLONS	THROUGHPUT
4-03-001-23	WORKING-HEPTANE	0.	0.	0.	1.20	0.	1000 GALLONS	THROUGHPUT
4-03-001-24	WORKING-HEXANE	0.	0.	0.	3.60	0.	1000 GALLONS	THROUGHPUT
4-03-001-25	WORKING-ISOCETANE	0.	0.	0.	1.50	0.	1000 GALLONS	THROUGHPUT
4-03-001-26	WORKING-ISOPENTANE	0.	0.	0.	15.7	0.	1000 GALLONS	THROUGHPUT
4-03-001-27	WORKING-PENTANE	0.	0.	0.	10.4	0.	1000 GALLONS	THROUGHPUT
4-03-001-28	WORKING-TOLUENE	0.	0.	0.	0.64	0.	1000 GALLONS	THROUGHPUT
FLOATING HOUF								
4-03-002-01	STAND STG-GASOLN	0.	0.	0.	12.0	0.	1000 GALLONS	STORAGE CAPACITY
4-03-002-02	WORKING-PRODUCT	0.	0.	0.	0.	0.	1000 GALLONS	THROUGHPUT
4-03-002-03	STAND STG-CRUDE	0.	0.	0.	10.6	0.	1000 GALLONS	STORAGE CAPACITY
4-03-002-04	WORKING-CRUDE	0.	0.	0.	0.	0.	1000 GALLONS	THROUGHPUT
4-03-002-05	STAND STG-JET FUEL	0.	0.	0.	4.38	0.	1000 GALLONS	STORAGE CAPACITY
4-03-002-06	STAND STG-KEROSENE	0.	0.	0.	1.90	0.	1000 GALLONS	STORAGE CAPACITY
4-03-002-07	STAND STG-DIST FL	0.	0.	0.	1.90	0.	1000 GALLONS	STORAGE CAPACITY
4-03-002-08	STAND STG-BENZENE	0.	0.	0.	2.70	0.	1000 GALLONS	STORAGE CAPACITY
4-03-002-09	STAND STG-CYCLOHEX	0.	0.	0.	3.03	0.	1000 GALLONS	STORAGE CAPACITY
4-03-002-10	STAND STG-CYCLOPENT	0.	0.	0.	8.76	0.	1000 GALLONS	STORAGE CAPACITY
4-03-002-11	STAND STG-HEPTANE	0.	0.	0.	1.64	0.	1000 GALLONS	STORAGE CAPACITY
4-03-002-12	STAND STG-HEXANE	0.	0.	0.	4.75	0.	1000 GALLONS	STORAGE CAPACITY
4-03-002-13	STAND STG-ISOCETANE	0.	0.	0.	2.01	0.	1000 GALLONS	STORAGE CAPACITY
4-03-002-14	STAND STG-ISOPENTANE	0.	0.	0.	20.8	0.	1000 GALLONS	STORAGE CAPACITY
4-03-002-15	STAND STG-PENTANE	0.	0.	0.	13.9	0.	1000 GALLONS	STORAGE CAPACITY
4-03-002-16	STAND STG-TOLUENE	0.	0.	0.	0.88	0.	1000 GALLONS	STORAGE CAPACITY
VAR-VAPOR SPACE								
4-03-003-01	WORKING-GASOLINE	0.	0.	0.	10.2	0.	1000 GALLONS	THROUGHPUT
4-03-003-02	WORKING-JET FUEL	0.	0.	0.	2.30	0.	1000 GALLONS	THROUGHPUT
4-03-003-03	WORKING-KEROSENE	0.	0.	0.	1.00	0.	1000 GALLONS	THROUGHPUT
4-03-003-04	WORKING-DIST FUEL	0.	0.	0.	1.00	0.	1000 GALLONS	THROUGHPUT
4-03-003-05	WORKING-BENZENE	0.	0.	0.	2.30	0.	1000 GALLONS	THROUGHPUT
4-03-003-06	WORKING-CYCLOHEX	0.	0.	0.	2.60	0.	1000 GALLONS	THROUGHPUT
4-03-003-07	WORKING-CYCLOPENT	0.	0.	0.	7.20	0.	1000 GALLONS	THROUGHPUT
4-03-003-08	WORKING-HEPTANE	0.	0.	0.	1.40	0.	1000 GALLONS	THROUGHPUT
4-03-003-09	WORKING-HEXANE	0.	0.	0.	4.00	0.	1000 GALLONS	THROUGHPUT
4-03-003-10	WORKING-ISOCETANE	0.	0.	0.	1.70	0.	1000 GALLONS	THROUGHPUT
4-03-003-11	WORKING-ISOPENTANE	0.	0.	0.	17.9	0.	1000 GALLONS	THROUGHPUT
4-03-003-12	WORKING-PENTANE	0.	0.	0.	12.0	0.	1000 GALLONS	THROUGHPUT
4-03-003-13	WORKING-TOLUENE	0.	0.	0.	0.73	0.	1000 GALLONS	THROUGHPUT
OTHER/NOT CLASIFO								
4-03-999-99	SPECIFY IN REMARK						1000 GAL	STORED

Hydrocarbon emissions from fuel combustion sources are part of the RAPS hourly emission inventory. Data for evaporative emissions, which account for approximately 40 percent of the point source hydrocarbon emission, are only gathered as part of inventory or production control and are presented as annual data.

Base data, such as storage capacity, throughput, production, consumption, etc., for the St. Louis Air Quality Control Region (AQCR-70) were obtained from 64 companies with emissions in excess of one ton per year. This represents about 450 points. Thirty-seven of the companies emit in excess of 100 tons per year, ten in excess of 10 tons per year, and seventeen in excess of one ton per year. Gas stations and dry cleaning establishments may emit greater than one ton per year hydrocarbons. However, they are included in the area sources inventory. Locations of the stacks, accurate to ten meters, were obtained from visiting plant sites and pinpointing the location of sources on U.S. Geological Survey maps. In addition, stack parameters and operating patterns were obtained from individual companies.

Emission patterns for hydrocarbon sources vary widely due to the variety of types of hydrocarbon sources. As mentioned before, emissions from combustion sources were received continuously as part of the RAPS Point Source Inventory, generally on an hourly basis. Hydrocarbon data from sources which produce or use coatings and solvents are accompanied with hourly use patterns based on working hours during a year. Evaporative emissions from petroleum storage are assumed to be generated on a continuous basis and are, therefore, spread equally throughout the year.

All of this information has been stored in the RAPS emission inventory data bank at EPA/RTP.

## 2.2 AREA SOURCES

Area sources of hydrocarbons include industrial area sources, residential and commercial sources, highway vehicles both as line and area sources, railroads and river vessels, airports, and off-highway mobile sources. All of the emissions from these sources have been spatially distributed into 1989 grids in accordance with the RAPS grid network (1).

Industrial area sources which are too small to be considered as point sources were determined by contacting individual companies and obtaining fuel consumption or throughput data. From these data, emissions were calculated using emission factors. These emissions were then assigned to the grid square in which the company was located. This category includes 53 companies.

Stationary residential and commercial sources include fuel combustion for heating, evaporative emissions from dry cleaning plants, surface coating operations and gasoline marketing, structural fires, and solid waste disposal. These emissions have been determined and distributed to each grid square according to residential and commercial land use.

Highway vehicle line source emissions have been determined and distributed over the AQCR according to the location of the line sources within the RAPS gridding system. Highway vehicle area sources have been determined as an off-shoot of the highway line sources and the emissions have been assigned to the appropriate grid square.

Airport emissions have been determined and distributed to those grids containing airports and in which flight operations take place, such as take-off and approach.

Off-highway mobile sources include motorcycles, lawn, garden and farm equipment, construction equipment, industrial equipment and outboard motors. The emissions from these sources have been distributed based on registrations; residential, farm and commercial land use; and navigable waters, respectively.

River vessel emissions were based on towboat traffic and determined primarily from records taken by the Corps of Engineers at Lock 27 near St. Louis and on emission factors derived for similar engines of the Coast Guard fleet and railroad locomotives.

Railroad fuel use and emissions were determined for two types of operations: line-haul operations and switch-yard activities. The former are described as line sources consisting of a series of links within the study area. Switch-yard operations utilize an area source concept.

For details of methodologies, the reader is referred to the reports listed in Section 2.0. The area source inventory also has been stored in the RAPS emission inventory data bank at EPA/RTP.

### 3.0 HYDROCARBON CLASSIFICATION

In order to make a breakdown of hydrocarbon emissions according to chemical structure, an appropriate compositional analysis must be applied to each category of emissions within the available total hydrocarbon inventory. Such an analysis has been applied by J. C. Trijonis and R. W. Arledge (2) to organic emissions in Los Angeles.

The work described in that study appears to be applicable to St. Louis with three major exceptions:

- (1) Trijonis' "reactivity classes" do not coincide completely with the breakdown required for this report.
- (2) Compositions of petroleum products and solvent usage may be appreciably different between St. Louis and Los Angeles.
- (3) There are sources in St. Louis which are not considered in the Los Angeles study, such as coal combustion and coke ovens.

To make the information contained in the report applicable to the present study, the following modifications were made:

1. The Trijonis report is organized according to reactivity classes with 5-class reactivity categorization for organics. Each category contains groups of compounds by name, e.g.  $C_1$ - $C_3$  paraffins in Class I, mono and tertiary alkyl benzenes in Class II,  $C_4$ + paraffins in Class III, primary and secondary alkyl benzenes in Class IV, and aliphatic olefins in Class IV.

All of the various organic emission sources in the Los Angeles area are discussed and analyzed to determine what chemical compounds are emitted. Each source is then tabulated to determine the extent of emissions in each reactivity class. The results are expressed in mole percent. In addition, the average molecular weights for each type of organic were determined and included in the report.

Since most of the source types exist both in Los Angeles and St. Louis, the report has been useful in classifying RAPS data. The tabulations have been reorganized by rearranging the chemical compounds into the broader classes of paraffins, olefins, aromatics, aldehydes and non-reactives. The non-reactives group includes all of the compounds in Class I of the Trijonis classification. The paraffins group includes  $C_4+$  paraffins and alcohols, ketones, acetates and cellosolves. The aromatics group is composed of all aromatics with the exception of benzene, which is included with the non-reactives. The hydrocarbon classification tables developed for each type of source in the RAPS study area are included in the Appendix to this report.

The RAPS inventory presents emissions on a weight per unit time basis. For this reason, the classification of hydrocarbons was reported on a weight percent basis. This was accomplished by utilizing the molar percent tabulations and the average molecular weights presented in the Los Angeles study. The resulting tables are shown in Appendix A.

2. The composition of petroleum products in the St. Louis area was ascertained and adjustments were made in the tabulation of emissions arising from refinery operations, evaporative losses and automotive exhaust. These changes are discussed in detail in the text of the report.

3. Emissions from coal combustion and coke ovens were investigated and the results incorporated in this report.

### 3.1 POINT SOURCE INVENTORY

Once total hydrocarbon emissions were determined for each source, the hydrocarbon classification was applied to determine the non-reactives, paraffins, olefins, aromatics and aldehydes. The classification of hydrocarbon emissions from point sources is shown in Table 4.

#### 3.1.1 Fuel Combustion

The nature of fuel combustion for power generation or steam production is similar at Los Angeles and at St. Louis; therefore, the same breakdown has been used here for oil and gas consumption. The hydrocarbon classification is shown in Table 1 of the Appendix.

TABLE 4. HYDROCARBON BREAKDOWN--POINT SOURCES

SCC	Weight %				
	Non-Reactive	Paraffins	Olefins	Aromatics	Aldehydes
1-XX-XXX-XX	66	10	9	5	10
2-XX-XXX-XX	66	10	9	5	10
3-01-018-99	0	0	0	100	0
3-01-026-99	0	0	0	100	0
3-01-999-99	0	0	0	100	0
3-03-003-01	83	1	13	3	0
3-03-003-02	83	1	13	3	0
3-03-003-03	83	1	13	3	0
3-06-001-02 to	66	10	9	5	10
3-06-001-09					
3-06-002-01	5	95	0	0	0
3-06-004-01 to	5	74	15	6	0
3-06-008-05					
3-90-XXX-XX	66	10	9	5	10
4-01-002-02	100	0	0	0	0
4-01-002-05	0	0	100	0	0
4-02-001-01	6	78	0	16	0
4-02-003-01	0	100	0	0	0
4-02-004-01	0	89	0	11	0
4-02-005-01	6	78	0	16	0
4-02-006-01	6	81	0	13	0
4-02-008-01	8	24	1	67	0
4-02-009-01	9	70	0	21	0
4-02-999-99	9	70	0	21	0
4-03-001-01	8	68	24	0	0
4-03-001-03	8	68	24	0	0
4-03-001-07	8	68	24	0	0
4-03-001-56	0	100	0	0	0
4-03-002-01	8	68	24	0	0
4-03-002-03	5	74	15	6	0
4-03-002-07	8	68	24	0	0
4-03-999-99	8	68	24	0	0
4-06-001-26	8	68	24	0	0
4-06-001-30	8	68	24	0	0
4-06-002-01	8	68	24	0	0
4-06-002-05	8	68	24	0	0
5-01-001-01	42	16	31	4	7

Hydrocarbon emissions from coal combustion were not studied by Trijonis, and the only literature data found on this subject referred only to total hydrocarbons and polynuclear hydrocarbons. Because of this lack of information, the classification reported for oil combustion was also used for emissions from coal combustion. This should be reasonably satisfactory considering the similarity of conditions of high temperature and residence time in a boiler, as well as the small amounts emitted. Two percent of the total hydrocarbons in the AQCR originates from boiler operations; moreover, most of it is methane.

### 3.1.2 Industrial Processes

Industrial sources of hydrocarbon emissions in AQCR 70 include some chemical manufacturing, coke production, refinery operations (which include fuel combustion covered previously), and evaporative emissions from degreasing operations, petroleum product storage and bulk marketing.

Emissions from chemical manufacturing in the St. Louis area occur primarily from manufacture of products used for plastic and rubber formulations. In all processes examined, the products are derivatives of benzene or phenol. The emissions are, therefore, entirely aromatics. This classification is shown in Table 2 of the Appendix.

Coke oven emissions result from several points in a coking plant including charging holes, pushing doors and many leaks. The best available sources (3-5) indicate that the composition of the emissions is similar to the coke oven gas which is produced in a coking plant. The composition of a typical coke oven gas is given in Table 5. This analysis has been reorganized and the hydrocarbon classification is included as Table 3 in the Appendix.

TABLE 5. COKE OVEN GAS ANALYSIS

Hydrogen Sulfide	0.7% by vol.	Ethylene	2.45% by vol.
Carbon Dioxide	1.7% by vol.	Propylene	0.34% by vol.
Nitrogen	0.9% by vol.	Propane	0.08% by vol.
Hydrogen	56.7% by vol.	Butylene	0.16% by vol.
Carbon Monoxide	5.7% by vol.	Butane	0.02% by vol.
Methane	29.6% by vol.	Acetylene	0.05% by vol.
Ethane	1.28% by vol.	Light Oil	0.65% by vol.

Refinery emissions arise from a variety of sources. Emissions from power house boilers and process heaters are included in the previous section on fuel combustion. Other emissions are from leaks or vents connected with transfers, drains, blow-downs, vacuum jets, compressors, valves, seals, and flanges. The Los Angeles study was very complete for refinery emissions. The operation of refineries is very similar at St. Louis and at Los Angeles. The basic difference is that crude oil in St. Louis is obtained from mid-continent and Arabian sources whereas the crude processed in Los Angeles is primarily from West Coast and Indonesian sources. Crude oil processed in California is generally of a much higher aromatic content, typically 20 to 35 percent versus 10 to 15 percent in the Midwest (6).

The Petroleum Chemicals Division of DuPont reports biannually on the characteristics of gasolines sampled across the country (7). Gasoline from St. Louis is not included in the survey, but Kansas City is, and the composition of gasoline in St. Louis is much like that in Kansas City (8). The average hydrocarbon analyses of gasolines from Los Angeles and Kansas City are given in Table 6. It can be seen that the aromatics are considerably higher in Los Angeles.

TABLE 6. DUPONT GASOLINE ANALYSIS

	<u>Research Octane</u>	<u>Aromatics</u>	<u>Olefins</u>	<u>Saturates</u>
		Percent		
<u>Winter 1975-1976</u>				
Los Angeles--leaded regular	93.2	27.0	7.0	65.0
unleaded regular	93.2	30.0	7.0	63.0
premium	98.6	26.0	4.0	70.0
Kansas City--leaded regular	92.9	14.5	13.0	72.5
unleaded regular	91.7	13.5	15.0	71.5
premium	98.8	14.0	7.5	78.5
<u>Summer 1976</u>				
Los Angeles--leaded regular	93.3	29.0	6.0	65.0
unleaded regular	93.5	35.0	7.0	58.0
premium	98.7	29.0	5.0	66.0
Kansas City--leaded regular	93.7	22.0	7.5	70.5
unleaded regular	91.5	21.0	12.0	67.0
premium	98.6	14.5	6.5	79.0

Combining the values for summer and winter as well as leaded and unleaded regular gasolines gives the values shown in Table 7. Since in 1975-1976 about 55 percent of the gasoline sold was regular, 45 percent premium, the averages were weighted by this proportion, which gave the values shown in columns 3 and 6 of Table 7. The percentage difference between Los Angeles and Kansas City is shown in the next column. These values were used to adjust gasoline related emissions and are reflected in Tables 4, 20 and 21 in Appendix A.

TABLE 7. AVERAGE COMPOSITION OF GASOLINES

	<u>Los Angeles</u>			<u>Kansas City</u>			
	1	2	3	4	5	6	7
	Regular	Premium	Weighted	Regular	Premium	Weighted	Percentage
	%	%	Average	%	%	Average	Difference
Aromatics	30.25	27.50	29.00	17.75	14.25	16.17	0.557
Olefins	6.75	4.50	5.75	11.88	7.00	9.68	1.686
Saturates	63.00	68.00	65.25	70.37	78.75	74.15	1.136

The classification of hydrocarbons emitted from catalytic crackers was determined by source test results and is included as Table 5 in the Appendix.

Degreasing operations are very straightforward. The solvents used are either trichloroethane or trichloroethylene. Trichloroethane is a partially halogenated paraffin, whereas trichloroethylene is a partially halogenated olefin. These sources are shown in the hydrocarbon classification scheme in Tables 6 and 7 in the Appendix.

Surface coating emissions occur from coating operations which include automobile and truck body and parts coating, appliances coating, and can manufacturing. A few of the companies have purely air-dried operations, but most of the coating operations involve a heat curing step. Each company involved in surface coating was evaluated to determine what percentage of the emitted hydrocarbons are evolved in the spray booths versus the curing ovens. This involved estimating the percentage of overspray and the time allowed for "flash-off" of a portion of the solvents used in formulation before the piece entered the curing oven. The values reported by Trijonis for heat treated coatings were applied to the hydrocarbons emitted in the curing ovens. The SCC codes differentiate between the types of surface coatings applied; i.e., lacquers, enamels, varnish, etc. Each type of coating was studied to determine the approximate hydrocarbon composition used in formulation (9, 10) and these compositions were used to classify the hydrocarbons emitted during the air drying part of the surface coating operation - the spray booths. The hydrocarbon classification for each type of surface coating included in the inventory is shown in Tables 8 through 12 in the Appendix.

Petroleum product storage and bulk marketing facilities have emissions which are typical of the vapors which exist over the liquids stored. All volatile petroleum products such as gasoline and crude oil are stored in floating-roof storage tanks. Emissions from these are solely due to leakage around the seals within the tanks. The other source of emissions is the filling of tank trucks and barges as vapors are displaced as the tank fills. The composition of the vapors accumulated over the gasoline approaches the equilibrium composition of gasoline vapor. The hydrocarbon classifications for emissions from gasoline storage tanks are shown in Table 13 of the

## Appendix.

### 3.2 AREA SOURCES

The classification of hydrocarbon emissions from area sources is shown in Table 8.

River vessels and railroads are assumed to have diesel engines which produce all of the hydrocarbon emissions. Emissions from diesel engines were studied extensively by Battelle Labs (11). The results should be applicable to St. Louis. The classification of hydrocarbons used here is the same as for diesel engines presented in Table 22 in the Appendix.

Airport emissions include aircraft operations, exhaust emissions from service vehicles and evaporative emissions from fuel handling. Hydrocarbon emissions are distributed 79 percent, 13 percent and 8 percent, respectively, to these sources (12). Lambert International and Scott Air Force Base contributed 96.2 percent of the total hydrocarbons. Since, within the bounds of this study, it was not possible to classify the hydrocarbons from all airports individually, the hydrocarbon classification was based on the operations at Lambert International and Scott Air Force Base.

Table 9 shows the classification of emissions for each of the hydrocarbon sources and the weighted average for the airport. The complete classification of these emissions is presented in Table 14 of the Appendix. The aircraft emissions are based on the assumption of originating entirely from jet engines; 98 percent of the aircraft emissions occur during the taxi and idle modes of operation. The service vehicle emissions are assumed to be the same as automotive exhaust emissions. Fuel handling emissions are the same as the evaporative emissions from storing jet fuel.

TABLE 9. AIRPORT HYDROCARBON EMISSIONS

TYPE	% OF TOTAL	NON-REACTIVE	PARAFFINS	OLEFINS	AROMATICS	ALDEHYDES
Aircraft	79	11	44	27	15	3
Service Vehicle	13	12	47	15	26	0
Fuel Handling	8	0	70	5	25	0
Weighted Average		10	47	24	17	2

TABLE 8. HYDROCARBON BREAKDOWN--AREA SOURCES

	<u>Weight %</u>				
	<u>Non-Reactive</u>	<u>Paraffins</u>	<u>Olefins</u>	<u>Aromatics</u>	<u>Aldehydes</u>
River Vessels	3	53	12	12	20
Railroads	3	53	12	12	20
Residential and Commercial Fuel Combustion	66	10	9	5	10
Evaporative Surface Coating					
Missouri	6	57	0	37	0
Illinois	9	70	0	21	0
Gasoline Marketing	8	68	24	0	0
Dry Cleaning	76	23	0	1	0
Structural Fires	42	16	31	4	7
Solid Waste Disposal	42	16	31	4	7
Stationary Industrial	26	52	3	16	3
Airports	10	47	24	17	2
Highway					
Light Duty Vehicle					
Exhaust	11	48	21	20	0
Evaporative	4	60	20	16	0
Heavy Duty - Gas					
Exhaust	11	48	21	20	0
Evaporative	4	60	20	16	0
Heavy Duty - Diesel					
Exhaust	3	53	12	12	20
Off-Highway Sources					
Motorcycles	12	47	15	26	0
Lawn & Garden	12	47	15	26	0
Farm Equipment	8	49	14	21	8
Construction Equip.	7	50	13	18	11
Industrial Equip.	10	49	14	23	4
Outboard Motors	12	47	15	26	0

Stationary residential and commercial fuel combustion sources include combustion of coal, oil, natural gas, and liquified petroleum gas. For these emissions the same classification used with point source fuel combustion was applied (Table 1, Appendix).

Evaporative hydrocarbons from surface coating include emissions due to the solvent content of retail paints. Illinois has a state regulation restricting photochemically reactive solvents which is very similar to Los Angeles APCD Rule 66 (13). Trijonis' report includes a table of the national average solvent composition which is given in Table 10. According to Mr. Raymond Connor of the National Paint and Coating Association (14), this table of values is still the best available information. The State of Missouri does not have a hydrocarbon regulation similar to Illinois; therefore, the data in Table 10, column 3, were used for the Missouri portion of the hydrocarbons from surface coating. The composition in the last column of Table 10 was used for the Illinois portion of the hydrocarbons. The individual classifications of hydrocarbons in each state are presented in Tables 15 and 16 in the Appendix.

Evaporative hydrocarbons from service stations are generated from filling the underground storage tanks at service stations and from filling automobile tanks. The volume of these emissions is considered as being split equally from the filling of the underground tanks and automobile tanks (15). The DuPont analyses of gasoline in Kansas City and Los Angeles have been used to modify the emissions classification.

Evaporative hydrocarbons from dry cleaning operations are the result of using cleaning solvents which are either perchloroethylene or petroleum based solvents. Based on a 1974 study in St. Louis city, the usage is 76 weight percent perchloroethylene and 23 weight percent petroleum based solvents. Table 11 gives the hydrocarbon compositions from each of these solvent types and the weighted average which is used for classifying the cumulative emissions in the AQCR. This classification is presented in further detail in Table 17 in the Appendix.

TABLE 10. COMPOSITION OF SURFACE COATING SOLVENTS

ALIPHATIC HYDROCARBONS	ACTUAL OR ESTIMATED MOLECULAR WEIGHT	1972 AVERAGE NATIONAL WIDE CONSUMPTION: LBS. PER CAPITA	COMPOSITION OF SOLVENTS: NATIONAL AVERAGE MOLE % OF TOTAL HYDROCARBONS	REACTANTS REQUIRED BY LAC APCD - RULE 46	SENSITIZATION BY OTHER COMPOUNDS	ESTIMATED COMPOSITION OF COATING SOLVENTS IN THE LOS ANGELES AREA: MOLE % OF TOTAL HYDROCARBONS
Mineral spirits, regular, low odor ...	86 <sup>a</sup> (C <sub>6</sub> )	2.005	14.9			
Mineral spirits, odorless ...	86 <sup>a</sup> (C <sub>6</sub> )	0.286	2.9			
Kerosene ...	162 (C <sub>12</sub> )	0.053	0.3			
Mineral spirits, heavy, coal-oil ...	86 <sup>a</sup> (C <sub>6</sub> )	0.165	1.2			
Other aliphatic hydrocarbons ...	86 (C <sub>6</sub> )	1.342	8.9			
		2.751	27.3		1.3	36.7
AROMATIC & HALOGENATED HYDROCARBONS						
Benzene ...	78 (-)	0.033	0.3			0.3
Toluene (Rule 66-E-2) ...	92 (-)	1.002	12.1	3.4		0.7
Xylene (Rule 66-E-2) ...	106 (-)	2.277	13.8	7.8		6.0
Naphtha, high flash ...	138 (C <sub>10</sub> )	0.462	2.1			2.1
Other aromatics (Rule 66-E-2) ...	120 (C <sub>9</sub> )	0.946	2.6	1.5		1.1
Nonaromatic hydrocarbons ...	140 (C <sub>10</sub> )	5.502	31.2	12.7		2.3
						20.3
TERPENE HYDROCARBONS						
(Pine oil & Turpentine) ...	136 (C <sub>10</sub> )	0.033	0.1			0.1
		0.033	0.1			0.1
ALCOHOLS (MONOHYDRIC)						
Methyl alcohol (methanol) ...	32 (-)	0.091	1.0		2.0	3.8
Ethyl alcohol (inc. all denatured grades) ...	46 (-)	0.072	1.0			1.0
Propyl alcohol (n & iso.) ...	60 (-)	0.264	2.8			2.8
n-Butyl alcohol ...	74 (-)	0.378	3.3			3.3
Other butyl alcohols ...	74 (-)	0.033	0.3			0.3
Other monohydric alcohols ...	162 (C <sub>12</sub> )	0.134	0.8		7.0	0.8
		0.572	10.8			12.0
GLYCOLS & DERIVATIVES						
Glycols ...	90 <sup>a</sup> (C <sub>6</sub> )	0.566	4.8			4.8
Glycol ethers (cellulosics) ...	90 (C <sub>6</sub> )	0.627	6.5			6.5
		1.195	8.3			8.3
KETONES & ESTERS						
Acetone (di-methyl ketone) ...	58 (-)	0.642	7.1		2.5	9.6
Methyl ethyl ketone (M.E.K.) ...	72 (-)	0.090	0.2			6.2
Methyl isobutyl ketone (Rule 66-E-3) ...	100 (-)	0.275	1.8	0.5		1.3
Other ketones (Rule 66-E-3) ...	120 (C <sub>9</sub> )	0.082	0.4	0.1		0.3
Ethyl acetate ...	88 (-)	0.029	0.2			0.2
Isopropyl acetate ...	102 (-)	0.028	0.2			0.2
Normal butyl acetate ...	116 (-)	0.311	1.7			1.7
Other esters ...	166 (C <sub>12</sub> )	0.295	0.9	0.3		0.2
		2.262	18.5	0.3	7.5	20.4
CHLORINATED SOLVENTS						
Perchloroethylene ...	98 (-)	0.049	0.4			0.4
Tri-chloroethylene (Rule 66-E-3) ...	134 (-)	0.036	0.2	0.1		0.1
Other chlorinated solvents ...	150 (C <sub>10</sub> )	0.008	0.1	0.1		0.1
		0.093	0.7	0.1		0.3
OTHER SOLVENTS & DILUENTS						
C <sub>10</sub> + Cyclohexane ...	140 (C <sub>10</sub> )	0.278	0.6			0.6
C <sub>10</sub> + Paraffins ...	140 (C <sub>10</sub> )	0.278	0.6			0.6
		0.556	1.2			1.2
		0.747	10.8	7.8	7.5	26.1

\* Estimated or assumed

\* Use of these compounds limited by Los Angeles County Air Pollution Control District Rule 66-E

† Rule 3 assumed to equal volume 3

TABLE 11. DRY CLEANING HYDROCARBON EMISSIONS

<u>SOLVENT</u>	<u>NON-REACTIVE</u>	<u>PARAFFINS</u>	<u>OLEFINS</u>	<u>AROMATICS</u>	<u>ALDEHYDES</u>
Perchloroethylene	100	0	0	0	0
Petroleum Based	0	94	0	6	0
Weighted Average	76	23	0	1	0

Hydrocarbon emissions from structural fires and solid waste disposal are the last type of residential and commercial sources. The only data available for this source are reported by Trijonis and are reflected in Table 8. The detailed classification of hydrocarbons from waste incineration is shown in Table 18 in the Appendix.

Emissions from stationary industrial sources include a variety of types of activities. The best approximation of these sources indicates that 70 percent consists of air dried surface coating and 30 percent of combustion (16). The classification in Table 8 reflects these percentages. A detailed classification of hydrocarbons from this combination of sources is shown in Table 19 in the Appendix.

As stated earlier, gasoline in Los Angeles has a much higher aromatic content than gasoline in St. Louis. The effect of higher aromatic content in gasoline on exhaust emissions has been heavily studied. A numerical relationship has been expressed by Wigg, et al (17), which states that there is a linear relationship between aromatic hydrocarbon emissions and fuel aromatic content and an inverse relationship between olefin emissions and fuel aromatic content. This relationship is reported to be in relatively good agreement with other studies on the same subject (18, 19). The equations which were developed in this study are:

$$\text{Exhaust (aromatic - benzene), \%} = 0.49 \text{ fuel aromatic, \%}$$

and

$$\text{Exhaust olefin \%} = 39 - (0.30 \text{ fuel aromatic}), \%$$

These equations and the DuPont analyses have been used to modify the composition of hydrocarbons in automotive exhaust. The exhaust composition thus derived is also in agreement with results reported by Kopczynski, et al,

in a planning study in preparation for the RAPS project (20).

Evaporative hydrocarbon emissions from automobiles are comprised of emissions from fuel tank breathing and the evaporation of gasoline from the carburetor fuel bowl. These emissions have been determined by modifying the values reported by Trijonis by decreasing the aromatic content by 44 percent and increasing the olefin content.

The composition of hydrocarbons from automobile exhaust and evaporative emissions are given in Table 8. The composition of the exhaust and evaporative emissions of heavy duty gasoline powered trucks have been assumed to be identical to those for light duty vehicles since there is no fundamental difference between the engines and fuels used. The composition of the exhaust emissions for heavy duty diesel powered trucks are classified in Table 8. These are the same as those used for railroads which use diesel engines. Evaporative emissions from diesel engines are considered negligible. The classifications of exhaust and evaporative hydrocarbon emissions are presented in Tables 20, 21 and 22 in the Appendix.

Off-highway mobile sources are comprised of a mix of gasoline and diesel engines (22). Motorcycles, lawn and garden, and outboards are all gasoline engines. Farm equipment is 61.9 percent gasoline powered, construction equipment is 44 percent gasoline powered, and industrial equipment is 78 percent gasoline powered. The exhaust hydrocarbon classification data in Table 8 expresses these percentages. The exhaust emissions from gasoline engines are the same as the previously discussed automotive emissions, and the exhaust emissions from diesel engines are the same as the previously discussed diesel truck engines. The reclassifications of the hydrocarbons from the groups of combined gasoline and diesel engines are presented in Tables 23, 24, and 25 in the Appendix.

#### 4.0 SUMMARY

A detailed inventory of organic emissions has been developed for the St. Louis AQCR. The inventory has been incorporated into the RAPS data base and is stored on EPA's Univac 1110 computer at Research Triangle Park, North Carolina.

The inventory consists of a listing of all industrial point source emissions in excess of one ton per year, a listing of stationary area sources such as gasoline marketing and dry cleaning operations, and a compilation of mobile sources including surface transportation, railroad, river vessels, airports and off-highway mobile sources.

Emission data are available for each source category, either as total hydrocarbons or broken down into five structural categories: paraffins, olefins, aromatics, aldehydes and non-reactives. Appropriate factors were developed for the St. Louis area and applied to the hydrocarbon emission data. These classification factors are also stored on the Univac computer. As a consequence, an emission inventory for the five categories of organics is now available for the St. Louis AQCR. A summary of the total emission broken down into the five structural categories is shown in Table 12.

TABLE 12. SUMMARY OF TOTAL ORGANIC EMISSIONS INVENTORY BY CLASS

SOURCE CATEGORY	ANNUAL EMISSIONS, TONS/YR.					TOTALS
	NON REACTIVE	PARAFFINS	OLEFINS	AROMATICS	ALDEHYDES	
<u>Point Sources</u>						
Fuel Combustion	1,793	272	245	136	271	2,717
Chem. Manufacturing	-	-	-	6,702	-	6,702
Primary Metals	1,941	23	305	70	-	2,339
Refinery Operations	358	5,299	1,074	430	-	7,161
Surface Coatings	843	15,593	-	4,636	-	21,072
Petroleum Storage & Marketing	597	5,070	1,790	-	-	7,457
Solid Waste Disposal	57	22	42	5	10	136
Miscellaneous	12	-	12	-	-	-
Point Source Totals						47,610
<u>Area Sources</u>						
Industrial Area Sources	29	57	3	18	3	110
Residential & Commercial	14,923	2,261	2,035	1,130	2,261	22,610
Vehicles, Line Sources, Exhaust	8,093	35,314	15,450	14,714	-	73,570
Vehicles, Line Sources, Evap.	1,021	15,321	5,107	4,086	-	25,535
Vehicles, Line Sources, Diesel	40	708	160	160	267	1,335
Vehicles, Area Sources	1,257	6,283	2,010	2,890	125	12,565
Railroads	127	2,237	506	506	844	4,220
River Vessels	28	498	113	113	188	940
Airports	146	686	350	248	30	1,460
Off-Highway Mobile	1,628	7,977	2,279	3,744	652	16,280
Gas Marketing	1,092	9,282	3,276	-	-	13,650
Dry Cleaning	490	148	-	7	-	645
Surface Coating	255	2,271	-	1,231	-	3,757
Area Source Totals						176,677
GRAND TOTAL						224,287

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## APPENDIX A

### RAPS Hydrocarbon Classification for Types of Sources

Aver. Mol. Wt. 25  
T&A 3-13 & A-5

27

TABLE A-2  
RAPs HYDROCARBON CLASSIFICATION  
ORGANIC CHEMICAL MANUFACTURING  
Plasticizers, Rubber Chemicals, Pesticides, etc.

[illegible]

TABLE A-3  
RAPS HYDROCARBON CLASSIFICATION  
COKE OVENS

Aver. Mol. Wt. 35

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES		
	mol %	wt %	mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %	
C <sub>1</sub> - C <sub>3</sub> paraffins	89.4	77	C <sub>4</sub> <sup>+</sup> paraffins	0.1	1	Aliphatic olefins	8.6	13	Prim. & Sec.-alkyl benzenes	0.5	3			0
Benzene	1.4	6												
Acetylene	0.1	<1												
		83			1			13			3			

TABLE A-4  
RAPS HYDROCARBON CLASSIFICATION  
REFINERY OPERATIONS

Aver. Mol. Wt. 93  
T&A 3-6 & A-2 (Adjusted)

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES		
	mol %	wt %	mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %	
C <sub>1</sub> - C <sub>3</sub> paraffins Acetylene Benzene	6 2 3	1.9	C <sub>4</sub> <sup>+</sup> paraffins 67	72	Aliphatic olefins 14	13	Prim. & Sec.- alkyl benzenes 3	4	5	6	10			
		.6												
		2.5												
		5		72		13								
		5		74*		15*				6*				

\* Adjusted for Midwestern crudes

Aver. Mol. Wt. 120

31

TABLE A-6  
RAPS HYDROCARBON CLASSIFICATION  
DEGREASING - Trichloroethane

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES		
	mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %
Partially halogenated paraffin	100	100												

TABLE A-7

[illegible]

TABLE A-8  
RAPS HYDROCARBON CLASSIFICATION  
SURFACE COATING -AIR DRIED - Paint, Enamel

Aver. Mol. Wt. 100

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES		
	mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %
Acetone	7	4	C <sub>4</sub> <sup>+</sup>	41	41				Prim. & Sec. - alkyl benzenes	6	7			
Methanol	2	1	paraffins						Dialkyl benzenes	4	7			
Partially halogenated paraffins	1	1	Cycloparaffins	6	9				Tri & tetra - alkyl benzenes	1	2			
			N-alkyl ketones	7	6									
			Prim. & Sec. - alkyl acetates	5	5									
			Branched alkyl ketones	3	2									
			Prim. & Sec. - alkyl alcohols	13	11									
			Cellosolves	4	4									
		6			78			0			16			0

TABLE A-9

[illegible]

Aver. Mol. Wt. 70

[illegible]

TABLE A-11  
RAPS HYDROCARBON CLASSIFICATION  
SURFACE COATING - AIR DRIED - Primers

Aver. Mol. Wt. 82

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES									
	mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %							
Acetone	6	4	C <sub>4</sub> <sup>+</sup> paraffins Alcohols Ketones Esters Ethers	47	47				Aromatics	10	13										
	Methanol	4		2	13					13	13										
				11	11																
				7	8																
				2	2																
		6			81									0							

Aver. Mol. Wt. 82  
T&A 3-17 & A-7

38

# RAPS HYDROCARBON CLASSIFICATION

## PETROLEUM STORAGE TANKS - Gasoline

# PETROLEUM STORAGE TANKS - Gasoline

[illegible]

TABLE A-14

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES		
	mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %
C <sub>1</sub> - C <sub>3</sub> paraffins Benzene Acetylene		10	C <sub>4</sub> <sup>+</sup> paraffins Naphthenes		47	Aliphatic olefins		24	Alkyl benzenes		17	Aliphatic aldehydes		2
		10			47			24			17			2

TABLE A-15

RAPS HYDROCARBON CLASSIFICATION

SURFACE COATING -AIR DRIED -General

Missouri

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES		
	mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %
Acetone	7	4	C <sub>4</sub> <sup>+</sup> paraffins						Prim. & Sec. - alkyl benzenes					
Methanol	2	1		30	28					12	14			
Partially halogenated paraffins			Cycloparaffins	2	3				Dialkyl benzenes	14	18			
	1	1	N-alkyl ketones	6	5				Tri & tetra - alkyl benzenes	3	5			
			Prim. & Sec. - alkyl acetates	3	4									
			Branched alkyl ketones	2	2									
			Prim. & Sec. - alkyl alcohols	14	11									
			Cellulosives	4	4									
		6			57			0			37			0

TABLE A-16  
RAPS HYDROCARBON CLASSIFICATION  
SURFACE COATING -AIR DRIED - General  
Illinois

Aver. Mol. Wt. 87  
T&A 3-19 & A-9

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES		
	mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %
Acetone	10	7	C <sub>4</sub> <sup>+</sup>						Prim. & Sec. - alkyl benzenes	9	11			
Methanol	4	1	paraffins	37	37				Dialkyl benzenes	6	8			
Partially halogenated paraffins	1	1	Cycloparaffins	5	8				Tri & tetra - alkyl benzenes	1	2			
			N-alkyl ketones	6	5									
			Prim. & Sec. - alkyl acetates	3	4									
			Branched alkyl ketones	2	2									
			Prim. & Sec. - alkyl alcohols	12	10									
			Cellulosolves	4	4									
					70			0			21			0
		9												

TABLE A-17

[illegible]

TABLE A-18

Aver. Mol. Wt. 33  
T&A 3-15 & A-6

[illegible]

TABLE A-19  
RAPS HYDROCARBON CLASSIFICATION  
STATIONERY INDUSTRIAL

Aver. Mol. Wt. 86

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES		
	mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %
C <sub>1</sub> - C <sub>3</sub> paraffins	75	18	C <sub>4</sub> <sup>+</sup> paraffins	27	29	Aliphatic olefins	1	3	Prim. & Sec. - alkyl benzenes	7	9	Aliphatic aldehydes	1	3
Acetylene	1	1	Cycloparaffins	3	6				Dialkyl benzenes	4	6			
Acetone	7	5	N-alkyl ketones	4	3				Tri & tetra - alkyl benzenes	1	1			
Methanol	3	1	Prim. & Sec. - alkyl acetates	2	3									
Partially hydrogenated paraffins	1	1	Branched alkyl ketones	1	1									
			Prim. & Sec. - alkyl alcohols	8	7									
			Cellosolves	3	3									
					52						16			3
		26						3						

TABLE A-20  
RAPS HYDROCARBON CLASSIFICATION  
LIGHT DUTY VEHICLE and HEAVY DUTY -  
Gas Exhaust

Aver. Mol. Wt. 69  
T&A 3-41, 3-46 & A-18, A-20 \*

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES					
	mol %	wt %	C <sub>4</sub> <sup>+</sup> paraffins	mol %	wt %	Aliphatic olefins	mol %	wt %	Prim. & Sec.-alkyl benzenes	mol %	wt %		mol %	wt %			
C <sub>1</sub> - C <sub>3</sub> paraffins	14	4		30	42		20	12	Dialkyl benzenes	6	8						
Acetylene	11	4									Tri & tetra - alkyl benzenes		13	22			
Benzene	3	3												3		5	
					42			12		35							
					48*			21*		20*				0			
		11															

\* Adjusted for Midwestern crudes

TABLE A-21

Aver. Mol. Wt. 91  
T&A 3-47 & A-21 \*

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES		
	mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %
C <sub>1</sub> - C <sub>3</sub> paraffins	1	1	C <sub>4</sub> <sup>+</sup> paraffins	57	55	Aliphatic olefins	13	12	Prim. & Sec. - alkyl benzenes	9	9			
Benzene	4	3	Cycloparaffins	1	1				Dialkyl benzenes	12	15			
									Tri & tetra - alkyl benzenes	3	4			
		4			56			12			28			
					60*									16*
		4												

\* Adjusted for Midwestern crudes

TABLE A-22

RAPS HYDROCARBON CLASSIFICATION

DIESEL ENGINE EXHAUST

Aver. Mol. Wt. 89  
T&A 3-52 & A-24

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES		
	mol %	wt %	mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %	
C <sub>1</sub> - C <sub>3</sub> paraffins	11	2	24	53	C <sub>4</sub> <sup>+</sup> paraffins	27	12	Aliphatic olefins	1	2	Prim.& Sec.- alkyl benzenes	30	20	Aliphatic aldehydes
Acetylene	2	1							5	10	Dialkyl benzenes			
		3		53			12			12			20	

TABLE A-23

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES		
			wt %		mol %		Aliphatic olefins		wt %		mol %		Aliphatic aldehydes	
			mol %	wt %	mol %	wt %			mol %	wt %				
C <sub>1</sub> - C <sub>3</sub> paraffins	13	3	C <sub>4</sub> <sup>+</sup> paraffins	28	49	25	14	Prim. & Sec. - alkyl benzenes	3	5	11	8		
Acetylene	8	3						Dialkyl benzenes	9	15				
Benzene	2	2						Tri & tetra - alkyl benzenes	1	1				
					49		14					8		

TABLE A-24

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES		
	mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %
C <sub>1</sub> - C <sub>3</sub> paraffins	12	3	C <sub>4</sub> + paraffins	28	50	Aliphatic olefins	25	13	Prim. & Sec.-alkyl benzenes	2	4	Aliphatic aldehydes	17	11
Acetylene	6	2							Dialkyl benzenes	8	13			
Benzene	1	2							Tri & tetra - alkyl benzenes	1	1			
					50			13			18			11
		7												

TABLE A-25

NON-REACTIVES			PARAFFINS			OLEFINS			AROMATICS			ALDEHYDES		
	mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %		mol %	wt %
C <sub>1</sub> - C <sub>3</sub> paraffins	13	4	C <sub>4+</sub> paraffins	30	49	Aliphatic olefins	25	14	Prim. & Sec.- alkyl benzenes	3	5	Aliphatic aldehydes	7	4
Acetylene	9	3							Dialkyl benzenes	10	16			
Benzene	2	3							Tri & tetra - alkyl benzenes	1	2			
		10			49			14			23			4

<b>TECHNICAL REPORT DATA</b> <i>(Please read Instructions on the reverse before completing)</i>		
1. REPORT NO. EPA-600/4-78-028	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE REGIONAL AIR POLLUTION STUDY Point and Area Source Organic Emission Inventory	5. REPORT DATE June 1978	
	6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) R.W. Griscom	8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Rockwell International Air Monitoring Center 11640 Administration Drive Creve Coeur, MO 63141	10. PROGRAM ELEMENT NO. 1AA603 AA-09 (FY-77)	
	11. CONTRACT/GRANT NO. 68-02-2093 Task Order 108 I	
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED Final	
	14. SPONSORING AGENCY CODE EPA/600/09	
15. SUPPLEMENTARY NOTES		
16. ABSTRACT <p>An inventory of organic emissions from stationary and mobile sources has been assembled for the St. Louis Air Quality Control Region. The inventory covers point and area sources for process, combustion and evaporative emissions. A breakdown into five categories had been assigned to each source type. The categories are (1) paraffins, (2) olefins, (3) aromatics, (4) aldehydes, and (5) non-reactives. This report describes how this classification has been determined for hydrocarbon emissions in the St. Louis AQCR and provides sufficient reference data to derive alternative schemes as required. The breakdown was made part of the RAPS Emission Inventory System, which is stored on the EPA's Univac computer at Research Triangle Park, N.C.</p>		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Air pollution *Organic compounds *Emission *Environmental surveys *Sources	St. Louis, MO	13 B 07 C 05 J
18. DISTRIBUTION STATEMENT  RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED	21. NO. OF PAGES 58
	20. SECURITY CLASS (This page) UNCLASSIFIED	22. PRICE