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Identification and determination of biogenic and anthropogenic volatile organic compounds in forest areas of Northern and Southern Europe and a remote site of the Himalaya region by high-resolution gas chromatography–mass spectrometry

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ABSTRACT

More than 100 volatile organic compounds of natural and man-made origin were identified and determined in air samples collected in forest and remote areas. The combined use of carbon adsorption traps and high-resolution gas chromatography–mass spectrometry made possible the selective determination of polar compounds such as organic acids, alcohols and carbonyl compounds by selected-ion detection. A comparison between the distribution and composition of volatile organic components recorded in Northern Europe, the Mediterranean basin and the Himalaya region seem to be indicative of the ubiquitous occurrence of some polar organic compounds of biogenic origin. The determinations carried out in the Italian Station built by the National Research Council (CNR) of Italy at the foot of Mount Everest show clearly that, under favourable conditions, substantial amounts of organic pollutants of man-made origin can be transported over unpolluted areas.

INTRODUCTION

Emission of large amounts of chemical compounds into the atmosphere as a result of anthropogenic and biogenic processes results in a complex array of chemical transformations ultimately leading to diverse effects on man and the environment. Among them, photochemical air pollution, acid deposition, changes in the stratospheric ozone layer and global weather modifications are the most important [1]. For a long time, volatile organic com-

pounds (VOC) have been recognized to be important primary pollutants, acting as precursors of atmospheric pollution either in tropospheric and stratospheric layers [1]. Because of the great complexity of chemical reactions and emission, transport and deposition processes, computer models have been developed to predict the possible adverse effects associated with increased emission of VOC into the atmosphere [1–2].

In the last 15–20 years, validation of the chemical mechanisms by computer models has been regarded as one of the fundamental tasks to be pursued in order to make model predictions sufficiently accurate to be used for a targeted decrease in atmo-

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spheric pollution [2,3]. The comparison of observations with predictions implies, however, that both the composition and concentrations of VOC present in different air parcels are known in great detail and with high accuracy. Particularly important is the capability to detect biogenic components whose emission from vegetation and microbial processes is still largely unknown [4]. This is possible only if analytical techniques capable of detecting both precursors and products of atmospheric reactions at trace levels (pptv) are available.

Recently, the use of adsorption traps filled with graphitic carbons combined with high-resolution gas chromatography-mass spectrometry (HRGC-MS) has been proposed as a suitable method for investigating the composition of the organic fraction with carbon numbers ranging between 4 and 14 [5]. More than 140 compounds exhibiting different polarities (mainly alkanes, alkenes, arenes, alcohols, aldehydes and ketones) were identified in samples collected in urban and suburban areas of the Italian peninsula and a pine forest located in Central Italy [5,6]. To test further the accuracy of this method and extend its capability to the identification and determination of components emitted by natural sources or formed by their photochemical oxidation in air, additional experiments were carried out in relatively unpolluted areas of Northern Europe, the Mediterranean basin and in the Himalaya region close to the Mount Everest where a permanent station has recently been set up by the National Research Council of Italy (CNR).

The analysis of these samples confirmed that the method proposed is suitable for evaluating in a single run a large number different classes of organic components useful to assess the relative importance of biogenic vs. man-made emission, investigate atmospheric processes and detect the influence of transport in remote areas. In this paper the full methodology for determining the various classes of organic components that can be present in the atmosphere is described. The observations made are discussed on the light of the present knowledge on VOC emission and reactivity. Evidence for the importance of transport in determining the levels of organic pollutants in remote areas of the Himalaya region is presented.

EXPERIMENTAL

Adsorption Traps

VOC present in volumes of air varying from 1 to 6 l were collected on two-stage traps consisting of glass tubes (15 cm × 0.3 cm I.D.) filled with Carbotrap C (0.034 g) and Carbotrap (0.17 g) particles ranging between 20 and 40 mesh. Both adsorbents were supplied by Supelco (Bellefonte, PA, USA). Graphitic carbons were preferred to more adsorbing carbon materials (such as Carbosieve III) as their hydrophobic surface and low specific surface area prevented the adsorption of large amounts of water and carbon dioxide on the traps, thus allowing the mass spectrometric identification of volatile components with carbon numbers higher than 2 [5]. Before sample collection, the traps were cleaned by passage of a stream of pure helium at a flow-rate of 300 ml/min for 10 min at 285°C. After purging, the traps were sealed with metal connectors equipped with PTFE ferrules, wrapped in aluminium foil and stored in a tightly closed glass container (3 l) in the presence of open cartridges filled with a desiccant and active charcoal to prevent contamination of the trapping materials during transport. One sealed trap in each container was used as a blank to check whether accidental exposure of the container to contaminants would have caused passive collection of hydrocarbons in the sampled traps.

A high precision, battery-operated sampling device (Genesis Air Sampler; DuPont, Kenneth Square, PA, USA) was used for the parallel collection of the same volume of air in two different traps. After sampling, the traps were sealed and stored in the glass container for shipment to the laboratory. By adopting this procedure, VOC adsorbed on traps were found to be stable for more than 2 months.

Desorption unit, GC-MS apparatus and columns

Hydrocarbon components retained on the carbon traps were transferred to the GC unit by thermal desorption. A Chrompack (Middelburg, Netherlands) purge and trap injector was adapted for this purpose by eliminating the purging and drying units. The unit operates according to a two-step mechanism involving a cryofocusing process at the column inlet to prevent band broadening of the GC peaks in the capillary column. After the trap has

been back-flushed at a flow-rate of 10 ml/min for 1 min, the gas stream is diverted to the cryofocusing unit (-150°C) containing a fused silica liner. The flow-rate is then increased to 20 ml/min and maintained for 5 min through both the trap and liner while the temperature of the trap is ballistically increased to 250°C . The desorbed sample enriched on the cryofocusing unit is subsequently transferred to the GC column by increasing the temperature of the fused-silica liner from -150 to 230°C .

All separations were performed on a $60\text{ m} \times 0.32\text{ mm}$ I.D. capillary column (J&W Rancho Cordoba, CA, USA) coated with a $0.25\text{-}\mu\text{m}$ film of DB-1. After transfer of the sample, the column oven was maintained at 5°C for 3 min, programmed to 50°C at $3^{\circ}\text{C}/\text{min}$ and then to 220°C at $5^{\circ}\text{C}/\text{min}$. A Model 5890 gas chromatograph (Hewlett-Packard, Palo Alto, CA, USA) connected to a Hewlett-Packard Model 5970 B mass spectrometer (mass-selective detector, MSD) was employed for all GC-MS determinations. Positive identification of the various components was carried out by combining the information obtained through the analysis of mass spectra with those acquired through the determination of the elution sequence determined by measuring the retention indices of a large number of pure components. When standards were not available, retention indices reported in the literature were used for peak identification [7]. Selected-ion detection was preferred for identification and quantification purposes whenever eluted compounds were characterized by fragmentation patterns where specific ions could have been used for unambiguous determinations.

Sites investigated

Forest samples were collected in eastern Germany and Central Italy. Eastern Germany was selected because it is covered by large wooded areas highly representative of the vegetation present in the northern hemisphere at high latitudes (*i.e.*, Northern Europe, USA and Canada).

Sampling was carried out inside a large pine forest located at Storkow, 30 km south east of Berlin and not far from the Polish border. More than 30 samples were collected during daytime and at night during the second half of July.

The site located in Central Italy was representative of the "Mediterranean Macchia", a wooded

area mainly characterized by deciduous trees mixed with short plants growing near the sea shore. The presence of pine trees (*Pinus pinea*, *Pinus aleppensis*, *Douglasia*) is also frequent. This type of forest, common in Southern Europe from Spain to Greece, gives rise to an intense smell associated with a strong emission of VOC caused by the presence of aromatic and scented herbs and the occurrence of the high temperatures typical of temperate regions. Sampling was performed in a large, protected area located 25 km west of Rome. Also in this case, a large number of samples were collected during the winter season when reduced impact from the urban area occurred.

The VOC distribution existing in remote areas was investigated by collecting air samples at the Italian Station installed by CNR in Nepal. Established since 1990, it is located at an altitude of 5050 m at the foot of Mount Everest (8848 m) in the middle of the National Park of Sagarmatha. It can be reached from the Lobuche camp in a 6-day trek and only during the favourable season (end of the monsoon season). The station consists of a glass pyramid built on a small hill next to a gorge between two large glaciers. As power generation is partly ensured by solar cells covering the glass windows and partly by a small hydroelectric generator, no direct emission of man-made VOC could have affected the determinations. Air samples were taken during the 1991 expedition that started at the beginning of September and ended in the middle of October. This activity was part of a larger programme (Ev-K2-CNR) involving research in geological, environmental and biological fields and studies on advanced technologies.

RESULTS AND DISCUSSION

Figs. 1–3 show the total ion current (TIC, m/z 34–200) profiles obtained by submitting to GC-MS analysis air samples collected at the three different sites. The peak numbers refer to the compounds listed in Table I, where the retention time, retention index and amount detected are also reported for each component identified in the various samples.

The VOC are grouped into classes in order to distinguish better compounds released by anthropogenic sources (alkanes, arenes and partly alkenes) from those suspected to be associated with biogenic

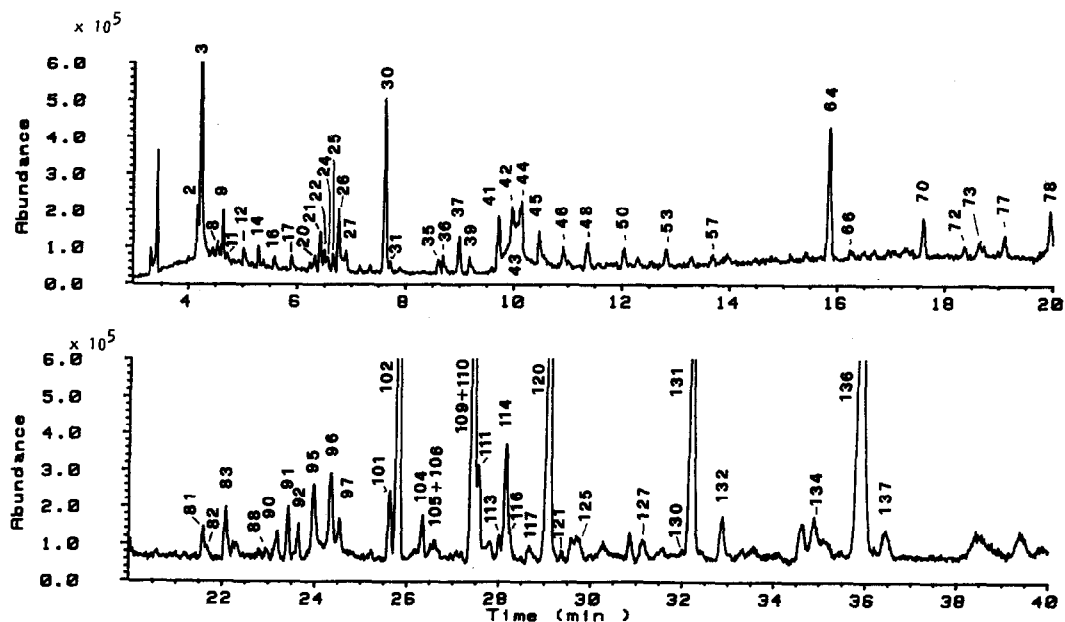


Fig. 1. GC-MS profile of a sample collected in a Northern European pine forest (Storkow, Germany). The trace is the reconstructed chromatogram obtained by using a mass window ranging from m/z 34 to 200. Peak numbers refer to the compounds listed in Table I.

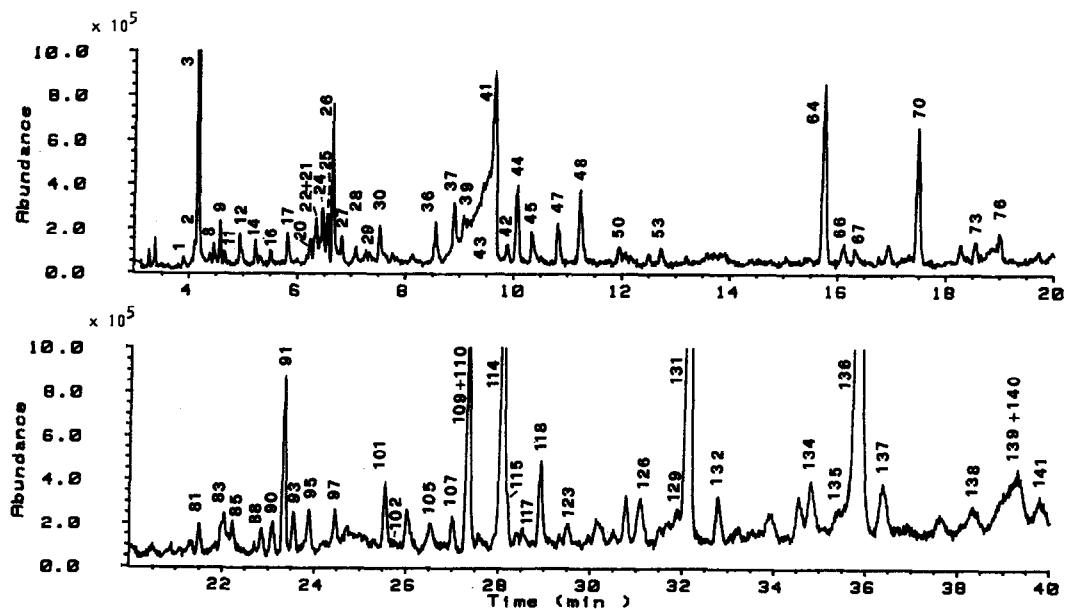


Fig. 2. GC-MS profile of a sample collected in a "Mediterranean Macchia" in Central Italy (Castel Porziano). The trace is the reconstructed chromatogram obtained by using a mass window ranging from m/z 34 to 200. Peak numbers refer the compounds listed in Table I.

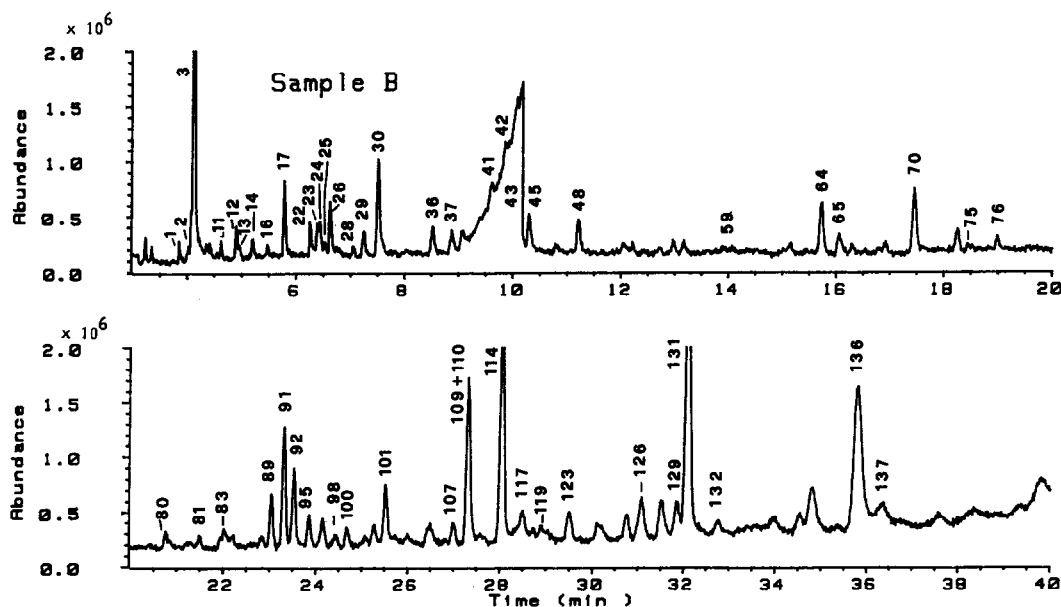


Fig. 3. GC-MS profile of a sample collected at the Italian Station in Nepal. The trace is the reconstructed chromatogram obtained by using a mass window ranging from m/z 34 to 200. Peak numbers refer to the compounds listed in Table I.

emission (some alcohols, aldehydes and ketones). Monoterpenes are listed separately as together with isoprene they are the most abundant organic components emitted by trees, being present in large amounts in the oil cells of leaves [8]. In Table I, the number of individual components identified in each class into which the VOC were grouped is reported and the net and relative contributions of the various classes to the whole organic fraction are also given.

The GC-MS profiles in Figs. 1–3 were accurately selected from more than 70 samples in order to highlight the complexity of the VOC distribution found in each of the areas investigated. As both natural and man-made emissions and photochemical reactions taking place in the atmosphere change rapidly from day- to night-time, and are strongly influenced by the meteorological conditions and seasonal variations, it is not surprising that the greatest complexity of the VOC distribution of the samples shown in Figs. 1–3 was realized at different times of the day. For the pine forest sample, the largest number of components was recorded at night when polar components remaining from the daytime hours were still present in the air together

with monoterpene compounds not removed by reaction with OH radicals and ozone. In the “Mediterranean Macchia”, where monoterpene emission was restricted to α -pinene released by some pine trees, the greatest complexity was rather realized in the middle of the day when high temperatures promoted substantial emissions of polar components from plants and/or photochemical reactions led to their formation. In this instance, low emission combined with fast removal by reaction with OH radicals can reasonably explain the low levels of α -pinene found in this sample. Although some day-to-day variations occurred in the VOC concentrations in forest samples collected in Northern and Southern Europe, they were mainly affecting the anthropogenic fraction and thus are attributed to the variable extent to which man-made emissions and their transport were influencing the sites. Daily profiles of natural components were, instead, fairly regular with a high abundance of monoterpene compounds at night and maximum levels of polar compounds around noon.

Within the above-mentioned limitations, the mass chromatograms shown in Figs. 1 and 2 can be

TABLE I
 VOC IDENTIFIED AND DETERMINED BY GC-MS IN THE PINE FOREST AREA OF STORKOW (GERMANY) THE "MEDITERRANEAN MAC-
 CHIA" OF CASTEL PORZIANO (ITALY) AND THE ITALIAN STATION LOCATED AT THE FOOT OF EVEREST (K2,CNR-PYRAMID, 5050 m) IN
 NEPAL

Peak No.	Compound	Retention index						Storkow (July 18, 1991, 3 a.m.)	Castel Feb. 27, 1992, noon)	K2-A (Sept. 28, 1991, 7 p.m.)	K2-B (Oct. 3, 1991, 7.30 a.m.)	K2-C1 (Oct. 4, 1991, 8 a.m.)	K2-C2 (Oct. 4, 1991, 6 p.m.)
		time (min)	VOC ($\mu\text{g}/\text{m}^3$)	Storkow (July 18, 1991, 3 a.m.)	Castel Feb. 27, 1992, noon)	K2-A (Sept. 28, 1991, 7 p.m.)	K2-B (Oct. 3, 1991, 7.30 a.m.)						
<i>Alkanes</i>													
9	<i>n</i> -C ₅	4.555	500.00	0.38	0.53	3.74							
15	Butane, 2,2-dimethyl-	5.292	524.77			0.09							
19	Butane, 2,3-dimethyl-	6.147	553.48			1.54							
21	Pentane, 2-methyl-	6.338	559.88	0.41	0.71	10.32						0.31	
27	Pentane, 3-methyl-	6.818	576.01	0.23	0.51	10.54						0.34	
30	<i>n</i> -C ₆	7.532	600.00	1.85	0.45	25.84			2.60	1.04		0.86	
46	Hexane, 2-methyl-	10.778	662.46	0.31									
50	Pentane, 2,2,4-trimethyl-	11.942	684.86	0.29	0.25	1.38							
53	<i>n</i> -C ₇	12.729	700.00	0.27	0.50	1.88							
76	<i>n</i> -C ₈	18.998	800.00		0.49	2.36			0.35				
97	<i>n</i> -C ₉	24.449	900.00	0.40	1.01	0.88			1.47				
119	<i>n</i> -C ₁₀	28.908	1000.00		2.71	0.82			0.68			0.22	
132	<i>n</i> -C ₁₁	32.768	1100.00	1.24	1.74	0.78			1.53				
137	<i>n</i> -C ₁₂	36.359	1200.00	0.89	2.78	0.79			3.22				
141	<i>n</i> -C ₁₃	39.795	1300.00		1.53	0.61							
Total amount				6.27	13.21	61.57			9.85	1.04		1.73	
% of total				6.9	7.7	23.0			5.7	0.8		7.7	
No. of compounds				10	12	14			6	1		4	
<i>Alkenes</i>													
6	1-Pentene	4.351							0.92				
8	1-Butene, 2-methyl-	4.441											
11	Isoprene	4.631	502.55	0.19	0.35	0.12							
28	1-Hexene	7.057	584.04	0.12	0.23	0.12			0.33	0.34		0.16	
38	2,4-Hexadiene	9.050	629.21		0.26	1.47			0.24	0.15		0.27	
51	1-Heptene	12.070	687.33							0.36		0.10	
55	1-Pentene, 2,2,4-trimethyl-	13.203	707.57										
58	1,4-Heptadiene, 3-methyl-	13.691	715.35							0.49			
72	1-Octene	18.269	788.38	0.26					2.70				
Total amount				0.57	0.84	9.6			0.57	1.34		0.53	
% of total				0.6	0.5	3.6			0.3	1.1		2.3	
No. of compounds				3	3	6			2	4		3	

<i>Arenes</i>												
41	Benzene	9.615	640.08	0.54	3.08	1.99	0.42	0.27	0.50			
64	Toluene	15.778	748.64	1.87	4.02	31.38	1.80	0.28	0.14			
81	Ethylbenzene	21.488	845.68	0.47	0.66	2.09	0.51					
83	(<i>m</i> + <i>p</i>)-Xylene	22.009	855.24	0.77	1.54	3.48	1.99					
88	Vinylbenzene	22.851	870.69	0.16	0.79	1.44						
90	<i>o</i> -Xylene	23.095	875.16	0.41	0.95	0.93						
99	Isopropylbenzene	24.797	907.81			0.07						
100	Benzene, 1-methoxy-4-methyl-	25.077	914.09				0.42	1.32				
103	<i>n</i> -Propylbenzene	26.146	938.06			0.33						
105	Benzene, 1-methyl-3-ethyl-	26.531	946.41	0.11	1.14	0.38						
106	Benzene, 1-methyl-4-ethyl-	26.536	946.81	0.14								
108	Benzene, 1,3,5-trimethyl-	26.859	954.05			0.30						
112	Benzene, 1-methyl-2-ethyl-	27.268	963.22			0.09						
113	Benzene, 1,2,4-trimethyl-	27.925	977.96	0.39								
121	<i>p</i> -Cymene	29.355	1011.58	0.06								
122	Indane	29.410	1013.00	0.07								
	Total amount			4.99	12.18	42.48	5.14	1.87	0.64			
	% of total			5.5	7.1	15.9	3.0	1.5	2.8			
	No. of compounds			11	7	11	5	3	2			
<i>Monoterpenes</i>												
102	α -Pinene	25.707	928.22	9.28	0.05	0.84						
104	Camphene	26.238	940.13	0.61		0.51						
111	β -Pinene	27.540	969.32	1.77								
116	Myrcene	28.240	985.02	0.33		0.09						
118	Terpene	28.583	992.71			0.63						
120	<i>A</i> ³ -Carene	29.071	1004.22	9.08		0.20						
124	β -Phellandrene	29.591	1017.69	0.41								
125	Limonene	29.661	1019.51	0.34		1.16						
130	α -Terpinolene	32.004	1080.20	0.51								
133	Camphor	33.408	1117.81			2.66						
	Total amount			22.33	0.05	6.09	0	0	0			
	% of total			24.6	0.0	2.3	0.0	0.0	0.0			
	No. of compounds			8	1	7	0	0	0			
<i>Alkyl halides and CFCs</i>												
4	CFC 11 ^b	4.224				0.06						
14	CFC 113 ^b	5.206	521.87	0.18	0.34	0.04	0.47	0.24	0.25			
32	Chloroform ^b	7.577	600.86	0.12		1.40			0.22			
37	1,1,1-Trichloroethane	8.890	626.13	0.49	0.83	1.48	0.52	0.37	0.40			
42	Carbon tetrachloride	9.873	645.05	0.29	0.31	0.29	0.03	0.72	0.67			
49	Trichloroethene	11.731	680.80			0.36						
73	Tetrachloroethene	18.549	792.84	0.30	0.45	1.60						
	Total amount			1.38	1.93	5.23	1.02	1.33	1.54			
	% of total			1.5	1.1	2.0	0.6	1.1	6.8			
	No. of compounds			5	4	7	3	3	4			

(Continued on p. 62)

TABLE I (continued)

Peak No.	Compound	Retention Retention VOC ($\mu\text{g}/\text{m}^3$)							
		time (min)	index	Storkow (July 18, 1991, 3 a.m.)	Castel (Feb. 27, 1992, noon)	K2-A (Sept. 28, 1991, 7 p.m.)	K2-B (Oct. 3, 1991, 7.30 a.m.)	K2-C1 (Oct. 4, 1991, 8 a.m.)	K2-C2 (Oct. 4, 1991, 6 p.m.)
<i>Sulphur compounds</i>									
13	Carbon disulphide ^b	4.957	513.50	0	0	1.03	0.28	0	0
54	Methane isothiocyanate ^b	12.984	704.08	0.0	0.0	1.10	0.28	0.0	0.0
Total amount									
% of total									
No. of compounds									
<i>Alcohols</i>									
1	Ethanol ^b	3.857		0.19	0.19	0.46	0.31	0.12	0.06
7	2-Propanol ^b	4.408		0.54	0.54	1.42	0.60	0.71	0.33
12	2-Propanol, 2-methyl-	4.914	512.06	0.22	0.22	2.32	0.79	0.24	0.38
18	1-Propanol	5.913	545.62			0.86		0.84	
31	3-Buten-2-ol, 2-methyl-	7.533	600.00					0.25	
36	1-Propanol, 2-methyl-	8.537	619.33	0.23	0.23	21.13	0.90	0.11	
45	1-Butanol	10.439	655.95	0.52	0.67	0.35		0.36	
63	1-Butanol, 3-methyl-	15.712	747.59			0.92		0.22	
67	1-Pentanol	16.355	757.85	0.44	0.68	0.45		0.36	
85	1-Hexanol	22.138	857.61			0.10	1.35	1.59	
87	2-Propanol, 1,3-dichloro-	22.418	862.75	0.40	0.40				
95	Ethanol, 2-butoxy-	23.800	888.09			0.28		0.68	
96	2,4-Pentanediol, 2-methyl-	24.344	898.08	1.25	1.34			1.06	
107	1-Heptanol	26.996	957.11	0.87	0.87			2.07	
123	1-Hexanol, 2-ethyl-	29.494	1015.18	0.44	0.90			1.92	
126	1-Octanol	31.079	1056.24	2.28	2.28				
134	1-Nonanol	34.802	1156.62	0.77	2.41				
138	1-Decanol	38.327	1257.28	2.12	2.12				
Total amount									
% of total									
No. of compounds									
<i>Aldehydes</i>									
2	2-Propenal ^b	4.044		0.27	0.27	0.08	0.25	0.13	0.15
16	2-Propanal, 2-methyl-	5.479	531.03	0.16	0.29	0.74	0.29	0.13	0.10
17	2-Butenal	5.791	541.52	0.19	0.49	3.32	1.41	2.19	0.24
24	Butanal	6.444	563.45	0.17	0.84	4.29	0.18	1.52	0.12
39	Butanal, 3-methyl-	9.073	629.65	0.24	0.13	2.16			
48	Pentanal	11.228	671.12	0.41	1.52	7.96		0.93	
61	Pentanal, 2-methyl-	14.299	725.05			0.19			

TABLE I (continued)

Peak Compound No.	Retention time (min)	Retention index	Retention VOC ($\mu\text{g}/\text{m}^3$)					
			Storkow (July 18, 1991, 3 a.m.)	Castel (Feb. 27, 1992, noon)	K2-A (Sept. 28, 1991, 7 p.m.)	K2-B (Oct. 3, 1991, 7.30 a.m.)	K2-C1 (Oct. 4, 1991, 8 a.m.)	K2-C2 (Oct. 4, 1991, 6 p.m.)
<i>Acids</i>								
43	10.011	(648) ^a	2.90	12.12	8.55	25.46	20.24	0.40
59	13.731	(716)	0.12	0.59	0.70	0.41	0.26	
75	18.819	(797)	0.09	1.14	0.99	0.09	0.23	
82	21.766	(851)	0.20	0.85	0.14	0.01	0.20	
94	23.792	(888)	0.01	1.09	0.24	0.27	0.22	
115	28.076	(981)	0.17	2.11	0.31	0.76	0.73	
129	31.903	(1078)	0.12	1.66	0.15	0.79	0.77	
135	35.475	(1175)	0.39	2.65	0.39	2.29	1.14	
139	39.082	(1279)	0.66	2.20	0.48	3.72	0.86	
Total amount			4.66	24.41	11.95	33.8	24.65	0.4
% of total			5.1	14.2	4.5	19.6	20.1	1.8
No. of compounds			9	9	9	9	9	1
<i>Esters</i>								
10	4.619	502.17			0.30			
23	6.400	561.97				0.16		
34	7.728	603.77			0.51			
56	13.389	710.54			0.67			
68	16.584	761.50			0.82			
77	19.101	801.90	0.40					
Total amount			0.4	0	2.3	0.16	0	0
% of total			0.4	0.0	0.9	0.1	0.0	0.0
No. of compounds			1	0	4	1	0	0
<i>Cycloalkanes</i>								
35	8.533	619.26	0.19					0.49
44	10.061	648.66	0.36	1.44	7.11	7.99	0.10	
57	13.591	713.76	0.18		0.79			
71	17.873	782.06						0.27
79	20.451	826.66			0.46			
127	31.145	1057.95	0.74					
Total amount			1.47	1.44	16.35	0	0	0.86
% of total			1.6	0.8	6.1	0.0	0.0	3.8
No. of compounds			4	1	4	0	0	3

<i>Phenols</i>									
110	Phenol								
	Total amount	27.323	964.46	0.67	0.33	0.35			
	% of total		0.67	0.33	0.35	0	0	0	0
	No. of compounds		0.7	0.2	0.1	0	0	0	0
			1	1	1				
<i>Alkylsilanols</i>									
25	Trimethylsilanol	6.537	566.56	0.17	0.80	0.13	0.05		
	Total amount		0.17	0.8	0.55	0.13	0.05	0	0
	% of total		0.2	0.5	0.2	0.1	0.0	0.0	0.0
	No. of compounds		1	1	1	1	1	0	0
	Total VOC amount		90.72	171.87	267.29	172.10	122.56	22.57	
	Total VOC identified		86.57	159.51	254.07	145.15	98.56	11.98	
	Total VOC not identified		4.15	12.36	13.22	26.95	24.00	10.59	
	Total number of VOC identified		81	74	101	59	58	33	

^a Retention indices are reported in parentheses to indicate the uncertainty associated with peak overloading.
^b Compounds characterized by a break-through volume lower than 1 l. Only qualitative determination was possible. Values in the table refer to the portion retained on the trap.

taken as reasonably representative of the areas investigated. In particular, the monoterpene and carbonyl fractions observed in the German forest seem to reflect well the composition that can be found in almost any pine forest, being similar to that measured in the wooden area of Monti Cimini Park (Central Italy), also characterized by a high density of pine trees [5].

It was difficult to define a “typical” situation for the samples collected in Nepal. At an altitude of 5050 m the vegetation is restricted to musks and lichens, the fauna is scarce and anthropogenic emissions are almost non-existent, hence the composition and levels of VOC are mainly determined by transport phenomena and are thus strongly influenced by the meteorological conditions occurring during sampling. In the 1991 expedition, some days were dominated by strong ascending currents carrying VOC emitted by natural and man-made sources located far down in the valley up to the station (southern winds), whereas other days were characterized by the descent of cold air masses moving from the mountains downward to the valley (northern winds). In the latter instance, a substantial removal of VOC away from the sampling site was taking place. Owing to the dramatic difference in the VOC composition and concentration associated with these two circulation patterns, we have reported in Fig. 3 the mass chromatogram of a sample collected when only light winds (< 1–2 m/s) were blowing (sample B, 7.30 a.m.). Under these conditions, the concentration of VOC in air was mainly determined by local emissions and the organic species remaining from the previous days.

To give an idea of the levels associated with the different air mass circulation occurring at the Himalaya station, we have also reported in Table I the VOC concentrations measured when prevailing winds were blowing from the southern (sample K2-A, 7 p.m.) and northern sectors (sample K2-C2, 6 p.m.).

Although the number of individual components found in forest and remote sites was usually lower than that observed in urban areas [5,6], all samples were characterized by a higher complexity than that existing in heavily impacted airsheds because of the numerous classes of polar organic compounds present in the atmosphere. In addition to alkanes, alkenes, arenes, aldehydes, ketones, isoprene and

some monoterpene components also detected at different levels in many urban and suburban samples, a complex array of free acids, esters, alcohols and furans was found. Although some of these polar components were sometimes found in urban and suburban airsheds [5,6], their abundance was not such that specific detection was required.

The huge amounts of acids present in the chromatograms in Figs. 2 and 3 giving rise to a large, overloaded peak in the first part of the chromatogram (peak No. 43), coupled with the constant and detectable presence of alcohols from ethanol to hexanol and numerous aliphatic esters in the samples collected in the “Mediterranean Macchia” and the Himalaya region, suggested that selected-ion detection was necessary to elucidate better the complex array of polar and non-polar components present in forest and remote areas. This approach was found to be particularly useful for investigating the presence of organic acids, aldehydes, alcohols and terpenes.

An example of the information provided by mass spectrometry with selected-ion detection is reported in Fig. 4, where the total ion current profile of a sample collected at the Himalaya station (K2-A, 7 p.m.) is displayed together with the mass chromatograms used for the identification of some specific classes of components listed in Table I. The ion at m/z 31, corresponding to the oxonium ion ($[\text{CH}_2\text{OH}]^+$) formed by the cleavage of the carbon-carbon bond next to the α -carbon atom, was specific for the identification of many primary and secondary alcohols whereas the ion at m/z 44 ($[\text{CHCHOH}]^+$), coming from the rearrangement of the γ -hydrogen available for transfer to the carbon oxygen followed by the cleavage of the carbon bond in the β -position (McLafferty rearrangement), allowed the selective determination of all aldehydes with carbon numbers > 3. The ion at m/z 60 corresponding to the molecular ion of acetic acid and to a fragment coming from the McLafferty rearrangement ($[\text{CH}_2\text{C}(\text{OH})_2]^+$) typical of aliphatic acids with carbon numbers > 4 was used for the selective detection of many acidic components. Recording of the molecular ion (m/z 74 not displayed in Fig. 4) was, instead, necessary for the identification and evaluation of propionic acid. The HRGC-MS profile of the cyclic ion at m/z 93, derived from the sequential loss of aliphatic chains from the terpen-

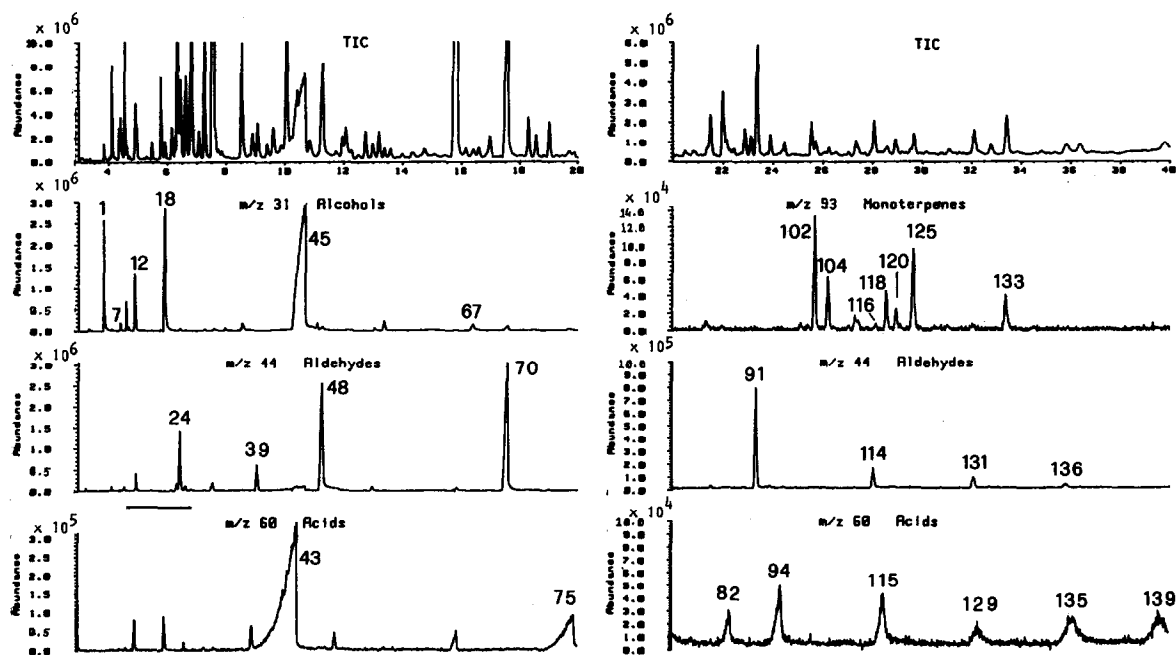


Fig. 4. Total ion current (m/z 34–200) and selected-ion detection profiles used for the identification of alcohols, aldehydes, acids and monoterpene compounds present in a sample collected at the Italian station in Nepal. The profile refers to sample K2-A in Table I. For peak identification, see Table I.

oid structure, allowed the specific detection of monoterpene compounds present at trace levels in the air samples.

Selected-ion detection was also extensively applied to the determination of other co-eluted components of natural and man-made origin (*i.e.*, alkylbenzene isomers or 6-methyl-5-hepten-2-one and phenol). Profiles relative to these organic species are not shown in Fig. 4 as the approach followed was the same as that used for investigating urban and suburban airsheds and examples of selected-ion mass chromatograms already published [5].

The analysis of samples characterized by substantial amounts of polar components was extremely useful from the methodological viewpoint as it showed the capability of carbon traps to retain and release in a quantitative way very polar organic compounds (particularly alcohols, aldehydes, ketones, esters and free acids) with a wider range of carbon numbers than reported previously (C_2 – C_3 , depending on the functional group). It also suggested that HRGC–MS determination of aliphatic acids might be competitive with methods based on

denuder collection followed by liquid ion chromatography [9], as it makes it possible to detect all homologues members from acetic to nonanoic acid and to distinguish between isomeric components (see the peaks 82 and 94 in Fig. 4). Of course, a different column from that used for generating the mass chromatograms in Fig. 4 would be necessary for better identification and quantification purposes.

A detailed knowledge of the VOC distribution and composition present in forest and remote areas was also useful for assessing the possible origin of individual components. The high abundance of semi-volatile aldehydes, ketones (particularly 6-methyl-5-hepten-2-one, known to be emitted by flowers and fruits), esters, alcohols and acids with respect to isoprene and monoterpene components of natural origin, alkanes, alkenes, arenes, chlorofluorocarbons and trimethylsilanol of anthropogenic origin and benzaldehyde of photochemical origin seem to be highly indicative that the largest proportion of polar components comes from natural processes. Whereas carbonyl compounds, esters

and alcohols are common constituents of the essential oils and fragrances extracted from plants and flowers [10] and some of them have been already detected in natural emission [4,11–13] and forest environments [5,14], organic acids might arise from either photochemical oxidation or microbial degradation of organic compounds [15].

The prevalence of aliphatic acids with an even number of carbon atoms found in many of the samples investigated and the low concentrations of ozone present in the European forest during the monitoring campaign seem to be highly suggestive of microbial origin. Also, the presence of carbon disulphide in one of the samples collected at the Himalaya site is not surprising as it is emitted together with carbonyl sulphide from different soils and plants [16]. It is more difficult to assign a definite source to 2-methylfuran, although the lack of this component in the urban and suburban airsheds [5,6] might be highly indicative of its biogenic origin.

Although the classes of polar VOC and levels measured in the wooded areas of Northern and Southern Europe were basically the same as those found at the Himalaya station, different distributions of the individual components present in each class were observed. This difference is particularly evident for aldehydes, as nonanal and decanal were the most abundant components recorded in the European forests whereas an almost Gaussian distribution centred on hexanal was found at the Himalaya station. This difference might be attributed either to the type of biogenic emission prevailing in the various sites (*i.e.* trees *vs.* short vegetation) or condensation processes that selectively removed high-boiling components from the air masses carrying VOC to the Himalaya station. The first hypothesis is supported by some laboratory experiments showing that aldehydes and ketones with carbon numbers ranging from 4 to 8 can be emitted by short vegetation growing under the canopy of Northern European forests [11] or plants growing in the California basin [4]. However, these results are somehow in contrast with the aerometric determinations carried out in forest areas [5,6,14] showing that, similarly to the results in Figs. 1 and 2, nonanal and decanal are the most abundant carbonyl components present in air and they account for a large proportion of the whole organic fraction.

In our opinion, the predominance of hexanal at the samples collected in the Himalaya station can be better explained by the progressive depletion of high-boiling components taking place into the air masses during their travel towards the site. It is likely that the lowering of temperature associated with ascent of the air masses from the valley to the mountains, where daytime temperatures are close or below to 0°C, caused an efficient conversion of high boiling VOC into particles, thus promoting their removal from the airshed by wet and dry deposition processes. Evidence of transport of VOC into the station is provided by the data recorded when southern winds were blowing over the monitoring site. If we consider the concentrations measured on September 28th at the Himalaya station (sample K2-A in Table I, the chromatogram of which is reported in Fig. 4), we can see that levels of man-made emitted VOC (alkanes, alkenes, arenes, trimethylsilanol and some chlorinated hydrocarbons) much higher than those existing in the European forests were reached during the afternoon. This, combined with the occurrence of substantial amounts of monoterpene hydrocarbons known to be emitted by pine trees not growing at such high altitudes, can be taken as highly indicative of the fact that VOC present in the samples from the Himalaya station were actually emitted far away from the site where natural emission from forests was mixed with organic emissions released by anthropogenic processes (mainly combustion of biomass fuels for house heating and charbroiling or meat-cooking operations).

The dramatic difference with the VOC composition measured when Northern winds were removing VOC from the station is clear if we compare the results for the sample collected on September 29th with that taken on October 4th at 6 p.m. (sample K2-C2 in Table I). In the latter instance a total VOC content one order of magnitude lower than that measured when polluted airsheds reached the site was measured. No presence of monoterpene hydrocarbons was detected and negligible amounts of arenes (benzene and toluene) were present in the sample. The major components were oxygenated compounds of natural origin whereas much lower levels of halogenated hydrocarbons of man-made origin were detected. Trimethylsilanol was below the detection limit. A comparison with the levels

obtained on October 4th in the morning (sample K2-C1 in Table I) when low circulation occurred seems to suggest that the prevalence of northern winds in the afternoon hours caused a substantial removal of VOC from the sampling site by transporting them back to the valley. Although the observation that pollution levels recorded in the remote Himalaya station can be much higher than those measured in forest areas of heavy industrialized countries of Europe might appear surprising, it is perfectly in line with the observations of Davidson *et al.* [17], who found that the excessive per capita use of biomass fuels in Nepalese houses gives rise to quite high levels of pollution in the Himalaya region. Owing to the high indoor concentrations of organic compounds existing in Nepal, levels as high as 5 and 8 $\mu\text{g}/\text{m}^3$ were measured in outdoor samples collected outside one house in Sundarjal. The indications given by the sample collected on September 28th, 1991, seem to suggest, however, that anthropogenic emission might be even higher than that measured by Davidson *et al.*, giving rise to toluene concentrations as high as 30 $\mu\text{g}/\text{m}^3$. It is also possible that further injection of organic pollutants into polluted air masses coming from the Indian peninsula might be responsible for the levels reached at the Himalaya station when southern winds were dominating the air mass circulation. The observation that levels of benzene and toluene measured on the following days were close to those expected to be present in unpolluted atmospheres (ca. 0.5 and 0.6 $\mu\text{g}/\text{m}^3$, respectively) highlights the importance of transport phenomena in affecting the air quality of remote Himalaya regions. Whatever the cause (local emissions, long-range transport or a combination of both) leading to high levels of organic pollutants is, it must be regarded a serious source of concern for the preservation of the Everest environment owing to the possible formation of photochemical pollution and enhanced acid deposition arising from the exposure of such pollutants to the intense UV radiation existing at high altitudes.

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REFERENCES

- 1 B. J. Finlayson-Pitts and J. N. Pitts, Jr., *Atmospheric Chemistry: Fundamentals and Experimental Techniques* Wiley, New York, 1984.
- 2 R. G. Derwent, *Atmos. Environ.*, 24A, (1990) 2615-2624.
- 3 R. Atkinson, *Atmos. Environ.*, 24A, (1990) 1-41.
- 4 A. M. Winer, J. Arey, R. Atkinson, R. S. M. Aschmann, W. D. Long, C. L. Morrison and D. M. Olszyk, *Atmos. Environ.*, 26A, (1992) 2647-2659.
- 5 P. Ciccioli, A. Cecinato, E. Brancaleoni, M. Frattoni and A. Liberti, *J. High Resolut. Chromatogr.*, 15, (1992) 75-84.
- 6 P. Ciccioli, A. Cecinato, E. Brancaleoni and M. Frattoni, *Fresenius Environ. Bull.*, 1, (1992) 73-78.
- 7 *The Sadtler Standard Gas Chromatography Retention Index Library*, Sadtler Research Laboratories, Division of Bio-Rad Laboratories, Philadelphia, 1985.
- 8 Y. Yokouchi and Y. Ambe, *Research Report No. 76. R-76-85*, National Institute for Environmental Studies, Tsukuba, 1985.
- 9 H. Puxbaum, C. Rosemberg, M. Gregori, Lanzerstorfer, E. Ober and W. Winiwarter, *Atmos. Environ.*, 22 (1988) 2841-2850.
- 10 R. G. Buttery, in R. Teranishi, R. A. Flath and H. Sugisawa (Editors), *Flavor Research Recent Advances*, Marcel Dekker, New York, 1981, pp. 175-216.
- 11 V. A. Isidorov, I. G. Zenkevich and B. V. Joffe, *Atmos. Environ.*, 19, (1985) 1-8.
- 12 T. E. Graedel, D. T. Hawkins and L. D. Claxton, *Atmospheric Chemical Compounds—Sources, Occurrence and Bioassay*, Academic Press, Orlando, FL, 1972.
- 13 A. Latrasse, E. Sémon, and J. L. Le Quéré, *J. High Resolut. Chromatogr.*, 14, (1991) 549-553, (1991).
- 14 Y. Yokouchi, H. Mukai, K. Nakajima and Y. Ambe, *Atmos. Environ.*, 24A, (1990) 439-442.
- 15 B. R. T. Simoneit and M. A. Mazurek, *Aerosol Sci. Technol.*, 10, (1989) 267-291.
- 16 R. Staubes, H. W. Georgii and G. Ockelmann, *Tellus*, 41B, (1989) 305-313.
- 17 C. I. Davidson, L. Shaw-Feng, J. F. Osborn, M. R. Pandey, R. A. Rasmussen and M. A. K. Khalil, *Environ. Sci. Technol.*, 20, (1986) 561-567.