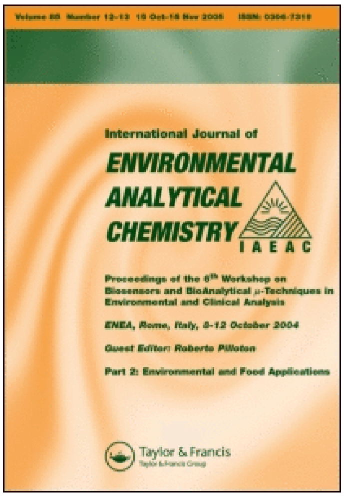

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Occurrence of Oxygenated Volatile Organic Compounds (VOC) in Antarctica

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OCCURRENCE OF OXYGENATED VOLATILE ORGANIC COMPOUNDS (VOC) IN ANTARCTICA

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Polar and non-polar VOC present in six different sites located near Terra Nova Bay in Antarctica were determined by HRGC-MS. 76 different components were positively identified. Among them, particularly important are oxygenated components (free acids, aldehydes, ketones, alcohols, esters, ethers and furanes) as they account for the largest portion of the organic fraction. Biogenic emission seem to be the major source for many of them. This would explain their ubiquitous occurrence in the troposphere.

KEY WORDS: Oxygenated VOC, Antarctica, biogenic emission, ubiquitous air components.

INTRODUCTION

The ubiquitous occurrence of semi-volatile carbonyl compounds in the atmosphere has been recently proposed[1] on the basis of field investigations carried out in urban[1,2], rural[1], forest[1,2] and remote areas[2,3]. Levels in air have been attributed most to biogenic emission from vegetation[1]. Results of research carried out in the Arctic region (Spitzbergen Islands)[4] and Nepal (Himalaya)[4,5] have also shown that, in addition to carbonyl compounds, many other classes of oxygenated VOC are present in remote environments. More than 33 different components including free acids, alcohols, metoxy-alcohols, esters, ethers and furans were positively identified[4–6] in these samples. Since many of them have been also found in plant[7–10] and ocean emissions[11], release from biogenic sources provides a reasonable explanation for their occurrence in remote areas. Due the high levels reached by oxygenated VOC in air, it is possible that VOC emissions from biogenic sources are much larger than what is presently believed and it can strongly contribute to tropospheric ozone formation[6]. Since Antarctica does not possess significant man-made sources of its own and its long distance from polluted areas largely prevent transport of compounds characterized by short-lifetime in the atmosphere, it represents the ideal site for investigating whether biogenic emissions are truly responsible for the occurrence of oxygenated VOC in the troposphere. In this paper, the

VOC composition found in 6 different sites located near the Italian Base installed at Terra Nova Bay will be reported. Data on oxygenated VOC will be discussed and compared with the results obtained in other remote sites.

EXPERIMENTAL

Site description

All samples were collected in the Ross Sea region (Northern Victoria Land) in an area ranging between 74 to 75°S and 162 to 165°E. Six sites were chosen and they are listed in Table 1. Distance and direction from the Italian Base and elevation from the sea level were the main criteria used for their selection. A map showing their location is reported in Figure 1. In Table 1 the exact position of sites, data of sampling and atmospheric conditions in which collection occurred are reported.

Sampling and analysis of VOC

Air samples were collected in stainless steel canisters (BRC, Rasmussen, Hillboro, OR, USA) whose internal surfaces were electro-polished to provide a passivated chromium-nickel oxide layer chemically inert toward polar VOC. Air was transferred into the canisters by using an ultra-clean pump (model FC1121, BRC, Rasmussen, Hillboro, OR, USA) whose contact surfaces were also made in stainless steel. The various parts of the sampling apparatus were assembled according to the scheme reported in Figure 2a. Nupro valves (Nupro Co., Willoughby, OH, USA) were used for connecting canisters with the pump and outlet air and for preventing their contamination from outdoor and indoor sources before and after sampling. Canisters having volumes of 0.85 and 16 L were used in this campaign. They were washed three times with external air before samples were collected at 3 atm. After sampling, canisters were tightly closed, stored in special boxes at room temperature and sent to the laboratory for the analysis.

Aliquots of the total sample (1–2 L) were enriched on traps filled with solid sorbents to meet the sensitivity of the analytical system. They were connected to the canisters according to the scheme reported in Figure 2b. A needle valve was used to keep the flow

Table 1 Sampling sites of VOC at Terra Nova Bay and experimental conditions in which collection was performed.

No.	*Station*	*Lat.* *°S*	*Long.* *°E*	*Altitude* *m*	*Day*	*Volume* *L*	*T* *°C*	*W.S.* *m/s*
1	Tourmaline Pl.	74°08'	163°26'	1650	11.21.93	16	−10	< 1
2	Kay Island	74°04'	165°19'	s.l.	11.22.93	0.85	−10	< 1
3	Edmonson Point	74°20'	165°07'	s.l.	10.27.93	0.85	−6	< 1
4	Mount Melbourne	74°20'	163°20'	1130	11.04.93	0.85	−20	< 1
5	Starr Nunatak	75°54'	162°33'	96	11.18.93	0.85	0	< 1
6	Cape Russel	74°55'	163°50'	70	11.25.93	0.85	0	> 8 SW

All sites were located 30 to 150 km away from the Italian Station at Terra Nova Bay to reduce the influence of man-made sources.

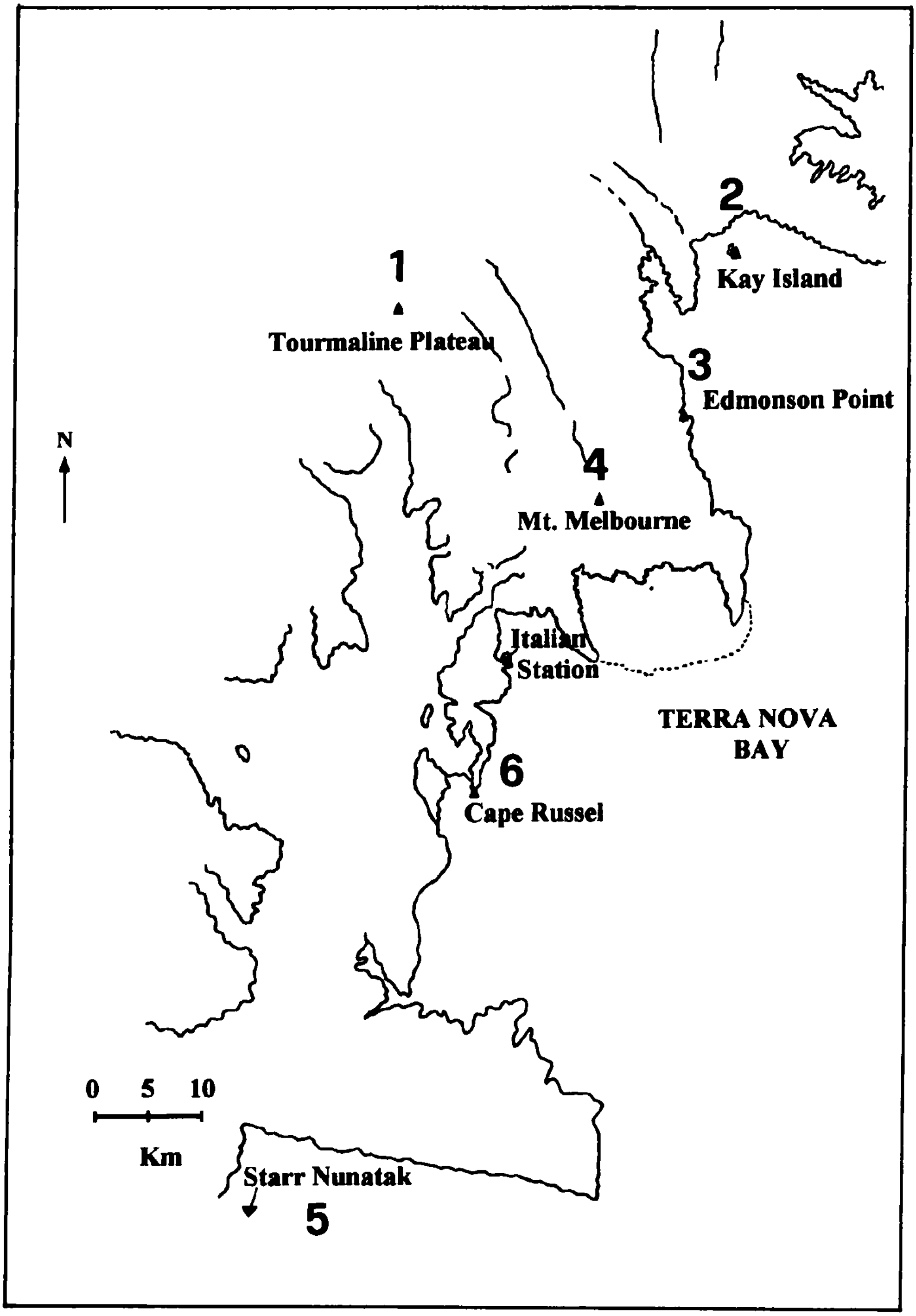

Figure 1 Map showing the location of the VOC sampling sites at Terra Nova Bay.

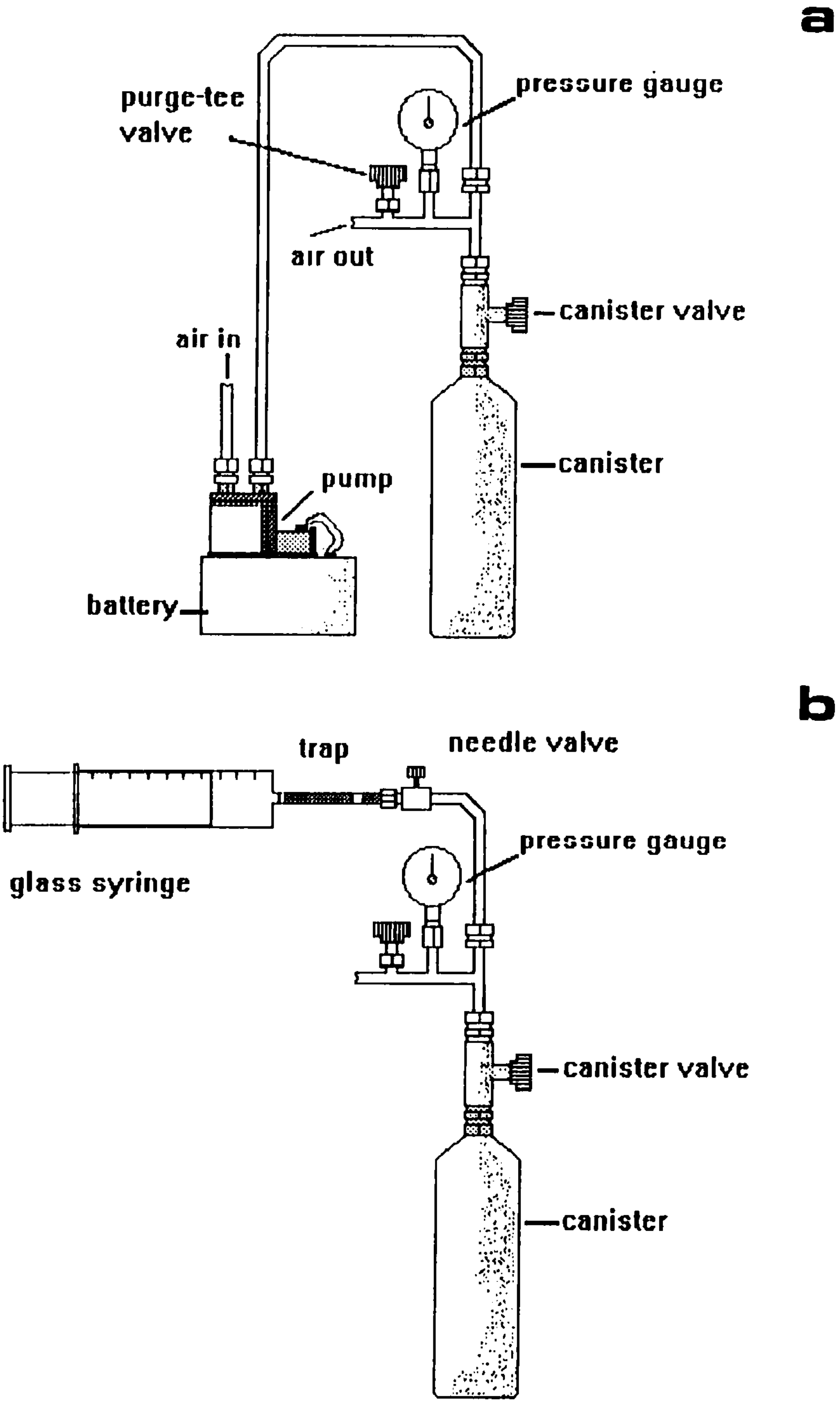

Figure 2 Diagram showing the collection of VOC on canisters (a) and procedure used to transfer them into adsorption traps (b).

rate constant through the trap at a rate of ca. 100 mL/min. The volume sampled was measured with a 250 mL glass syringe connected to the trap outlet. Cartridges were made by glass tubes filled with Carbotrap C (0.034 g) and Carbotrap (0.17 g) supplied by Supelco (Supelco Co, Bellefonte PA, USA). Particles ranging between 20 and 40 mesh were used.

VOC were injected into the GC unit by means of a Chrompack (Chrompack, Middleburg, The Netherlands) purge and trap injector adapted for air analysis. The desorption unit was connected to a Hewlett Packard gas chromatograph (Hewlett Packard, Palo Alto, CA, USA) model 5890 using a 5970 quadrupole mass spectrometer as detection system. GC separations were carried out on a 60 m, 0.32 mm i.d. capillary column internally coated with a 0.25 um film of DB-1. The column was supplied by J&W Scientific (Folsom, CA, USA). A full description of the conditions used for the desorption and analysis of VOC can be found in the literature cited[12]. Reconstructed mass chromatography combined with a detailed knowledge of the elution sequence on DB-1 columns was used for peak identification[12,13]. With this technique more than 300 components with a number of carbon atoms from 4 to 11 present in air samples can be easily identified and quantified in a single GC-MS run[13].

RESULTS AND DISCUSSION

Figure 3 shows the Total Ion Current (TIC) profile obtained by submitting to GC-MS analysis the sample where the highest levels of VOC were measured (Tourmaline Plateau). By combining the information collected in the various sites investigated, a total number of 76 different VOC were unambiguously identified. They are listed in Table 2 together with the concentrations measured in each site. Since enrichment of VOC was carried out at room temperature, reliable values of the mixing ratios were obtained only

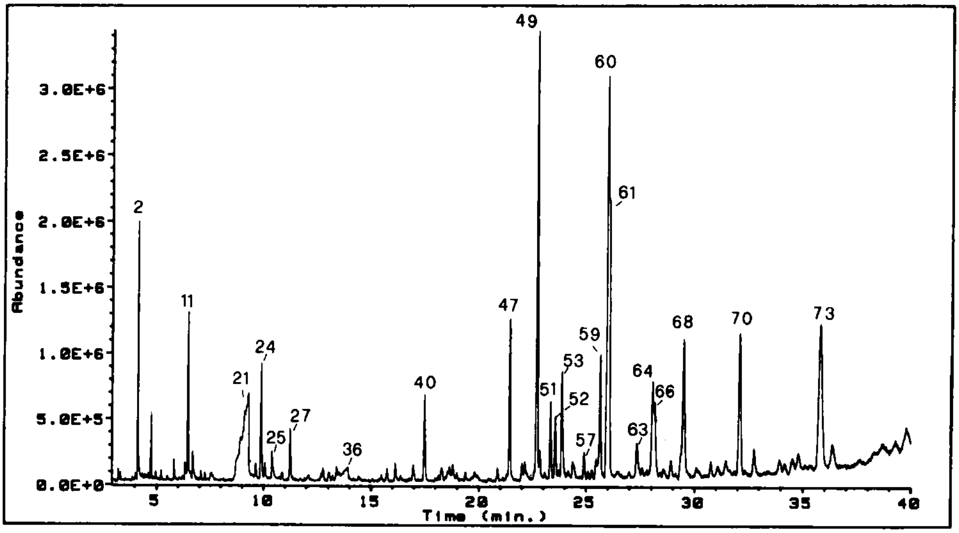

Figure 3 HRGC-MS profile of VOC present at Tourmaline Plateau. For peak identification see Table 2.

Table 2 Concentrations ($\mu g/m^3$) of VOC measured at 6 different sites located near Terra Nova Bay in Antarctica. (For site identification see Figure 1).

N.	*Compound*	*Ret. time*	*Site 1*	*Site 2*	*Site 3*	*Site 4*	*Site 5*	*Site 6*
1	2-Propenal	4.04	0.35	0.45	0.32	0.60	0.91	0.63
2	Acetone	4.12	16.08	9.62	6.86	8.93	26.82	40.26
3	n-C5	4.55	0.11	–	0.12	0.18	0.57	0.14
4	Isoprene	4.63	0.21	0.21	–	0.36	–	0.48
5	2-Propanol,2-methyl	4.91	0.49	1.52	0.30	0.73	–	–
6	CFC 113	5.21	0.21	0.25	0.13	0.19	0.09	0.13
7	Propanal,2-methyl	5.48	0.27	–	–	0.26	0.38	–
8	2-Propenal,2-methyl	5.79	0.92	0.83	0.61	0.68	1.64	–
9	Furan,2,5-dihydro	6.25	0.25	–	–	–	–	–
10	3-Buten,2-one	6.36	1.28	0.52	0.40	0.84	2.43	2.41
11	Butanal	6.44	9.06	0.72	–	0.90	1.92	1.08
12	2-Butanone	6.63	2.48	1.40	0.85	2.16	4.81	0.98
13	1-Hexene	7.06	0.27	–	–	0.26	0.35	–
14	Furan,2-methyl	7.25	0.29	–	0.20	0.19	0.26	0.47
15	n-C6	7.53	0.14	–	0.13	0.31	0.79	0.21
16	cis-3-Hexene	7.64	0.03	–	–	–	–	–
17	cis-2-Hexene	7.73	0.04	–	–	–	–	–
18	1-Propanol,2-methyl	8.54	–	–	–	1.88	–	–
19	1,1,1-Trichloroethane	8.89	0.51	0.42	0.42	0.51	0.49	0.53
20	2-Butenal	9.20	0.33	0.50	1.12	–	1.16	0.44
21	Acetic acid	(9.5)	27.87	4.02	–	–	8.95	–
22	Benzene	9.62	0.24	–	0.20	0.26	1.27	–
23	CC14	9.87	0.53	0.50	0.54	0.66	0.55	0.59
24	2-Butenal,2-methyl	9.90	4.42	–	–	–	–	–
25	1-Butanol	10.44	1.81	–	–	1.47	1.74	–
26	2-Pentanone	10.82	0.57	0.53	–	0.51	1.20	0.38
27	Pentanal	11.23	2.28	0.69	0.57	0.82	1.89	1.09
28	Ethene, trichloro	11.73	–	–	–	1.04	–	–
29	3-Heptene	12.33	0.03	–	–	–	–	–
30	iso-Heptadiene	12.65	0.21	–	–	–	–	–
31	n-C7	12.73	0.28	–	0.12	0.27	0.56	0.15
32	2-Heptene	13.10	0.07	–	–	–	–	–
33	Formic acid, butyl ester	13.39	0.71	–	–	–	–	–
34	iso-Heptene	13.50	0.07	–	–	–	–	–
35	trans-2-Pentenal	14.05	0.25	–	–	–	–	–
36	Propanoic acid	(14.5)	4.87	–	–	–	–	–
37	Toluene	15.78	0.22	–	–	–	0.58	–
38	cis-2-Pentenal	16.25	0.94	0.52	0.39	0.84	1.29	1.80
39	2-Hexanone	16.98	1.56	0.54	–	1.03	1.15	0.79
40	Hexanal	17.51	3.88	1.61	1.63	1.48	3.81	3.41
41	iso-Octadiene	18.20	0.54	–	–	–	–	–
42	iso-Octene	18.30	0.61	0.32	0.32	0.83	0.76	0.98
43	Butanoic acid	(18.5)	0.84	–	–	0.14	0.60	–
44	iso-Octene	18.80	0.04	–	–	–	–	–
45	n-C8	19.00	0.23	0.52	0.08	0.77	0.69	0.18
46	iso-Octene	19.40	0.24	–	–	–	–	–
47	iso-Heptenal	21.40	5.23	–	–	–	–	–
48	4-Heptanone	22.00	1.31	0.42	–	–	–	–
49	3-Heptanone	22.74	28.18	0.64	–	0.68	–	–
50	2-Heptanone	22.88	1.70	0.50	0.21	0.21	–	–
51	Heptanal	23.33	2.34	0.78	0.74	1.42	2.33	2.32
52	3-Heptanol	23.55	2.32	–	–	–	–	–
53	2-Butoxy,ethanol	23.80	5.06	1.28	1.26	2.18	2.74	14.85
54	2(3H)Furanone,2,3-dihydro,5-methyl	24.35	1.79	–	–	–	–	–
55	n-C9	24.45	0.24	–	0.07	1.02	1.93	0.19

Table 2 *(cont.)* Concentrations (ug/m^3) of VOC measured at 6 different sites located near Terra Nova Bay in Antarctica. (For site identification see Figure 1).

N.	*Compound*	*Ret. time*	*Site 1*	*Site 2*	*Site 3*	*Site 4*	*Site 5*	*Site 6*
56	Pentanoic acid	(24.5)	0.32	–	–	0.05	0.67	–
57	2H-Pyran,2-carboxaldehyde,5,6-dihydro	24.80	1.25	–	–	–	–	–
58	Benzaldehyde	25.53	0.32	0.42	0.23	0.66	1.08	–
59	iso-Octenone	25.70	8.97	–	–	–	–	–
60	iso-Octenone	25.90	41.86	–	–	–	–	–
61	Hexanal,2-ethyl†	26.10	–	–	–	–	–	–
62	Hexanoic acid	(27)	0.37	–	–	0.14	1.01	–
63	5-Hepten,2-one,6-methyl	27.32	3.92	1.05	1.00	3.13	8.11	2.52
64	2-Hexenal,2-ethyl	27.90	3.80	–	–	–	–	–
65	Octanal	28.06	2.70	1.15	0.78	3.90	6.45	2.72
66	2-Octanone,3†-methyl	28.15	–	–	–	–	–	–
67	n-C10	28.91	0.36	–	–	1.32	4.01	0.27
68	1-Hexanol,2-ethyl	29.49	7.21	0.47	0.42	2.22	1.85	1.49
69	Heptanoic acid	(32)	0.14	–	–	0.13	–	–
70	Nonanal	32.10	4.67	3.36	3.42	9.34	8.00	5.25
71	n-C11	32.77	–	–	–	0.40	0.94	–
72	Octanoic acid	(35.5)	0.32	–	–	0.17	–	–
73	Decanal	35.81	6.13	2.98	3.48	9.06	7.29	6.13
74	n-C12	36.36	–	–	–	0.72	–	–
75	Nonanoic acid	(39)	0.58	–	–	0.54	–	–
76	n-C13	39.29	0.26	–	–	–	–	–

for hydrocarbons with a number of carbon atoms larger than ca. 4. The only exception to this general rule is represented by acetic and propionic acid and CCl_4 for which a quantitative collection and full recovery were obtained.

The first observation that can be made by looking at the data shown in Table 2 is that, similarly to what has been observed in the Arctic region, oxygenated components largely dominate the hydrocarbon composition in terms of number of compounds detected and levels reached. Consistently with reduced impact from anthropogenic sources, tiny levels of man-made VOC were found in Antarctica. Among them, only CFC_s, CCl_4 and benzene were present in all sites investigated.

If we focus the attention on components for which reliable values of the mixing ratio were obtained (CCl_4 and benzene), we can see that levels 50% lower than those recorded in the Spitzbergen Islands were detected in Antarctica[4] and they are fully consistent with the ones reported in the literature[14,15]. In addition to benzene, toluene was the only other volatile arene found in Antarctica. It was detected only in the canister sampled at Starr Nunatak. The concurrent presence of large amounts of n-alkanes from C_3 to C_{11} in this sample clearly indicates that the site was directly influenced by anthropogenic emissions. The most likely source of pollution was represented by engine-exhaust emission coming from drilling activities carried out at a remote station for geological studies located some kilometers away from the sampling site.

Although n-alkanes were also detected at Tourmaline Plateau, Edmonton Point, Mount Melbourne and Cape Russel, levels measured were so small that their occurrence in air might be also attributed to biogenic sources. The presence of tiny amounts of isoprene in four of the sites investigated suggets that one of them is probably represented by mosses and lichens as they are the only organisms leaving in Antarctica capable of performing a reduced photosynthetic activity. The possibility of transport can be, in fact, excluded due to short life-time of isoprene in the atmosphere and the long distances of Antarctica from vegetation covered areas.

Although some of the oxygenated compounds listed in Table 2 (such as acetone and 3-butene-2-one) are known to be formed by photochemical degradation of alkanes, alkenes and isoprene, it is unlikely that the low amounts of biomass and reduced photochemical activity occurring in this remote region are capable of producing polar VOC at the levels we measured. This is particularly true for components with number of carbon atoms larger than ca. 8 for which possible precursors and pathways leading to their formation are difficult to envision.

The low photochemical reactivity of the atmosphere is also confirmed by the occurrence of i-octene in all samples. Since this is a highly reactive component never found in more than 300 urban, suburban, rural, forest and remote samples worldwide collected, it can be regarded as a unique constituent of the Antarctic region.

In general, the composition and distribution of oxygenated VOC reported in Table 2 are so not much different from those occurring in the remote areas of the Northern Hemisphere. The organic composition is characterized by high concentrations of acetic acid and aldehydes from propenal to decanal. Only the relatively high abundance of alcohols and alkenals and the lack of esters make possible to distinguish samples from Antarctica from those collected in the Northern Hemisphere. In particular, the lack of esters should be emphasized as it is perfectly on line with the hypothesis that these components are indicators of lower plant (flowers, weeds) emissions not present in Antarctica.

Since vegetation emission and photochemical reactions do not represent a significant source for oxygenated compounds, ocean and/or biogenic activities occurring in it should be responsible for their levels in air. While ocean is known to emit acetic acid[11], it has never been suggested as a possible source for semi-volatile carbonyl components. Based on the results obtained, we believe that marine emission provides a better explanation than long-range transport from vegetation-covered areas for their occurrence in remote islands of the Atlantic[4] and Pacific Ocean[2,3].

As a final comment, it is important to stress here the capabilities afforded by the use of passivated canisters in the collection of polar components in remote areas. In clean environments where low levels of primary and secondary pollution exist, they provide results comparable to those given by adsorption traps. Particularly important is the observation that sticky components, such as free acids, are not significantly depleted by adsorption and/or reactions occurring on their walls.

CONCLUSIONS

Results obtained in Antarctica confirmed the ubiquitous occurrence of oxygenated VOC in the troposphere and the possibility that marine sources might strongly contribute to their atmospheric levels. Since some of these components are sufficiently reactive to participate actively in tropospheric ozone formation, their contribution should be taken into account whenever global changes arising from ozone production are investigated.

Acknowledgments

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