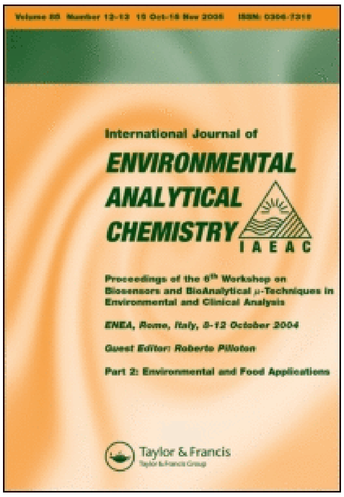

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Gröllert, C. , Kasper, A. and Puxbaum, H.(1997) 'Organic Compounds in High Alpine Snow', International Journal of Environmental Analytical Chemistry, 67: 1, 213 — 222

To link to this Article: DOI: 10.1080/03067319708031405

URL: http://dx.doi.org/10.1080/03067319708031405

Intern. J. Environ. Anal. Chem., Vol. 67, pp. 213-222
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ORGANIC COMPOUNDS IN HIGH ALPINE SNOW

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(Received 18 June 1996; In final form 15 November 1996)

Snow samples were taken in June 1995 at the Sonnblick Observatory located at the top of Mt. Sonnblick (3106 m a.s.l.) in the main ridge of the Austrian Alps, as part of the project "Organic Aerosol Scavenging". The main interest focused on the determination of aliphatic compounds and phenols. First the method for the extraction of the organic compounds was developed using standard samples prepared in the lab. The preconcentration of the samples was performed by liquid-liquid extraction with hexane and hexane/diethylether respectively. To characterize the analytical procedure, the efficiency of the extraction procedure, the reproducibility of the overall method and the detection limits were determined. Values for the recovery of the extraction method range from 57% (fatty acids) to 95% (aliphatic alcohols). Reproducibility was found to be between 3-5%, except for the fatty acids which gave a value of 16%. Detection limits were calculated for the various substances and are between 5μg/l (phenols) and 30μg/l (fatty acids). The analysis of the eight snow samples were performed using a GC-MS-FID system. The following compounds were identified as major compounds in the snow samples: 1-dodecanol, 1-tetradecanol, 1-hexadecanol, 1-octadecanol, 2-*iso*butyl-4-methoxy-phenol, di*iso*butylphenol and dibutylphthalate. The aliphatic alcohols are of biogenic origin and are present in a concentration range from 30 to 115 μg/l melted snow. The phenols show concentrations between 5 and 30 μg/l and the phthalates range up to 40 μg/l.

Keywords: Snow; organic compounds; background measurements; alkanols; phenols; phthalates

INTRODUCTION

The knowledge of organic precipitation chemistry is much less advanced compared to that of inorganic chemistry. Moreover, observations of organic compounds in snow are concentrated on urban areas or semi rural sites but they have

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not often been conducted at a background site to monitor the capabilities of long range transport.

The occurrence of organic material in snow has been reviewed by Jones[1]. Solvent extracted fatty acids and *n*-alkanes have been identified from a study conducted on snow in a semi rural area in the USA[2] to be the major species that can be measured analytically. The authors have found that 85 % of the identified organics is of biogenic origin. Lunde *et al.*[3] examined the wet deposition of organic micropollutants in Norway to monitor long range transport and chemical degradation of compounds. An analysis of their data shows that some of the identified major fatty acid components (e.g. C_{12}, C_{14}, C_{16}) were of natural origin. The concentrations of these classes of compounds in snowfall was very low (in the order of ten ng/l). In addition anthropogenic compounds such as polychlorinated biphenyls, polyaromatic hydrocarbons, phthalates and a range of fatty acid ethyl esters were identified. In the more polluted region of Southern California organic acids (mono- and dicarboxylic) and aldehydes were determined in rainwater samples using derivatization techniques (Kawamura *et al.*[4] and citations therein). Another discussion of organics in rainwater concerns the work of Czuczwa *et al.*[5]. More recently chlorinated organics have been analyzed in snow from remote areas[6-8]. Desideri *et al.*[9] have performed a study of organic compounds in Antarctic snow, they identified *n*-alkanes, PAH's, alkyl benzenes, phthalates and cholesterol in a range of samples, with alkanes being present in concentrations ranging between 369 – 1231 ng/l.

In this work we concentrated on the identification of neutral extractable organics in a glacier field at 3000 m in the Eastern Alps. Aerosol scavenging at this site takes place by nucleation scavenging into supercooled cloud droplets which are caught by falling snow flakes in the riming process as examined by Kalina and Puxbaum[10]. During winter the site is representative for tropospheric air, during summer also boundary layer air reaches the 3 km level[11].

EXPERIMENTAL

Site

The samples were taken near the Sonnblick Observatory (SBO) located at the top of Mt. Sonnblick (3106 m a.s.l.) in June 1995. Mt. Sonnblick (Figure 1) is situated in the main ridge of the Austrian Alps (Hohe Tauern, 12°57' E, 47°03' N). As Mt. Sonnblick is among the highest peaks in the area it is exposed to air masses from all directions. The observatory is surrounded by large glacier fields

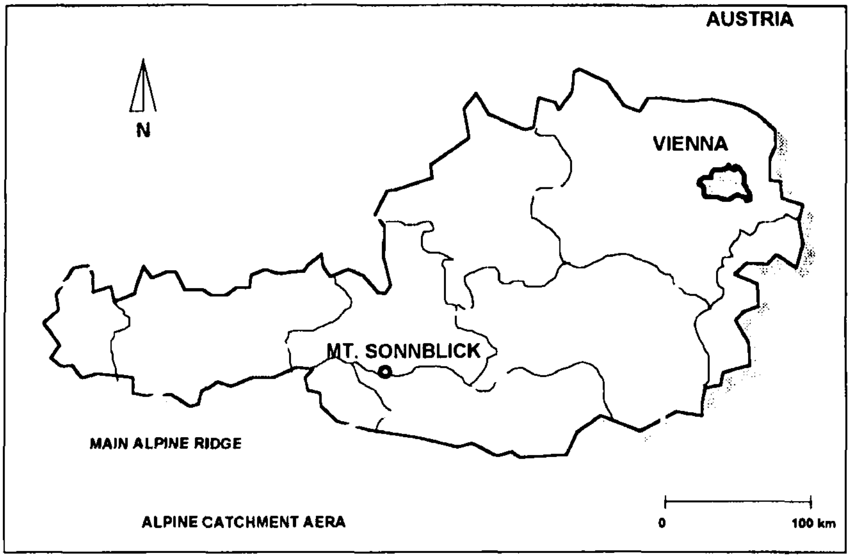

FIGURE 1 Location of Mount Sonnblick within the Austrian Alps

to the East and to the South. The Sonnblick Observatory has the ideal characteristics of a high alpine background station. Due to the lack of public transportation facilities there is hardly any tourism. The observatory itself is supplied with electricity and thus not a source for exhausts originating from fuel or heating.

Sampling

The surface snow samples were taken as follows: A snow layer of approximately 10cm thickness was collected and put into six liter polyethylene bags resulting in an approximate liquid volume of 2 liters per sample. Sample handling was performed with a poylethylene shovel. Samples were kept frozen in deep freeze until the time of analysis.

Sample pretreatment

The samples were melted at room temperature in closed PE flasks. Blanks were done for the PE bags and the PE flasks.

In literature several methods for the enrichment of organic compounds in aqueous solutions are reported. Many authors choose liquid/liquid extraction combined with various organic solvents as extractant, for example methylene chloride, benzene, *iso*propanol, *n*-hexane and diethylether[12,13]. Others have worked with solid phase extraction[14] which is already a selective method. For the analysis of PAHs a combination of solid phase extraction and SFE is reported[15]. For the work conducted liquid/liquid extraction with *n*-hexane was chosen, due to the intention to look for all classes of organic compounds.

The exact volume of the melted snow was measured and the sample was placed in a separating funnel together with 10ml of the extractant. The funnel was then shaken for 12min, after separation of the aqueous and the organic phase the funnel was rinsed with *n*-hexane. The organic fractions were combined and the solvent was evaporated at room temperature. To accelerate this process, a helium stream was used. After evaporation of the solvent a defined amount of *n*-hexane was added to achieve an enrichment factor of 5000 for each sample.

Solvents as *n*-hexane, methanol, and acetone were all p.a. grade purchased from Merck. Before use all glass vessels were rinsed thoroughly with demineralized water, methanol, acetone and *n*-hexane. Standard compounds were commercially available from Fluka, Sigma and Merck.

GC-FID-MS analysis

For identification of the compounds present in the snow samples a GC-FID-MS-system was used[16]. An HP 5890 Series II GC was equipped with a precolumn-splitter, two identical columns (J&W Scientific DB5-MS, 50m, 0.2mm ID, 0.33μm film thickness) with an FID at the end of the first column and a mass selective detector (HP 5971 A) at the end of the second. Helium 5.0 was used as carrier gas. The split/splitless injector was kept at 270°C, the split was 1:100.

The employed temperature program was as follows: 60°C for 1min, then a linear increase to 270°C at 6°C/min, and finally isothermal at 270°C for 34min. The FID was kept at 280°C as was the MS transferline.

Compounds were identified using both their mass spectra and their retention time. Mass spectra were compared to the Wiley library and standard substances were analyzed to check the retention times.

RESULTS AND DISCUSSION

Extraction method

To determine the overall recovery for the different classes of organic compounds, an "artificial snow sample" prepared from demineralized water containing aliphatic hydrocarbons, fatty acids, aliphatic alcohols, phenols and phthalates, each at a concentration of 200 µg/l. Extraction with n-hexane was performed as described above. Recoveries and reproducibilities for each class of compounds are given in Table I.

TABLE I Figures of merit

Classes of organic compounds	*Recovery[%]*	*Reproducibility [%]*	*Detection limits [µg/l]*	
			theoretical	*experimental*
Aliphatic hydrocarbons	74	4	11	14
Aliphatic alcohols	95	3	16	18
Phenols	87	3	5	
Phthalates	78	5	7	
Fatty acids	57	16	30	43

1-Octanol, 1-tetradecanol, 1-pentadecanol, 1-hexadecanol and 1-octadecanol were used as standard substances to check the extraction procedure for aliphatic alcohols. While only poor results could be obtained for 1-octanol (20%) much better recoveries in the range of 95% were found for *n*-alkanols with longer carbon chains. Fatty acids like palmitic and stearic acid could be extracted with a recovery of 55 - 59%. Thus, extraction from snow samples would be incomplete but should allow the determination of a lower limit. As far as the measured snow samples are concerned, no fatty acids were discovered. As aliphatic hydrocarbons undecane, dodecane and pentadecane were used, they showed only little variations in recovery and reproducibility compared to the average of 74% and 4%. Concerning the recovery of phenols, namely 2,4-di*iso*butyl-phenol, 2,6-di*iso*butyl-phenol, a recovery of 87% could be achieved. Dibutyl-phthalate and bis(2-ethylhexyl)-phthalate were used to determine the recovery of phthalates which was 78% with a reproducibility of 5%.

The reproducibility for the overall method (Table I) was found to be sufficient for alkanols, phenols, hydrocarbons and the phthalates while larger deviations were found for the fatty acids due to peak tailing. Since no fatty acids were found in the snow samples, no further work was conducted to improve this value.

Furthermore, the detection limits of the method were calculated. The theoretical detection limit (three times the standard deviation) was calculated out of the noise of the FID baseline. The experimental detection limit was investigated as well, based on repeated injections of standard solutions with concentrations near the theoretical detection limit (Table I).

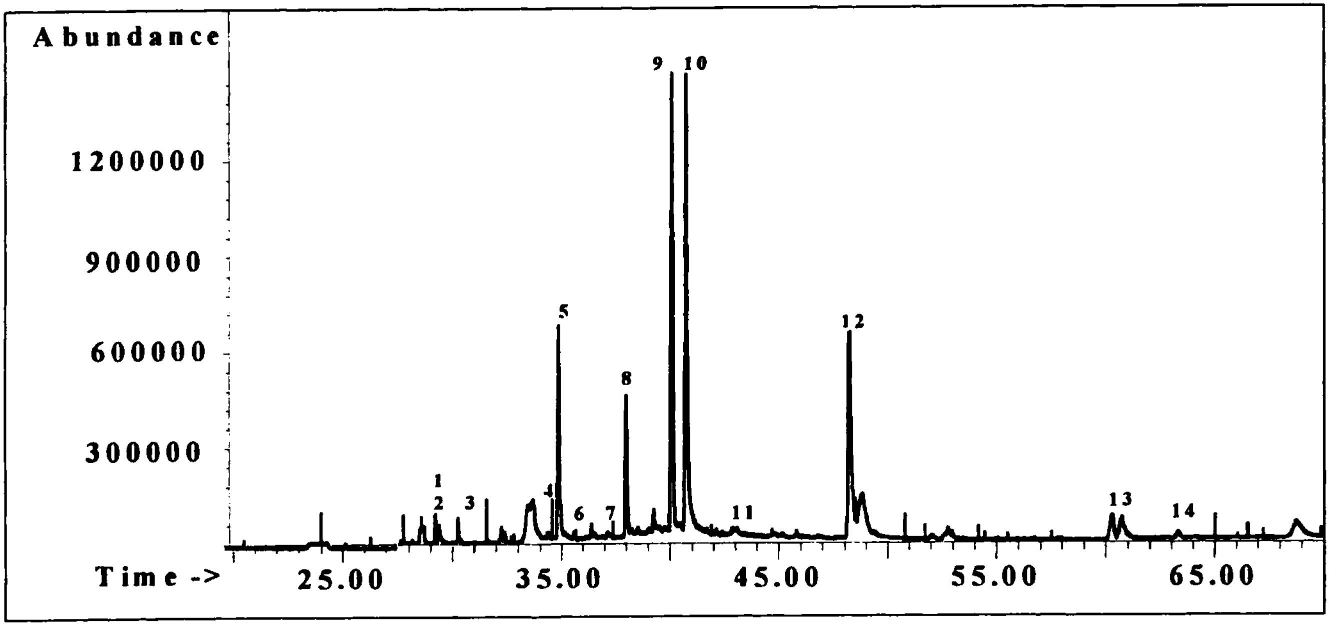

FIGURE 2 Total ion chromatogram of an SBO snow sample

The experiments with the artificial snow sample showed that extractions with *n*-hexane/diethylether did not provide any improvement of the recoveries than were found with pure *n*-hexane. Thus, all snow samples were extracted with pure *n*-hexane.

Snow Samples

Figure 2 shows a typical chromatogram of a snow sample obtained by analysis with a gas chromatograph – mass spectrometer system (GC-MS). The compounds detected in the sample were identified by comparison with a library (Wiley) and are listed in Table II. Peak numbers 10 and 12 in this chromatogram could not be identified with a quality factor of over 75%, but did enable the class of the substance to be assigned.

TABLE II Compounds found in an SBO snow sample

Peaknumber	*Ret.time [min]*	*Class of organic compound*	*Possible substance*
1	29,23	Phenol	2-*Iso*butyl-4-methoxy-phenol
2	29,39	Alcohol	1-Dodecanol
3	30,28	Phenol	2,4-Di*iso*butyl-phenol
4	34,38	Alkane	Heptadecane
5	34,88	Alcohol	2-(Dodecyloxy)-ethanol
6	36,43	Alkane	Octadecane
7	36,59	Alcohol	Pentadecanol
8	38,01	Phthalate	Di*iso*butyl-phthalic acid ester
9	40,11	Phthalate	Dibutyl-phthalic acid ester
10	40,75	Benzene	
11	42,93	Alcohol	1-Octadecanol
12	48,23	Phenol	
13	60,07	Phthalate	Di*iso*octyl-phthalic acid ester
14	63,31	Benzene	1-Methyl-4-*iso*propyl-benzene

Table III gives an overview of all identified compounds in the eight snow samples. Quantitative information is achieved by integration of the corresponding FID chromatogram. The alcohols were found to be present in the samples at a concentration range of 30 – 115 µg/l melted snow, aromatics (mainly phenols) at concentrations between 5 and 30 µg/l, with the phthalates being in a range of

TABLE III Compounds idenified in eight snow samples (s1-s8), concentrations given in $\mu g l^{-1}$

Compounds	*ID*	*s1*	*s2*	*s3*	*s4*	*s5*	*s6*	*s7*	*s8*
n-ALKANES									
Heptadecane	b	8							
Octadecane	b	9							
tot. alkanes		17							
ALCOHOLS									
1-Dodecanol	b	9			16	12	9		
1-Tetradecanol	b			11	10				
1-Pentadecanol	b	6							
1-Hexadecanol	b				23	18			
1-Octadecanol	b	10			36	25	10		
2-(dodecyloxy)-ethanol	a	22			28	18	13		
tot. alkohols		47			114	83	32		
PHTHALATES									
Dibutyl-phtalic acid ester	b	21	11	8	12	8	17	13	8
Di*iso*butyl-phthalic acid ester	a	16	5		9	12	7	6	5
Di*iso*octyl-phthalic acid ester	b		5		8				
tot. phthalates		37	21	8	29	20	24	19	13
AROMATICS									
2-*Iso*butyl-4-methoxy-phenol	b	9			11	7			
Di*iso*butyl-phenol	b	6			7	6	5		5
4-(*iso*butyl)-phenol	a				9	8			
Nonylphenyl Isomer	a					5			
1 Methyl-4-*iso*propyl-benzene	a	7							
tot. aromatics		22			27	26	5		5

[a] identified using a library

[b] identified using a library and retention time

5-40 µg/l. The dominant lipophilic components consist of *n*-alkanols, phenols and phthalates, and little amounts of *n*-alkanes in sample sl, where alkanes could be positively identified and quantified. These compounds indicate an input of anthropogenic sources[17].

Phthalates are present in each sample. They are ubiquitous plasticizers[18] and do occur in the urban atmosphere. As their degradation takes place very slowly[19], they can be transported to remote sites like the SBO. Although they are considered as common contaminants, some authors report that they might origin from biogenic sources, namely from the degradation of humic substances[20-22].

The aliphatic alcohols are the dominant components in the lipophilic fraction of all investigated snow samples reaching the highest sum concentration in sample s4. Concerning s4 and s5 only alcohols with even carbon numbers are detected. This predominance is characteristic for natural sources as there are vascular plant wax and microbial sources[23-24]. The distribution in all samples indicates an enhanced input of microbial matter (homologs $< n\text{-}C_{20}$). The formation of alcohols by atmospheric oxidation processes of hydrocarbons appears unlikely[25].

In the literature, only a few investigations of organic compounds in snow originating from a background site are reported. In Austria an investigation of snow quality of glaciers has been made[26], concerning the detection of phthalates, alkanes and one phenol compound in a sample collected near the Mt. Sonnblick site (Wurtenkees glacier). The sum concentration for alkanes found in this study is lower than 5μg/l melted snow. Other compounds have not been quantified. Another study involving snow analysis in Antarctica[9] reports high concentrations of phthalates, alkanes and benzenes being found as well as lower quantities of aliphatic alcohols. Also reported are large variations of the distributions of the homologs and the sum concentrations between the single samples, which are comparable to the differences that have been found in this study.

Acknowledgements

The financial support by the Austrian Science Foundation, P 10328 - CHE, is gratefully acknowledged. We are grateful to the sampling team during the measurement campaign.

References

[1] H. G. Jones, *Seasonal Snowpacks - Processes of Compositional Change* (NATO ASI Series Vol. G28, 1991) 173-227pp.
[2] P. A. Meyer and R. A. Hites, *Atmos Environ*, **16**, 2169-2175 (1982).
[3] G. Lunde, J. Gether, N. Gjos and M. S. Laude, *Atmos Environ*, **11**, 1007-1014 (1977).
[4] K. Kawamura, S. Steinberg and I. R. Kaplan, *Atmos Environ*, **30**, 1035-1052 (1996).
[5] J. Czuczwa, C. Leuenberger and W. Giger, *Atmos Environ*, **22**, 907-916 (1988).
[6] D. A. Peel, *Nature*, **254**, 324-325 (1975).
[7] S. Tanabe, H. Hidaka and R. Tatsukawa *Chemosphere*, **12**, 277-288 (1983).
[8] E. W. Wolff, *Antarctica Sci.*, **2**, 189-205 (1990).
[9] P. G. Desideri, L. Lepri, L. Checchini and D. Santianni, *Intern. J. Environ. Anal. Chem.*, **55**, 33-46 (1994).

[10] M. Kalina and H. Puxbaum, *Atmos Environ*, **28**, 3311-3328 (1994).

[11] A. Kasper and H. Puxbaum, *Anal Chim Acta*, **291**, 297-304 (1993).

[12] M. A. Mazurek, B. R. T. Simoneit, G. R. Cass and H. A. Gray, *Intern. J. Environ. Anal. Chem.*, **29**, 119-139 (1987).

[13] P. G. Desideri, L. Lepri and L. Checchini, *Microchim Acta*, **107**, 55-63 (1992).

[14] A. J. H. Louter, F. D. Rinkema, R. T. Ghijsen and U. A. Th. Brinkman, *Intern. J. Environ. Anal. Chem.*, **56**, 49-56 (1994).

[15] J. S. Ho, P. H. Tang, J. W. Eichelberger and W. L. Budde, *J. Chromtatogr. Sci.*, **33**, 1-8 (1995).

[16] G. König, *VOC Emissions from selected European Plant Species* (Thesis, Technische Universität Wien, 1995) 90pp.

[17] B.R.T. Simoneit, *Atmos Environ*, **18**, 51-67 (1984).

[18] C.S. Giam, E. Atlas, M.A. Powers, Jr. and J.E. Leonard, in: *The Handbook of Environmental Chemistry* (ed. O. Hutzinger, Springer Verlag, 1984) Vol.3 Part C, pp. 67-142.

[19] W.E. Gledhill, R.G. Kaley, W.J. Adams, O. Hicks, P.R. Michael, V.W. Saeger and G.A. Le Blanc, *Environ. Sci. Technol.*, **14**, 301-(1980).

[20] G.G. Choudhry in: *The Handbook of Environmental Chemistry* (ed. O. Hutzinger, Springer Verlag, 1984) Vol.1 Part C, pp. 1-24.

[21] G.G. Choudhry, *Toxicol. Environ. Chem.*, **4**, 209 (1981).

[22] W. Liao, R.F. Christma, J.J. Donald, D.S. Millington and J.R. Hass, *Environ. Sci. Technol.*, **16**, 403 (1982).

[23] B.R.T. Simoneit, *J. Atmos. Chem.*, **8**, 251-275 (1989).

[24] B.R.T. Simoneit, G. Sheng, X. Chen, J. Fu, J. Zhang and Y. Xu, *Atmos Environ*, **25A**, 2111-2129 (1991).

[25] P. Warneck, *Chemistry of the natural atmosphere* (Academic Press, Inc., 1988) 753pp.

[26] Federal Environmental Agency Austria (Umweltbundesamt), *Gletschergebiete Österreichs - Bestandsaufnahme und chemisch-analytische Untersuchungen (Glacier fields in Austria - a chemical-analytical investigation* (Bundesministerium für Umwelt, Jugend und Familie, 1993), Bd. 32, 220pp.