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Project Summary

Atmospheric Measurements of Selected Hazardous Organic Chemicals

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Methods were developed for the accurate analysis of an expanded list of hazardous organic chemicals in the ambient air. On-site analysis using an instrumented mobile laboratory was performed for a total of 44 organic chemicals. Twenty of these are suspected mutagens or carcinogens. Toxicity studies for several others are currently pending. Six important meteorological parameters were also measured. Four field studies, each about two-weeks duration, were conducted in Houston, Texas; St. Louis, Missouri; Denver, Colorado; and Riverside, California. An around-the-clock measurement schedule (24 hours per day, seven days a week) was followed at all sites, permitting extensive data collection. Widely varying weather conditions facilitated observations of pollutant accumulation and wide variabilities in concentrations of pollutants at a given site. Concentrations, variabilities, and human exposure (daily dosages) were determined for all measured pollutants. The diurnal behavior of pollutants was studied. Average daily outdoor exposure levels of all four sites were determined to be 197 μg/day for halomethanes (excluding chlorofluorocarbons), 140 μg/day for haloethanes and halopropanes, 89 μg/day for chloroalkenes, 32 μg/day for chloroaromatics, 1,394 μg/day for aromatic hydrocarbons, and 479 μg/day for secondary organics. Exposure levels at Houston, Denver, and Riverside were comparable, but levels were significantly lower at St. Louis.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Because a vast number of potentially harmful organic chemicals are released into the environment, it is becoming increasingly apparent that these chemicals contribute to the growing rate of cancer in industrialized countries. Despite recent and intense interest in toxic chemicals, the atmospheric abundance and fate of this important group of pollutants remains poorly understood. The purpose of this study is to characterize the concentrations of a wide range of toxic organic chemicals at several urban and source-specific locations under varying meteorological and source-strength conditions. The overall program of analytical methods development, field measurements, data collection, and analysis is expected to provide information that will permit determination of the atmospheric abundance and chemistry of this potentially harmful group of chemicals.

The research plan is primarily designed to answer the following basic questions:

- What are the concentration levels and variabilities of selected toxic organic chemicals in typical urban environments?
- What are the atmospheric fates of these chemicals?
- What is the extent of human exposure to selected toxic chemicals?

The answers to these questions will be sought through a combination of approaches:

- A comprehensive program of field measurements at several urban locations and near several source-specific locations.
- Analysis of data collected during the field measurements and integration of this information with data acquired from outside sources.
- Compilation of all available information dealing with the sources, sinks, chemistry, and effects (health as well as environmental) of the toxic chemicals of interest.

This report presents the results achieved during the second year of a three-year research effort. Analysis of data collected during the second year is by no means complete. Additional analysis will be presented in forthcoming reports and publications.

Procedures

The second-year research effort comprised a program of analytical methods development, field-data collection, data processing, and data interpretation for an expanded set of hazardous organic chemicals. All field measurements were conducted in-situ with the help of an instrumented mobile laboratory. After completion of the program of methods development, four field studies of roughly two-week duration each were conducted in Houston, Texas (Site 4); St. Louis, Missouri (Site 5); Denver, Colorado (Site 6); and Riverside, California (Site 7). These field studies were completed between early May and late July of 1980. The studies were designed to complement the three field studies conducted during the first year of this project at Los Angeles, California (Site 1); Phoenix, Arizona (Site 2); and Oakland, California (Site 3). Continuing practice of the first-year research, all field work in the second year was performed on a round-the-clock basis (24 hours per day, seven days a week), permitting the efficient collection of a large amount of data. A total of 44 organic chemicals and 5 meteorological parameters were measured. Over 20 of these chemicals are either mutagens or suspected carcinogens; in many other cases, toxicity studies are currently incomplete.

A total of 44 trace chemicals were targeted and are categorized in Table 1. The categories include chlorofluorocarbons, halomethanes, haloethanes, halopropanes, chloroalkenes, chloroaromatics, aromatic hydrocarbons, and oxygenated and nitrogenated species. The chlorofluorocarbons are considered to be nontoxic but are excellent tracers of polluted air masses. Formaldehyde was the only aldehyde measured, although work is in progress to develop measurement methods utilizing liquid chromatographic techniques for other aliphatic and aromatic aldehydes. A number of important meteorological parameters (wind speed, wind direction, temperature, pressure, relative humidity, and solar flux) were also measured.

For all halogenated species and organic nitrogen compounds shown in Table 1, electron-capture detector (ECD) gas chromatography (GC) was the primary means of analysis. The aromatic hydrocarbons were measured using flame-ionization detector (FID) gas chromatography. Formaldehyde was the only species measured by the wet chemical analysis technique utilizing the chromotropic acid procedure (U.S. Public Health Science, 1965).

The identity of trace constituents was established by using the following criteria:

- Retention times on multiple GC columns (minimum of two columns)
- EC thermal response
- EC ionization efficiency
- Limited GC/MS analysis.

Details of these comparisons for halocarbon species, organic nitrogen compounds, and aromatic hydrocarbons have already been published. The use of secondary standards nearly three times a day clearly demonstrated the excellent precision that was obtainable during field studies. The precision of reported field measurements is estimated to be ±5 percent. The measurements presented here have an overall estimated accuracy of better than ±15 percent.

The four selected sites in Houston, Texas; St. Louis, Missouri; Denver, Colorado; and Riverside, California, in all cases, represented an open urban atmosphere. There were no nearby sources or topographical features that could directly affect the representativeness of the measurements. Despite the logistical difficulty, a 24-hour measurement schedule offers the most efficient means of collecting the maximum amount of data to characterize the burden of toxic organic chemicals in the ambient air. In addition, night abundances of trace chemicals are likely to provide crucial information about the sources and sinks of measured species. Therefore, during all field programs a 24-hour-per-day, seven-days-a-week measurement schedule was followed.

During the sampling programs, general weather conditions were not unusually severe. In Houston, rainfall and passage of fronts did not allow for severe pollution episodes. St. Louis weather produced relatively clean environmental conditions. Weather in Denver was moderately hot and stagnant. At Riverside, the first half of the study period exhibited relatively clean conditions; the second half was more representative of hot and somewhat stagnant conditions.

Results

Experiments at all sites were performed satisfactorily, and no breakdowns were encountered. The entire data base was collected, validated, and compiled on our master data file. This file also contains the data that were collected in the first year of this research effort. All of the meteorological information is currently on chart papers and is easily accessible. The master data file will be updated as additional studies are conducted. While the collected data have been compiled, validated, and statistically treated, no detailed meteorological analyses have been conducted. The interpretation of data is therefore by no means complete, and further analysis and interpretations will continue.

Table 2 summarizes data on all of the organic chemicals measured during the four field studies; maximum, minimum, and average concentrations are presented for each of the measured species. The averages and the standard deviations associated with the concentration data are calculated from the actual data acquired and involve no interpolations. In addition, Table 2 presents an average daily outdoor exposure for each of the species and the standard deviations associated with this average daily exposure. The value is determined based on an average daily air intake of 23 m^3 at

Table 1. *Target Chemicals for Second-Year Research*

Chemical Name*	Chemical Formula	Toxicity†
Chloro-Fluorocarbons		
Trichloromonofluoromethane (F11)	CCl_3F	These chlorofluorocarbons
Dichlorodifluoromethane (F12)	CCl_2F_2	are nontoxic but have
Trichlorotrifluoroethane (F113)	CCl_2FCClF_2	excellent properties as tracers
Dichlorotetrafluoroethane (F114)	$CClF_2CClF_2$	of urban air masses
Halomethanes		
Methyl chloride	CH_3Cl	BM*
Methyl bromide	CH_3Br	BM
Methyl iodide	CH_3I	SC†,BM
Methylene chloride	CH_2Cl_2	BM
Chloroform	$CHCl_3$	SC,BM
Carbon tetrachloride	CCl_4	SC,NBM†
Haloethanes and halopropanes		
Ethyl chloride	C_2H_5Cl	—
1,1 Dichloroethane	$CHCl_2CH_3$	NBM
1,2 Dichloroethane	CH_2ClCH_2Cl	SC,BM
1,2 Dibromoethane	CH_2BrCH_2Br	SC
1,1,1 Trichloroethane	CH_3CCl_3	Weak BM
1,1,2 Trichloroethane	$CH_2ClCHCl_2$	SC,NBM
1,1,1,2 Tetrachloroethane	$CHClCCl_3$	NBM
1,1,2,2 Tetrachloroethane	$CHCl_2CHCl_2$	SC,BM
1,2 Dichloropropane	$CH_2ClCHClCH_3$	BM
Chloroalkenes		
Vinylidene chloride	$CH_2{=}CCl_2$	SC,BM
(cis) 1,2 Dichloroethylene	$CHCl{=}CHCl$	NBM
Trichloroethylene	$CHCl{=}CCl_2$	SC,BM
Tetrachloroethylene	$CCl_2{=}CCl_2$	SC
Allyl chloride	$ClCH_2CH{=}CH_2$	SC
Hexachloro-1,3 butadiene	$Cl_2C{=}CCl{-}CCl{=}CCl_2$	BM
Chloroaromatics		
Monochlorobenzene	C_6H_5Cl	—
α-Chlorotoluene	$C_6H_5CH_2Cl$	BM
o-Dichlorobenzene	$o{-}C_6H_4Cl_2$	—
m-Dichlorobenzene	$m{-}C_6H_4Cl_2$	—
p-Dichlorobenzene	$p{-}C_6H_4Cl_2$	—
1,2,4 Trichlorobenzene	1,2,4 $C_6H_3Cl_3$	—
Aromatic hydrocarbons		
Benzene	C_6H_6	SC
Toluene	$C_6H_5CH_3$	—
Ethyl benzene	$C_6H_5C_2H_5$	—
m/p-Xylene	$m/p{-}C_6H_4(CH_3)_2$	—
o-Xylene	$o{-}C_6H_4(CH_3)_2$	—
4-Ethyl toluene	$4{-}C_6H_4C_2H_5CH_3$	—
1,2,4 Trimethyl benzene	1,2,4 $C_6H_3(CH_3)_3$	—
1,3,5 Trimethyl benzene	1,3,5 $C_6H_3(CH_3)_3$	—
Oxygenated and nitrogenated species		
Formaldehyde	$HCHO$	SC,BM
Phosgene	$COCl_2$	—
Peroxyacetyl nitrate (PAN)	$CH_3COOONO_2$	Phytotoxic
Peroxypropionyl nitrate (PPN)	$CH_3CH_2COOONO_2$	Phytotoxic
Acrylonitrile‡	$CH{\equiv}CN$	SC

*In addition to chemical species, meteorological parameters were measured. These were: wind speed, wind direction, temperature, pressure, relative humidity and solar flux

†BM: Positive mutagenic activity based on Ames salmonella mutagenicity test (Bacterial Mutagens)
NBM: Not found to be mutagens in the Ames salmonella test (Not Bacterial Mutagens)
SC: Suspected Carcinogens

‡Satisfactory measurement method for ambient analysis is not available

Table 2. *Concentrations and Daily Outdoor Exposures of Measured Chemical Species*

Chemical Group and Species	Houston - Site 4 (14-25 May 1980) Concentration (ppt) Mean	S.D.†	Max.	Min.	Daily Exposure* (μg/day) Average	S.D.	St. Louis - Site 5 (29 May - 6 Jun 1980) Concentration (ppt) Mean	S.D.	Max.	Min.	Daily Exposure (μg/day) Average	S.D.
Chlorofluorocarbons												
Trichlorofluoromethane (F11)	474	178	1105	305	59.6	11.5	374	105	905	217	46.8	7.1
Dichlorofluoromethane (F12)	897	474	2817	482	103.5	30.2	622	182	1156	383	68.7	12.5
Trichlorotrifluoroethane (F113)	199	190	1664	37	37.7	26.5	132	171	1791	22	21.9	5.1
Dichlorotetrafluoroethane (F114)	28	10	58	12	4.5	0.9	25	6	37	13	4.0	0.5
Helomethanes												
Methyl chloride	955	403	2284	531	46.5	16.3	732	138	1015	531	34.1	1.2
Methyl bromide	100	58	278	45	9.3	3.3	81	25	125	7	7.2	1.2
Methyl iodide	3.6	2.2	11.2	0.6	0.4	0.2	2.6	1.6	7.2	0.2	0.4	0.2
Methylene chloride	574	553	3404	49	43.0	24.6	421	583	6402	82	29.3	10.5
Chloroform	423	749	5112	38	42.6	34.6	73	30	191	25	7.9	1.8
Carbon tetrachloride	404	449	2934	126	61.6	43.3	129	6	148	112	18.5	0.9
Haloethanes and halopropanes												
Ethyl chloride	227	273	1248	10	13.5	8.0	46	29	182	10	2.7	1.1
1,1 Dichloroethane	63	20	126	9	6.1	1.1	60	14	105	26	5.6	0.9
1,2 Dichloroethane	1512	1863	7300	50	125.0	81.1	124	101	607	45	11.4	4.7
1,2 Dibromoethane	59	72	368	10	9.9	5.6	16	4	26	8	2.8	0.4
1,1,1 Trichloroethane	353	263	1499	134	41.5	12.8	235	136	896	132	28.0	7.1
1,1,2 Trichloroethane	32	24	129	<5	3.1	1.8	15	6	45	6	1.9	0.4
1,1,1,2 Tetrachloroethane	12	15	80	2	1.1	0.8	6	3	18	4	0.3	0.3
1,1,2,2 Tetrachloroethane	11	9	77	2	1.6	0.7	6	2	12	4	0.3	0.2
1,2 Dichloropropane	81	37	253	22	8.5	1.4	53	12	88	22	5.6	0.7
Chloroalkenes												
Vinylidene chloride	25	36	136	<4	1.4	1.1	9	5	34	<4	0.4	0.2
(cis) 1,2 Dichloroethylene	71	59	429	21	6.3	2.6	39	8	66	25	3.5	0.5
Trichloroethylene	144	195	960	5	16.2	10.6	112	154	1040	8	13.5	7.4
Tetrachloroethylene	401	598	3215	34	61.4	61.9	326	955	7604	67	58.4	72.9
Allyl chloride	<5	—	<5	<5	<0.4	—	<5	—	<5	<5	<0.4	—
Hexachloro-1,3 butadiene	11	20	154	1	2.7	2.7	3	2	10	1	0.7	0.2
Chloroaromatics												
Monochlorobenzene	309	517	2785	9	34.4	24.8	240	243	1167	5	23.6	10.3
a-Chlorotoluene	<5	—	58	<5	<0.6	—	<5	—	25	<5	<0.6	—
o-Dichlorobenzene	7	9	67	1	1.0	0.7	6	11	95	1	0.8	0.6
m-Dichlorobenzene	7	8	47	1	0.7	0.3	4	8	55	1	0.3	0.3
p-Dichlorobenzene	—	—	—	—	—	—	—	—	—	—	—	—
1,2,4 Trichlorobenzene	2	2	13	1	0.4	0.1	1	1	4	1	0.2	0.0
Aromatic hydrocarbons												
Benzene	5780	5880	37700	840	449.2	283.3	1410	1190	5820	110	91.0	48.4
Toluene	10330	10850	65650	1040	822.4	419.9	1520	1250	6450	103	126.0	94.9
Ethyl benzene	1380	1400	7280	50	136.7	94.8	640	460	2100	50	44.9	23.9
m/p Xylene	3840	4270	23780	270	362.1	219.4	950	703	3230	110	86.8	50.9
o-Xylene	1307	1460	9790	80	123.7	65.8	310	300	1490	60	21.9	11.0
4-Ethyl toluene	870	1030	7470	60	90.3	44.0	240	180	1240	80	19.2	11.3
1,2,4 Trimethyl benzene	1150	1470	9260	50	118.6	54.2	370	370	2560	60	12.4	26.0
1,3,5 Trimethyl benzene	460	800	5350	70	27.1	21.5	530	490	1360	80	28.2	13.6
Oxygenated species												
Formaldehyde	—	—	—	—	—	—	11300	4500	18700	8100	319.0	127.0
Phosgene	<20	—	<20	—	<1	—	<20	—	<20	—	<1	—
Peroxyacetyinitrate (PAN)	438	835	4350	<10	44.0	45.4	277	203	890	40	24.4	8.0
Peroxyproponlynitrate (PPN)	110	140	630	<10	6.5	6.0	64	93	250	<10	0.5	1.2

Table 2. (continued)

Chemical Group and Species	Denver - Site 6 (15-28 Jun 1980) Concentration (ppt) Mean	S.D.	Max.	Min.	Daily Exposure (µg/day) Average	S.D.	Riverside - Site 7 (1-13 July 1980) Concentration (ppt) Mean	S.D.	Max.	Min.	Daily Exposure (µg/day) Average	S.D.
Chlorofluorocarbons												
Trichlorofluoromethane (F11)	637	255	1246	289	82.2	16.2	671	318	1880	201	87.8	19.9
Dichlorofluoromethane (F12)	1005	565	3178	471	107.9	24.5	1058	401	2804	667	125.2	35.0
Trichlorotrifluoroethane (F113)	221	235	1608	28	45.0	21.3	274	262	2211	26	44.6	11.5
Dichlorotetrafluoroethane (F114)	34	9	60	17	5.5	0.8	29	9	62	13	4.8	1.0
Halomethanes												
Methyl chloride	763	132	1157	519	36.8	4.8	703	179	1593	437	34.8	8.3
Methyl bromide	124	51	227	23	11.2	3.4	259	167	1033	43	23.5	12.3
Methyl iodide	1.8	1.0	4.8	0.6	0.2	0.1	2.8	1.2	6.2	0.6	0.4	0.2
Methylene chloride	967	926	4874	108	76.1	34.6	1949	1406	9426	478	159.1	53.7
Chloroform	185	206	1636	19	18.8	9.2	703	796	4747	109	76.1	44.3
Carbon tetrachloride	174	19	274	116	25.2	1.4	175	23	267	151	25.2	1.6
Haloethanes and halopropanes												
Ethyl chloride	41	24	125	10	2.4	0.8	87	65	312	16	5.1	1.9
1,1 Dichloroethane	65	31	142	11	6.3	1.6	66	22	147	8	6.1	1.1
1,2 Dichloroethane	241	297	2089	54	20.3	8.6	357	325	2505	63	31.8	12.3
1,2 Dibromoethane	31	15	78	10	5.5	0.9	22	7	47	10	3.9	0.5
1,1,1 Trichloroethane	713	553	2699	171	92.3	31.2	747	257	1349	205	92.8	17.8
1,1,2 Trichloroethane	27	10	56	7	3.4	0.6	41	21	89	<5	5.0	2.1
1,1,1,2 Tetrachloroethane	10	12	89	5	0.9	0.9	9	3	18	4	1.1	0.3
1,1,2,2 Tetrachloroethane	10	3	17	3	0.8	0.3	12	9	77	5	1.4	0.3
1,2 Dichloropropane	48	14	99	20	5.2	1.2	57	15	88	11	6.0	1.0
Chloroalkenes												
Vinylidene chloride	31	49	224	<4	1.4	3.3	9	6	56	<4	0.5	0.3
(cis) 1,2 Dichloroethylene	76	61	605	25	7.3	2.4	60	14	173	33	5.4	0.5
Trichloroethylene	196	313	2483	7	23.4	31.2	118	55	236	15	14.5	3.2
Tetrachloroethylene	394	158	1130	99	59.5	11.4	484	236	1626	173	76.7	20.8
Allyl chloride	<5	—	<5	<5	<0.4	—	<5	—	<5	<5	<0.4	—
Hexachloro-1,3 butadiene	2	1	7	0.4	0.5	0.2	4	3	16	1	1.1	0.3
Chloroaromatics												
Monochlorobenzene	290	217	1114	33	27.6	12.4	—	—	—	—	—	—
a-Chlorotoluene	<5	—	111	<5	<0.6	—	<5	—	38	<5	<0.6	—
o-Dichlorobenzene	26	34	227	2	4.3	2.9	10	8	76	3	1.4	0.4
m-Dichlorobenzene	8	7	36	1	1.0	0.6	6	4	21	1	0.6	0.3
p-Dichlorobenzene	—	—	—	—	—	—	—	—	—	—	—	—
1,2,4 Trichlorobenzene	6	4	35	1	1.0	0.5	10	7	40	2	1.7	0.3
Aromatic hydrocarbons												
Benzene	4390	3940	23910	110	302.4	129.9	3950	1910	10860	520	280.4	63.9
Toluene	6240	5280	24600	290	511.6	173.1	5800	3670	20070	450	496.9	155.8
Ethyl benzene	2220	3130	18520	90	195.5	94.8	1330	820	4000	250	127.7	30.9
m/p Xylene	2860	3320	20850	150	263.3	139.6	2231	1515	7340	260	215.5	52.9
o-Xylene	1280	1210	6000	<10	112.7	50.9	1100	650	3140	80	102.7	22.9
4-Ethyl toluene	900	760	4380	70	88.1	31.6	820	460	2650	70	85.8	22.6
1,2,4 Trimethyl benzene	1410	2310	15450	130	122.0	74.5	740	500	3120	100	78.4	50.7
1,3,5 Trimethyl benzene	340	240	1290	30	20.3	11.3	230	170	1260	70	13.6	5.6
Oxygenated species												
Formaldehyde	12300	5900	28700	6600	347.0	167.0	19000	7600	41000	10400	536.0	215.0
Phosgene	<20	—	<20	—	<1	—	~60	—	—	—	~2.5	—
Peroxyacetylnitrate (PAN)	443	1246	11647	12	45.0	21.4	1196	1249	5780	120	138.8	40.8
Petroxypropponylnitrate (PPN)	45	47	318	<10	4.4	2.7	193	197	900	<10	19.2	8.3

*Daily average exposure based on total air intake of 23 m^3/day at 25°C and 1 atm pressure
†Standard deviation

25°C and 1 atmosphere for a 70-kg male. The daily exposures were calculated by estimating hourly values by linear interpolations between measured data.

Much of the information presented in Table 2 is self-explanatory, so only salient observations will be made below. Table 3 summarizes the total average exposure for the four sites to each chemical category as defined in Table 2.

Chlorofluorocarbons (CFCs)

Four CFCs (fluorocarbon 11, 12, 113, and 114) were measured. As indicated earlier, CFCs are not expected to be toxic to the human body. They do, however, act as useful indicators of urban transport, and were, therefore, routinely measured throughout the sampling program.

Halomethanes

Six halomethanes were measured. As can be seen from Table 1, all six of these chemicals are either mutagens or suspected carcinogens. Chloroform levels are significantly elevated in the urban environments. Concentrations approaching 5 ppb were encountered at more than one site. The average daily intake of chloroform was as low as 9 μg/day in St. Louis and was close to 80 μg/day in Riverside (Table 2). While the sources of chloroform are still largely unknown, automobiles, chlorination of water, and direct emissions probably all contribute significantly. The variability of chloroform at Riverside is nearly identical to methylene chloride, further confirming its urban source.

Haloethanes and Halopropanes

Nine important chemicals in the haloethane and halopropane category were measured (Table 2). Since this is the first measurement of ethyl chloride, no comparative data are available. It is estimated that 0.01 million tons of ethyl chloride is released into the atmosphere every year in the United States. Measurements in this study suggested high levels of this chemical in Houston, where concentrations as high as 1.3 ppb were encountered. The average concentration (0.23 ppb) and the daily average exposure (14 μg/day) were also highest in Houston.

Chloroalkenes

Six chloroalkenes were sought. Of these, allyl chloride (a suspected carcinogen) was found to be present at concentrations of less than 5 parts per

Table 3. *Summary of Exposure to Hazardous Organic Chemical Groups*

	Total Average Daily Exposure (μg/day)				
*Chemical Category**	*Houston Site 4*	*St. Louis Site 5*	*Denver Site 6*	*Riverside Site 7*	*Average of Sites*
Chlorofluorocarbons†	*205*	*141*	*241*	*262*	*212*
Halomethanes	*203*	*97*	*168*	*319*	*197*
Haloethanes and halopropanes	*210*	*59*	*137*	*153*	*140*
Chloroalkenes	*88*	*78*	*92*	*98*	*89*
Chloroaromatics	*37*	*25*	*34*	—	*32*
Aromatic hydrocarbons	*2130*	*430*	*1616*	*1401*	*1394*
Oxygenated species	—	*344*	*396*	*696*	*479*

**As defined in Table 2*

†NOT suspected to be directly toxic

trillion at all sites. Vinylidene chloride (a bacterial mutagen and a suspected carcinogen) was measured at an average concentration of 10 to 30 parts per trillion at all sites.

There are two dominant chloroethylenes in the atmosphere: trichloroethylene and tetrachloroethylene. Trichloroethylene is a large-volume chemical (annual U.S. emissions = 0.15 million tons) that is also a suspected carcinogen. The highest concentration of 2.5 ppb was measured at Denver (Table 2). Typically the average concentrations were between 0.1 to 0.2 ppb.

The second large-volume chloroethylene that is also a suspected carcinogen is tetrachloroethylene. Its annual U.S. emissions are estimated to be about 0.3 million tons. At all sites, the tetrachloroethylene atmospheric abundance was 2 to 4 times that of trichloroethylene. This is due to larger emissions as well as its much longer lifetime when compared to trichloroethylene. The highest concentration of tetrachloroethylene was 7.6 ppb. The daily average exposure was determined to be between 60 and 80 μg/day at all sites.

Chloroaromatics

Six chloroaromatics were sought. No data are being reported of p-dichlorobenzene because of unknown interferences. Monochlorobenzene was the most dominant of the chlorobenzenes and its average concentration appeared to be close to 0.3 ppb. The highest concentration was 2.8 ppb in Houston. This is not inconsistent with its large source (0.1 to 0.15 million tons/year in the United States) and its moderately long lifetime.

Aromatic Hydrocarbons

Eight aromatic hydrocarbons were sought. The two most dominant aromatic hydrocarbons were benzene and toluene. The average abundance of toluene exceeded that of benzene at all sites: Average toluene/benzene concentration ratios at Sites 4, 5, 6, and 7 were respectively 1.8, 1.1, 1.4, and 1.5. As the air masses aged (or in cleaner environments) the toluene/benzene ratio decreases, largely because of the longer lifetime of benzene compared to toluene (8 days versus 2 days). Highest benzene and toluene concentrations of 38 ppb and 66 ppb were measured in Houston.

A common source of all measured aromatic hydrocarbons was indicated, as the diurnal variation of all the aromatic hydrocarbons at a given site was nearly identical.

As a whole, the aromatic hydrocarbon group is the most dominant, and daily intake of this group was the highest at all sites (Table 3).

Oxygenated Species

Four oxygenated species were sought: formaldehyde, phosgene, peroxyacetyl nitrate (PAN), and peroxypropionyl nitrate (PPN). Liquid chromatographic analysis of other aldehydes that are also toxic is currently underway. Formaldehyde was measured at relatively high concentrations that varied from 6 to 41 ppb. The abundance of formaldehyde compared to most other suspected carcinogens that were measured in urban atmospheres is significant. It is also found to be a bacteria mutagen and a suspected carcinogen (Table 1). Phosgene data are limited because of instrumental and meteorological parameters.

As is clear from Table 2, PAN and PPN levels were quite low at all sites. This was largely attributable to the prevailing weather. Maximum PAN levels at sites 4, 5, 6, and 7 were 4.4 ppb, 0.9 ppb, 11.5 ppb, and 5.6 ppb. The PPN levels were roughly lower by a factor of 5 when compared to those of PAN.

Conclusions and Recommendations

Table 2 summarizes the average concentrations measured at each of the sites and the daily average exposure based on a total air intake of 23 m^3/day for a 70 kg male. The corresponding standard deviations associated with these parameters are shown in Table 2. The mutagenicity and toxicity information for individual species is also summarized in Table 1. Table 3 summarizes average exposure (μg/day) to individual categories of chemical groups at each of the sites. Overall, the total exposure to measured toxic chemicals at Houston, Denver, and Riverside was comparable (it was significantly lower at St. Louis). As a category, exposure to aromatic hydrocarbons is the highest, and to chloroaromatics the lowest, at all sites.

Hot-spots for specific toxic chemicals are found at different locations. As is clear from Table 2, the ambient levels of 1,2-dichloroethane (a suspected carcinogen) were significantly elevated at the Houston site despite meteorological conditions that were unfavorable to pollutant accumulation. Hot-spots of methylene chloride (a weak mutagen) and chloroform (a suspected carcinogen) were observed at Riverside. The high concentrations of chloroform at Riverside are surprising. (No large sources are known.) Special tests were conducted to ensure the reliability of these data: Chloroform data were found to be accurate to within ± 10 percent. Formaldehyde, another suspected carcinogen, was measured at high concentrations at all sites.

In the third (final) year of this project, a significant emphasis will be placed on field measurements and on analysis and interpretation of the data set collected during this study. The major effort in the third year will be devoted to:

- Expanding the list of toxic chemicals to be measured
- Conducting additional field studies in selected U.S. cities
- Analyzing and interpreting all collected field data
- Preparing a final report.

During the end of the second year, and the early part of the third year of research, efforts will be directed to developing measurement methods for ambient aldehydes and ketones (as well as formaldehyde, which was measured in the second year). A high-pressure liquid chromatograph (HPLC) has been acquired and will be utilized. Attempts to identify currently unidentified species found to be nearly ubiquitously present will continue, and further efforts will be made to improve the separation of chlorinated aromatics (especially p-$C_6H_4Cl_2$).

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The complete report, entitled "Atmospheric Measurements of Selected Hazardous Organic Chemicals," (Order No. PB 81-200 628; Cost: ~~$8.00~~ subject to change) will be available only from: A04
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