

HYDROCARBONS IN THE ATMOSPHERE

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Summary

This contribution focuses on hydrocarbons in the atmosphere, covering methane and non-methane hydrocarbons, including volatile organic compounds and semi-volatile

organic compounds. Hydrocarbons play an essential role in atmospheric chemistry and atmospheric hydrocarbons are of high environmental relevance.

Their anthropogenic and natural sources are discussed. The main anthropogenic sources are applications of fossil resources, including production of fuels, combustion processes and solvent applications. With respect to natural resources, vegetation is the main emitter of hydrocarbons, with compounds such as ethylene, isoprene and monoterpenes.

Further on, their fate is discussed. This section shows the role of hydrocarbons in global atmospheric processes such as stratospheric ozone depletion, tropospheric ozone generation and global warming. Here, degradation mechanisms of different types of hydrocarbons are presented. Next, exchange with adjacent compartments, such as oceans, soils and vegetation is focused on.

Finally, analytical techniques and observed atmospheric hydrocarbons concentrations are discussed. This includes methods to sample hydrocarbons as free atmospheric molecules as well as hydrocarbons on aerosols. Subsequent separation, mainly based on gas chromatography, and detection methods are presented. Measurements of different subgroups of hydrocarbons at different locations are discussed, including factors explaining variations in the concentrations.

1. Introduction

In *sensu strictu* hydrocarbons (HCs) are organic compounds consisting of carbon and hydrogen atoms. In *sensu latu* the term hydrocarbons is also used for functionalized organic compounds, including oxygen, halogen (chlorine, bromine, iodine), nitrogen, phosphorous, sulfur ... atoms. They can be present in the atmosphere in two physical conditions, depending on their volatility or vapor pressure. If they are rather volatile, they are present as free molecules in the atmosphere. These types of hydrocarbons are classified as Volatile Organic Compounds (VOCs). On the other hand, if a compound's vapor pressure is low enough so that it partitions between the gas phase and aerosols, they are denoted as semi-volatile organic compounds (SVOCs). There is no global consensus on defining the exact boundary of the group of volatile organic compounds. In European and Australian legislation, volatile organic compounds are organic compounds with a vapor pressure at 25°C of, at least, 10 and 270 Pa respectively, whereas in the USA volatile organic compounds are defined as organic compounds which have negligible photochemical reactivity. Within the group of hydrocarbons in *sensu strictu*, methane takes a somewhat special position due to its relatively low reactivity and consequently high ambient mixing ratios. Therefore, hydrocarbons with exclusion of methane are sometimes considered as one group: the non-methane hydrocarbons (NMHCs). Figure 1 gives an overview of hydrocarbons with their environmental relevance.

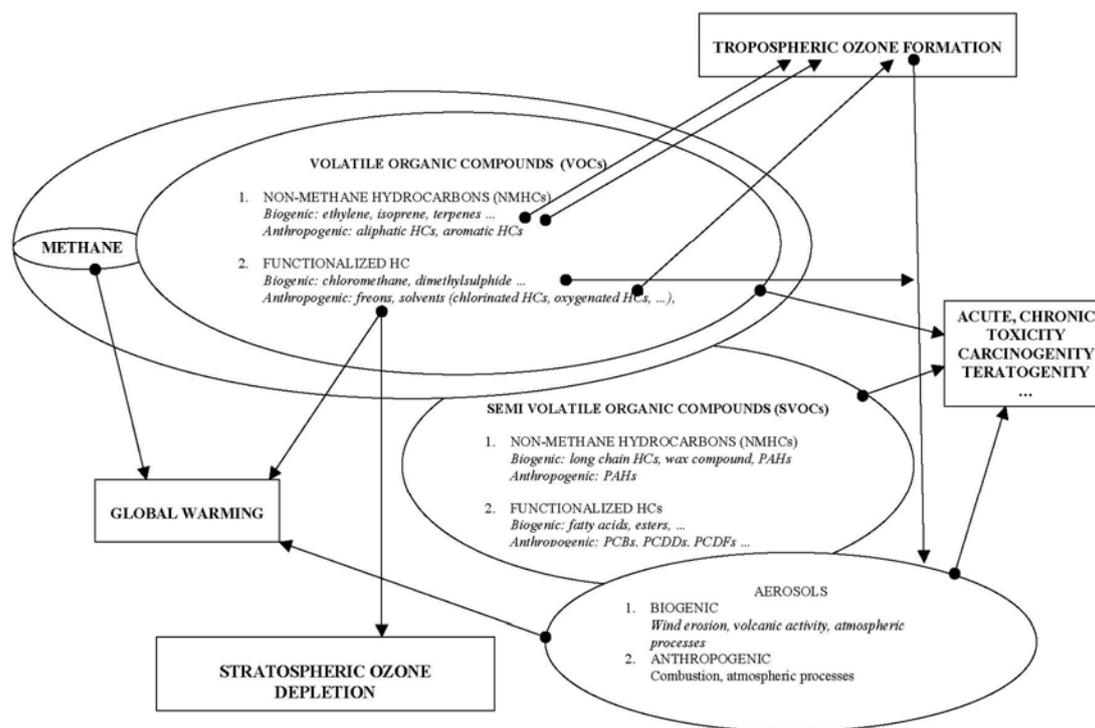


Figure 1: Overview of hydrocarbons in the atmosphere: subgroups, origin and environmental relevance

A number of subgroups of functionalized hydrocarbons, such as polychlorinated biphenyls (PCBs), chlorinated pesticides (e.g. 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT)), polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are considered as Persistent Organic Pollutants (POPs), because of their negative effects on the ecosystem and human health (Decision 18/32 of the UNEP Governing Council: Persistent Organic Pollutants, May 1995) (see *Persistent Organic Wastes*).

Hydrocarbons are present in the atmosphere as trace gases, with methane as the predominant hydrocarbon molecule (approximate concentration 1.7 ppmv). Measured concentrations of other hydrocarbons are in the parts per billion or parts per trillion range, e.g. isoprene (C_5H_8): 0.6-2.5 ppbv; and terpenes ($C_{10}H_{16}$): 0.03-2 ppbv.

Hydrocarbons which are reactive in conditions prevailing in the troposphere play an important role in photochemical air pollution. This fact has been recognized for more than 40 years. With the available knowledge of the fast photochemical reactions occurring in the atmospheric boundary layer, it is possible now to relate ozone formation quantitatively to atmospheric oxidation of reactive hydrocarbons (see *Formation and Effects of Smog*). Individual reactive hydrocarbons make a different contribution to ozone formation and hence it is possible to define a reactivity scale that orders hydrocarbons according to their relative importance as ozone precursors. Reactivity is being used in the policy process and hydrocarbons of negligible reactivity are exempt from regulations. The long-range atmospheric transport and multi-day photochemistry have led to combat regional ozone problems through international

action within the scope of the United Nations Economic Commission for Europe (UN ECE) and its international convention on Long-Range Transboundary Air Pollution.

In addition to natural causes, anthropogenic emissions of methane and chlorofluorohydrocarbons (CFCs), as well as carbon dioxide (CO₂) and laughing gas (or dinitrogen monoxide, N₂O), are expected to play an important role in earth's climate change within the next 50-100 years (see *Greenhouse Gases and Global Warming*). Chlorofluorohydrocarbons and related chlorinated compounds with tropospheric lifetimes exceeding several years are precursors of stratospheric ozone depletion (see *Stratospheric Ozone Depletion*). International actions have been worked out in the Montreal Protocol on the Protection of the Ozone Layer (1987), the subsequent London Revisions to the Protocol (1990) and the Protocol of Copenhagen (1992). More recently, there was the Kyoto climate change conference (1997) where a reduction of greenhouse gas emissions (mainly carbon dioxide, methane and nitrous oxide) is targeted. Finally, the work of the Intergovernmental Panel on Climate Change (IPCC) has to be mentioned in this context.

Hydrocarbons are emitted both from natural and anthropogenic sources. They can undergo advective transport through the atmosphere and exchange with adjacent compartments as water bodies, soils and vegetation. They can undergo photo-induced breakdown, in a direct or indirect way. The present contribution focuses on these aspects and on analytical methods to determine atmospheric concentrations. Finally, observed concentration ranges are discussed.

2. Sources

Sources of hydrocarbons can be divided into two main groups: natural and anthropogenic sources.

2.1. Anthropogenic Sources

Anthropogenic emissions comprise a broad spectrum of species, but also a wide variety of sources. They include production, treatment, storage and distribution of fossil fuels, combustion processes, applications of volatile organic solvents and solvent-containing products, industrial and biological processes. The currently available emission inventory data are presented in Table 1.

2.1.1. Fossil Fuels

Mining and processing of coal mainly lead to methane emission, but also ethane and propane are produced in minor amounts. Production, as well as storage and distribution of liquid fossil fuels, comprise a large variety of activities that result in hydrocarbon emissions to the atmosphere. Crude oil production platforms on land or offshore are point sources of hydrocarbons such as methane, ethane, propane, butanes, pentanes, hexanes, heptanes, octanes and cycloparaffins. Processing of petroleum products, resulting in fuels, feedstock and primary petrochemicals, includes separation, conversion and blending, and leads to emissions. Major sources are catalytic cracking

(0.25 to 0.63 kg per m³ of feed), cokes production (about 0.4 kg per m³ of feed) and asphalt blowing (about 27 kg of VOC per m³ of asphalt). Furthermore, so-called fugitive emissions occur from leaks from all types of equipment and installations, such as static and dynamic sealings, valves, flanges, pumps, and compressors. However, due to the variability of processes, emissions released from two petroleum refineries might be different in their specific amounts and in their composition. With respect to storage and distribution of petroleum products, gasoline is to be mentioned as the major source since it is handled in large amounts and because of its high volatility. Evaporative emissions are mainly determined by the vapor pressure of the liquids, construction and conditions of storage tanks and filling installations, meteorological conditions and amounts to be handled. For uncontrolled techniques, overall emission factors for refinery dispatch stations are in the range of 0.3 kg t⁻¹ of total gasoline handled, and transport and depots account for some 0.7 kg t⁻¹, whereas emission factors for service stations total 2.9 kg t⁻¹. Compounds here are mainly C₃-C₆ alkanes, C₄-C₅ alkenes and BTEX (benzene, toluene, ethylbenzene, xylenes).

2.1.2 Combustion Processes

Major products of complete combustion of fossil fuels are carbon dioxide and water. However, in practice, combustion leads to carbon monoxide (CO) and hydrocarbon by-products, mainly due to lack of oxygen, imperfect air/fuel mixing and inappropriate combustion temperatures. Hydrocarbons emitted can be partially oxidized as e.g. aldehydes, but also unoxidized compounds as alkanes and aromatics are emitted.

Country	METHANE						NMVOCs	
	Energy		Agriculture		Waste	Other	Total	Total
	Fuel combustion	Fugitive fuel	Livestock	Other				
Australia	116	1217	2970	376	737	180	5596	1851
Austria	14	6	157	35	248	0	460	238
Belgium	9	36	336	14	184	2	581	260
Bulgaria	4	171	111	2	362	3	653	89
Canada	245	1839	1097	no data	1038	42	4261	no data
Czech Rep.	23	281	121	no data	98	6	529	267
Denmark	33	15	184	no data	55	no data	287	140
Estonia	5	29	30	no data	36	0	100	25
Finland	22	1	81	no data	89	5	198	172
France	169	228	1504	31	549	104	2585	2420
Germany	88	1046	1530	26	794	no data	3484	1705
Greece	21	52	170	108	158	no data	509	382
Hungary	32	400	115	2	128	2	679	74
Ireland	5	4	564	no data	76	no data	649	102
Italy	93	285	811	82	686	13	1970	no data
Latvia	11	23	36	no data	27	0	97	67
Lithuania	8	17	83	no data	68	0	176	104
Monaco	0	no data	no data	no data	0	no data	0	1
Netherlands	30	150	435	no data	446	5	1066	302
New Zealand	11	43	1406	0	126	6	1592	181
Norway	15	30	110	no data	190	1	346	345
Poland	53	822	580	1	870	9	2335	730
Portugal	20	3	263	9	339	49	683	506
Romania	no data	no data	no data	no data	no data	no data	no data	529
Russian Fed.	no data	no data	no data	no data	no data	no data	no data	5990
Slovakia	8	122	66	no data	73	no data	269	149
Slovenia	no data	no data	no data	no data	no data	no data	no data	37
Spain	54	178	981	18	842	3	2076	2848
Sweden	35	no data	159	no data	61	0	255	516
Switzerland	6	12	137	no data	64	0	219	281
Ukraine	14	4387	1196	no data	859	0	6456	656
United Kingdom	94	738	995	no data	809	1	2637	2444

United States	627	10072	9875	511	10431	78	31594	18795
TOTAL	1865	22207	26103	1215	20443	509	72342	142819

Table 1: Anthropogenic emission inventory (Gg, 1 Gg = 1 kton) in 1998 of methane and non-methane hydrocarbons (NMHCs) (UN (2000) United Nations, Framework Convention on Climate Change. FCCC/SBI/2000/11. National Communications from parties included in Annex I to the convention: greenhouse gas inventory data from 1990 to 1998. 5 September 2000. <http://www.unfccc.de/resource/docs/2000/sbi/11.pdf>)

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Tailpipe emissions from gasoline passenger cars with and without three-way catalyst are estimated respectively as 0.68 and 18.92 g of hydrocarbon per kg of fuel, whereas passenger diesel cars (produced after 1996) emit about 1.32 g of hydrocarbon per kg of fuel. Similarly, diesel heavy-duty vehicle emissions are estimated as 5.4 g of hydrocarbon per kg of fuel. Exhaust gas emissions from motor vehicles strongly depend on parameters such as vehicle speed, motor load and engine temperature (cold start). Main emitted compounds for gasoline and diesel combustion engines are paraffins (C_1 - C_5 for gasoline cars, methane for diesel engines), C_2 - C_5 olefins, ethyne, aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes and C_9 aromatics), aldehydes (formaldehyde, acetaldehyde, acrolein, benzaldehyde, tolualdehyde), ketones (acetone) and others (mainly high molecular weight paraffins). A special feature of gasoline car fuel is the use of additives to improve the combustion process resulting in lower emissions, indicated by the 'octane rating'. Whereas previously lead compounds (tetra ethyl lead) was used, currently oxygenates (typically methyl tert butyl ether) are added in the US. These so-called reformulated gasolines result in less smog formation in urban areas. However, due to groundwater pollution by these oxygenates, it is expected that new additives will have to be introduced.

In space heating of households, the emissions per terajoule ($1 \text{ TJ} = 10^{12} \text{ J}$) of fuel largely depend on the type of fuel. Whereas emissions for gas and light fuel combustion are estimated as 5 kg TJ^{-1} , the emissions of combustion of solid fuels (coal, wood) are in the range of $350\text{-}400 \text{ kg TJ}^{-1}$. Coal, fuel oil and wood result in the emission of mainly C_1 - C_4 alkanes, C_2 - C_5 alkenes, C_2 - C_3 alkynes and BTEX (benzene, toluene, ethylbenzene and xylenes) compounds. Additionally, wood and fuel oil combustion gives rise to aldehydes and, in case of wood, also to ketones. Main exhaust compounds of gas combustion are C_1 - C_4 alkanes, C_2 - C_4 alkenes and C_2 - C_4 aldehydes.

Combustion processes are important emission sources for semi-volatile organic compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Due to their low chemical and biological degradation and their large octanol/water partitioning coefficients, these chemicals belong to the persistent organic pollutants (POPs). Mass balance investigation between known emission sources (mainly combustion) and deposition data have been made. A discrepancy of a factor of 2 was observed and attributed by the authors to octachlorodibenzo-p-dioxins produced by photochemical synthesis from pentachlorophenol.

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Biographical Sketches

Dr. ir. Jo Dewulf (18/7/1969) is post-doctoral researcher at the Faculty of Agricultural and Applied Biological Sciences at Ghent University. His research topics are environmental organic chemistry and technology. He graduated in 1992 and obtained his Ph.D. (Environmental Technology) at the same Faculty in 1997. Since his Ph.D., he is post-doctoral researcher with mainly research activities (1) in the assessment of sustainability of technology by exergy analysis, i.e. assessment of use of (non-)renewable resources, process efficiency and emissions (2) physical chemical environmental behavior and abatement of volatile organic compounds. He is also involved in teaching chemical and clean technology at the Faculty. He is (co-)author of over 30 publications in international peer reviewed journals and about 20 other scientific publications. He is referee for six international journals.

Prof. Dr. ir. Herman Van Langenhove (11/06/1953) is professor at the Faculty of Agricultural and Applied Biological Sciences at Ghent University. His discipline covers environmental chemistry and technology. He graduated at the Faculty of Agricultural and Applied Biological Sciences in 1976, obtained the post graduate diploma in Environmental sanitation (Ghent University, 1984). He obtained his Ph.D. at the same Faculty in 1986 on physicochemical techniques for the analysis of odors. Since 1992 Herman Van Langenhove is lecturing courses in analytical organic chemistry, environmental chemistry and physicochemical treatment of waste air. Research projects deal with the biogeochemistry of these compounds (specifically at the North Sea environment); the elimination of VOC from waste air using

chemical and biological techniques (biomembrane filter, advanced oxidation processes...); policy supporting research (odor nuisance, VOC inventories). Since a few years the concept of exergy is explored together with dr. ir. Jo Dewulf as a quantitative measure for sustainability. He authored or co-authored more than 250 scientific publications, more than 80 of which appeared in the highest ranking journals. He is a referee for more than ten journals and a member of the advisory board of two international journals.

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