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Air pollution

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN THE ATMOSPHERE OF THE CITY OF THESSALONIKI, GREECE

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Abstract. Volatile organic compounds (VOCs) are considered as important air pollutants playing a fundamental role in photochemical smog formation. The aim of this work is to study the atmospheric concentration levels of volatile hydrocarbons in the city of Thessaloniki at North Greece. The sampling was carried out during three weekly periods on 1995 and 1996. The hydrocarbons measured were the aliphatic and aromatic C6-C9 and naphthalene. The aromatic compounds were the most abundant followed by the aliphatics with corresponding maximum concentrations 79.2 ppb for toluene and 26 ppb for hexane.
Keywords: air pollution, volatile organic compounds, Thessaloniki, hydrocarbons.

AIMS AND BACKROUND

Hydrocarbons are a class of widespread organic air pollutants that play an important role in urban air quality deterioration for two main reasons: a) in the presence of nitrogen oxides they largely contribute to the formation of ozone and other photochemical oxidants[1,2], and b) some of them (especially benzene) are toxic and/or carcinogenic[3]. Hydrocarbons are present in the atmosphere as a result of human activities, arising mainly from motor vehicle exhausts and industrial processes. Emission from the vegetation is also an important source of atmospheric hydrocarbons[4].

In this work we study the diurnal and seasonal variation of the atmospheric concentration levels of hydrocarbons at two representative sites of the city of Thessaloniki: in the center of the city and at a second site close to the industrial zone. Twelve hydrocarbons were selected for measurement, namely the aliphatic hexane, heptane and octane, the aromatic benzene, toluene, ethylbenzene, *m*-, *p*-, *o*-xylenes, 1,2,4- and 1,3,5-trimethylbenzenes and the polycyclic aromatic naphthalene.

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MATERIALS AND METHODS

Three weekly campaigns were performed in Thessaloniki from September 21 to 26, 1995, from November 30 to December 5, 1995, and from June 6 to 11, 1996. Two representative sampling sites were selected, the first one (site A) in the center of the city along a relatively busy traffic road and the second (site B) close to the industrial zone. The samplers were located about 2 m above the ground, the sampling time was 20 min and the sampling frequency every 2 or 3 hours. Air samples were passed with the aid of personal pumps (Gillian) through preconditioned glass tubes filled with Tenax TA (Chrompack) at flow rates of about 100 ml/min. The tubes were then transferred to the laboratory and the volatile hydrocarbons were thermally desorbed (a Chrompack thermal desorption unit) and determined by gas chromatography and FID detection (a Hewlett Packard 5890 gas chromatograph).

RESULTS AND DISCUSSION

The mean, the minimum and the maximum concentrations measured during the three sampling periods are presented in Table 1. In all cases aromatic hydrocarbons, and mainly toluene, benzene, ethylbenzene and xylenes (BTEX), were the dominant compounds identified (concentration range 0.1-79.2 ppb at site A and 0.1-55.2 at site B). The measured aliphatic hydrocarbon concentrations were lower (0.1-21.4 ppb at site A and 0.1-26 ppb at site B) and hexane was the predominant alkane. The concentrations of naphthalene were always lower than 6.7 ppb. In Fig. 1 the diurnal variations of four representative compounds during the three measuring periods are shown: toluene, the most abundant compound, the toxic and known human carcinogen benzene, heptane from the class of aromatic and aliphatic compounds and naphthalene.

Table 1. Range and mean values of atmospheric concentration (ppb) of hydrocarbons in Thessaloniki during the three measuring periods

Compound	September 21-26, 1995				November 30-December 5, 1995				June 6-11, 1996			
	Site A		Site B		Site A		Site B		Site A		Site B	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Benzene	1.1-28.7	11.0	1.4-24.1	7.1	2.7-35.5	15.9	1.3-23.7	7.8	5.9-38.8	17.0	2.4-12.5	6.5
Toluene	1.7-55.1	22.7	2.2-55.2	13.5	5.4-78.0	32.0	1.3-53.7	15.9	11.4-79.2	36.0	5.4-28.0	15.9
Ethylbenzene	0.1-10.1	3.8	0.4-19.2	2.8	0.7-16.0	6.7	0.3-11.9	3.5	2.5-18.7	8.0	1.5-9.0	4.1
m-, *p*-xylenes	0.9-36.2	13.3	1.5-54.4	9.4	2.2-52.1	22.0	0.8-35.8	10.9	7.0-56.3	24.2	4.6-26.9	12.3
o-xylene	0.2-14.5	5.0	0.1-22.0	3.6	1.0-22.0	9.0	0.4-16.6	4.5	1.1-22.9	9.5	1.7-8.7	4.6
1,3,5-trimethylbenzene	0.1-4.5	1.5	0-4.1	1.1	0.4-5.8	2.7	0.2-4.6	1.3	0.5-8.4	3.7	0.8-3.8	2.1
1,2,4-trimethylbenzene	0.1-14.9	5.7	0.6-14.2	4.0	0.8-17.3	8.2	0.3-11.5	3.5	0.6-18.8	8.3	1.8-7.5	4.2
Hexane	0.1-13.1	4.9	0.8-13.3	3.9	1.3-18.7	5.0	0.5-19.0	3.3	1.2-21.4	6.3	1.6-7.0	3.9
Heptane	0.7-7.7	3.1	0.4-26.0	2.9	0.8-12.0	3.3	0.0-12.3	2.2	0.6-15.3	4.4	0.8-3.6	2.2
Octane	0.1-3.3	1.0	0.2-3.7	1.0	0.4-4.2	1.9	0.3-3.6	1.1	0.4-6.4	2.2	0.6-1.9	1.3
Naphtalene	0.0-6.9	1.0	0.0-2.6	0.6	0.0-4.2	1.0	0.0-5.0	0.9	0.0-4.9	1.0	0.0-2.8	0.7

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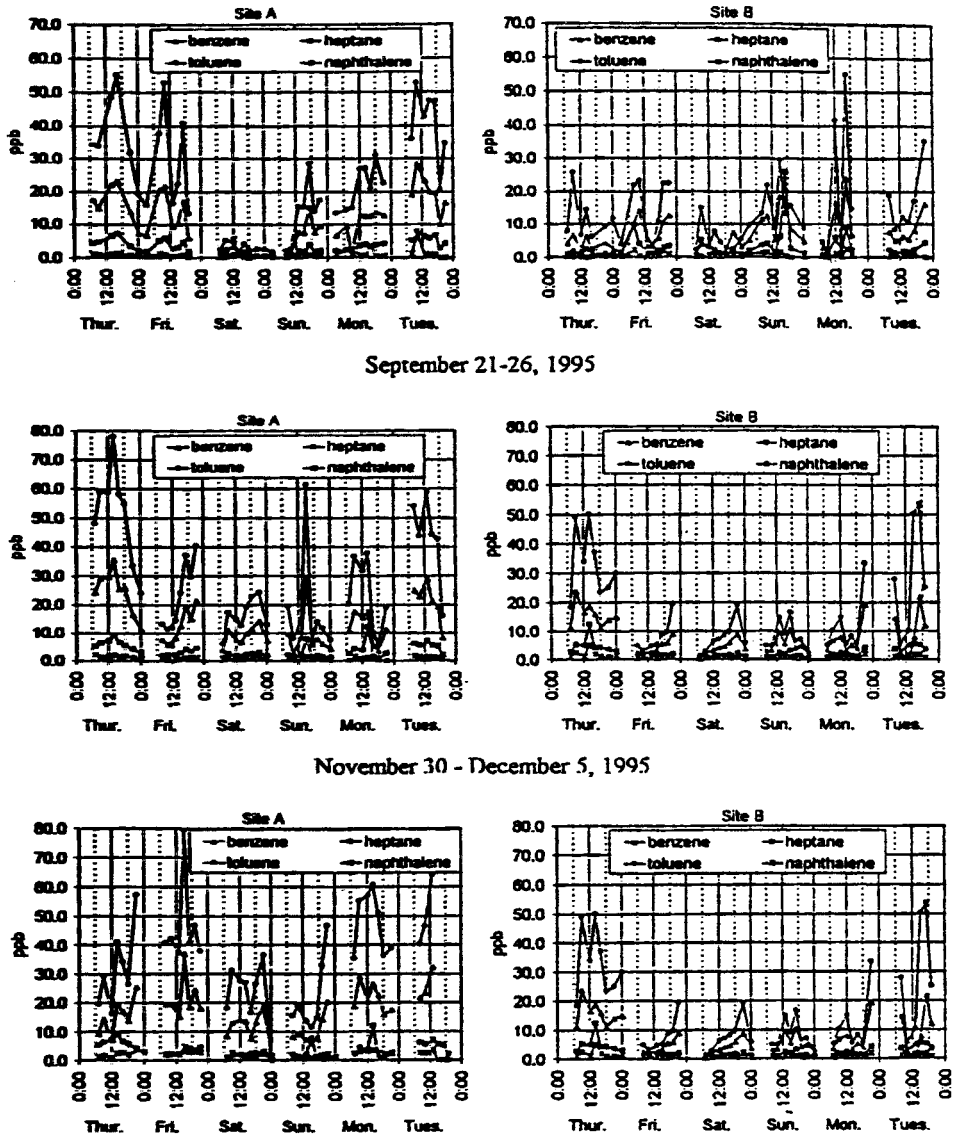

Fig. 1. Toluene, benzene, heptane and naphthalene diurnal variations during the three measuring periods

Site A (center of the city). The measured hydrocarbon concentrations in the center of the city, and especially the aromatic compound concentrations, were generally high. They are comparable with values found from measurements at urban sites in other European cities[5-7], but lower than concentrations obtained from measurements in the center of Athens during summer 1994[8,9].

Special care should be given to BTEX concentrations. These compounds are primary pollutants emitted mainly by the road traffic. From Fig. 1 it is evident that their daily maxima correspond to the increased traffic during the morning and afternoon rush hours, while during the night and weekends their concentrations are significantly lower. It is known that the only degradation pathways of benzene and toluene are transformations by chemical reactions when OH-radicals are formed by photochemical processes involving NO_x in presence of sunlight. Toluene is more reactive than benzene and it is transformed more rapidly[10], which means that the correlation between benzene and toluene will be getting worse as a function of age of the polluted air masses and the photochemical activity. In our case this correlation is very good even in the favourable for photochemical activities summer period (r=0.99 for the winter and 0.95 for the summer). This fact confirms that the almost exclusive source of the measured high BTEX concentrations at site A is the motor vehicle exhaust emissions from the nearby road. The correlation between aromatic and aliphatic hydrocarbons is rather poor indicating different sources for these compounds.

Site B (close to the industrial zone). At site B the measured concentrations were generally lower than the corresponding values at site A and this can be attributed to the reduced traffic. However, during weekend, and especially in the September sampling period, higher values for both the aromatic and aliphatic hydrocarbons were observed at site B. In addition, the correlation between benzene and toluene is not very good (r=0.83 for the winter and 0.71 for the summer) indicating dispersion and chemical transformation for these compounds. From these observations it can be concluded that some other sources (point sources and higher background pollution, traffic in other streets) except the direct emission from the street contribute to the air pollution at this site.

CONCLUSIONS

At site A, in the center of the city, high atmospheric concentrations of aromatic hydrocarbons were found with diurnal variations corresponding to traffic conditions and this was attributed to direct vehicle exhaust emissions. During the weekends the concentrations were significantly lower.

At site B, close to the industrial zone of the city, lower concentrations were measured due to better traffic conditions, but some other pollutant sources were detected contributing to the air pollution situation.

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