

Whole Air Sampling (WAS) from the DC-8 Aircraft during ARCTAS, 2008

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General Description

The UC-Irvine research group proposes to collect whole air samples aboard the DC-8 aircraft during both the spring and summer 2008 campaigns of the ARCTAS field mission. More than 60 trace gases will be identified and quantified at our Irvine laboratory – including C₂-C₁₀ NMHCs, C₁-C₂ halocarbons, C₁-C₅ alkyl nitrates, and selected sulfur compounds (Table 1). This will be achieved using our established technique of airborne whole air sampling followed by laboratory analysis using gas chromatography (GC) with flame ionization detection (FID), electron capture detection (ECD), and mass spectrometric detection (MSD). Our experimental procedures will build on those that have been successfully employed for numerous prior NASA field missions, most recently PEM-Tropics B [Blake *et al.*, 2001, 2003c; Colman *et al.*, 2001; Simpson *et al.*, 2001], TRACE-P [Blake *et al.*, 2003b, 2003d; Simpson *et al.*, 2003a, 2003b], and INTEX-A and B [Blake *et al.*, 2007, in press].

The ¹³C/¹²C and ¹⁴C content of CO₂ will also be determined, separately, in selected air samples using AMS. These measurements, which will be made by Stan Tyler (as described in Tyler *et al.* [1999]) in his UC-Irvine laboratory, can be readily obtained using the air that remains in selected canisters after we have finished our analysis of NMHCs.

As in previous missions, we are also prepared to provide back-up capability for the *in situ* CO and CH₄ measurements when the principal *in situ* CH₄ or CO measurements have gone off-line.

Sampling Frequency.

We propose to collect up to 168 air samples per flight, which (depending on the duration of the flight) allows us a 4-5-minute sampling during horizontal flight legs, and every 1-2 minutes during ascents and descents. The time taken to fill each sampling canister can be adjusted, but is usually about 1 minute. Sample collection on board the aircraft will be coordinated with other experiments and any intercomparison activities, so as to optimize sample overlap with other groups.

Sampling Equipment.

Our on-board sampling equipment includes seven foam-embedded sets of 24 linked, 2-L stainless steel samplings canisters (see photo in Figure 1), plus a metal bellows pump. We use a window-mounted ¼" forward-facing inlet and an aft-facing outlet.

Table 1. Compounds to be measured and archived by UC-Irvine during ARCTAS.

Compound	Formula	Lifetime	LOD	Precision (pptv)	Accuracy (%)
Hydrocarbons					
Ethane	C ₂ H ₆	2-3 mo	3	0.5	5
Ethene	C ₂ H ₄	1-2 d	3	0.7	5
Ethyne	C ₂ H ₂	12-17 d	3	0.5	5
Propane	C ₃ H ₈	10-15 d	3	0.7	5
Propene	C ₃ H ₆	8-12 hr	3	16	5
Propyne	C ₃ H ₄	2 d	3	2	5
<i>n</i> -Butane	C ₄ H ₁₀	4-6 d	3	0.6	5
<i>i</i> -Butane	C ₄ H ₁₀	5-7 d	3	1	5
1-Butene	C ₄ H ₈	9 hr	3	2	5
<i>cis</i> -2-Butene	C ₄ H ₈	5 hr	3	2	5
<i>trans</i> -2-Butene	C ₄ H ₈	5 hr	3	2	5
1,3-Butadiene	C ₄ H ₆	5 hr	3	2	5
<i>n</i> -Pentane	C ₅ H ₁₂	5 d	3	2	5
<i>i</i> -Pentane	C ₅ H ₁₂	5 d	3	2	5
Isoprene	C ₅ H ₈	1-2 hr	3	2	5
2-Methylpentane	C ₆ H ₁₄	2-3 d	3	2	5

3-Methylpentane	C ₆ H ₁₄	2-3 d	3	2	5
Benzene	C ₆ H ₆	9-13 d	3	2	5
Toluene	C ₇ H ₈	2-3 d	3	3	5
<i>m</i> -Xylene	C ₈ H ₁₀	1 d	3	5	5
<i>o</i> -Xylene	C ₈ H ₁₀	1-2 d	3	5	5
<i>p</i> -Xylene	C ₈ H ₁₀	1-2 d	3	5	5
Ethylbenzene	C ₈ H ₁₀	2 d	3	5	5
<i>m</i> -Ethyltoluene	C ₉ H ₁₂	17 hr	3	5	5
<i>o</i> -Ethyltoluene	C ₉ H ₁₂	1 d	3	5	5
<i>p</i> -Ethyltoluene	C ₉ H ₁₂	1 d	3	5	5
1,2,4-Trimethylbenzene	C ₉ H ₁₂	10 hr	3	5	5
1,3,5-Trimethylbenzene	C ₉ H ₁₂	5 hr	3	5	5
α -Pinene	C ₁₀ H ₁₆	6 hr	3	5	5
β -Pinene	C ₁₀ H ₁₆	4 hr	3	5	5

Alkyl Nitrates

Methyl nitrate	CH ₃ ONO ₂	1 mo	0.02	2	10
Ethyl nitrate	C ₂ H ₅ ONO ₂	2-4 wk	0.02	1	10
1-Propyl nitrate	C ₃ H ₇ ONO ₂	1-2 wk	0.02	1	10
2-Propyl nitrate	C ₃ H ₇ ONO ₂	1-3 wk	0.02	2	10
2-Butyl nitrate	C ₄ H ₉ ONO ₂	1-2 wk	0.02	1	10
2-Pentyl nitrate	C ₅ H ₁₁ ONO ₂	4-5 d	0.02	2	10
3-Pentyl nitrate	C ₅ H ₁₁ ONO ₂	4-5 d	0.02	2	10

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Table 1 continued. Compounds to be measured and archived by UC-Irvine during ARCTAS.

Compound	Formula	Lifetime	LOD	Precision (pptv)	Accuracy (%)
Halocarbons					
CFC-11	CFCl ₃	45 yr	1	0.8	2
CFC-12	CF ₂ Cl ₂	100 yr	10	0.7	2
CFC-113	CCl ₂ FCClF ₂	85 yr	1	1.2	2
CFC-114	CClF ₂ CClF ₂	300 yr	1	1.9	5
Methyl chloroform	CH ₃ CCl ₃	4.9 yr	1	1.0	5
Carbon tetrachloride	CCl ₄	35 yr	0.1	0.7	5
Halon-1211	CBrClF ₂	11 yr	0.05	1.1	5
Halon-2402	CBrF ₂ CBrF ₂	<20 yr	0.05	2.5	5
HCFC-22	CHF ₂ Cl	11.8 yr	1	2.0	5
HCF-134a	CH ₂ FCF ₃	13.6 yr	1	5.2	10-20
HCFC-141b	CH ₃ CCl ₂ F	9.2 yr	1	4.2	10-20
HCFC-142b	CH ₂ CClF ₂	18.5 yr	1	3.6	10-20
Methyl bromide	CH ₃ Br	9-10 mo	0.1	1.7	5
Methyl chloride	CH ₃ Cl	1.3 yr	5	1.5	5
Methyl iodide	CH ₃ I	4 d	0.01	1.1	10
Methylene bromide	CH ₂ Br ₂	3-4 mo	0.05	1.6	10-20
Methylene chloride	CH ₂ Cl ₂	3-5 mo	1	4.5	10
Chloroform	CHCl ₃	3-5 mo	0.1	1.1	5
Trichloroethene	C ₂ HCl ₃		0.05	1.5	5
Tetrachloroethene	C ₂ Cl ₄	2-3 mo	0.05	1.2	10
1,2-Dichloroethane	C ₂ H ₄ Cl ₂	1-2 mo	0.05	5.0	20
Bromodichloromethane	CHBrCl ₂	2-3 mo	0.01	2.0	10-20
Dibromochloromethane	CHBr ₂ Cl	2-3 mo	0.01	9.3	20
Bromochloromethane	CH ₂ BrCl	5 mo	0.01	7.4	20
Sulfur Compounds					
Carbonyl sulfide	OCS	16 yr	10	2	10
Dimethyl sulfide	CH ₃ SCH ₃	1-2 d	10	2	10
Dimethyl disulfide	CH ₃ SSCH ₃	1 hr	10	2	10
Carbon disulfide	CS ₂	2-3 d	10	2	10

References

Blake, N. J., D. R. Blake, I. J. Simpson, J. P. Lopez, N. A. C. Johnston, A. L. Swanson, A. S. Katzenstein, S. Meinardi, B. C. Sive, J. J. Colman, E. Atlas, F. Flocke, S. A. Vay, M. A. Avery and F. S. Rowland, Large scale latitudinal and vertical distributions of NMHCs and selected halocarbons in the troposphere over the Pacific Ocean during the March-April 1999 Pacific Exploratory Expedition (PEM-Tropics B), *J. Geophys. Res.*, 106, D23, 32,627-32,644, 2001.

- Blake, N. J., D. R. Blake, I. J. Simpson, S. Meinardi, A. L. Swanson, J. P. Lopez, A. S. Katzenstein, B. Barletta, T. Shirai, E. Atlas, G. Sachse, M. Avery, S. Vay, H. Fuelberg, C. M. Kiley, and F. S. Rowland, NMHCs and halocarbons in Asian continental outflow during TRACE-P: Comparison to PEM-West B, *J. Geophys. Res.* 108 (D20), 8806, doi: 10.1029/2002JD003367, 2003a.
- Blake, N. J., D. R. Blake, A. L. Swanson, E. Atlas, F. Flocke, and F. S. Rowland, Latitudinal, vertical, and seasonal variations of C₁-C₄ alkyl nitrates in the troposphere over the Pacific Ocean during PEM-Tropics A and B: Oceanic and continental sources, *J. Geophys. Res.* 108, D2, 10.1029/2001JD001444, 2003b.
- Blake, N. J., Streets, D., J.-H. Woo, I. J. Simpson, J. Green, S. Meinardi, K. Kita, E. Atlas, H. E. Fuelberg, G. Sachse, M. A. Avery, S. Vay, R. W. Talbot, J. E. Dibb, A. R. Bandy, D. C. Thornton, F. S. Rowland, and D. R. Blake, Carbonyl sulfide (OCS) and carbon disulfide (CS₂): Large scale distributions and emissions from Asia during TRACE-P, *J. Geophys. Res.*, 10.1029/2003JD004259, 2003c.
- Blake, N. J., E. Campbell, S. A. Vay, H. E. Fuelberg, L. G. Huey, G. Sachse, S. Meinardi, A. Beyersdorf, A. Baker, B. Barletta, J. Midyett, L. Doezema, M. Kamboures, J. McAdams, B. Novak, F. S. Rowland, and D. R. Blake, Carbonyl sulfide (OCS): Large scale distributions over North America during INTEX-NA and relationship to CO₂, submitted to *J. Geophys. Res.*, 2007.
- Colman, J. J., A. L. Swanson, S. Meinardi, B. C. Sive, D. R. Blake, and F. S. Rowland, Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B, *Anal. Chem.*, 73, 3723-3731, 2001.
- Simpson, I. J., J. J. Colman, A. L. Swanson, A. R. Bandy, D. C. Thornton, D. R. Blake and F. S. Rowland, Aircraft measurements of dimethyl sulfide (DMS) using a whole air sampling technique, *J. Atmos. Chem.* 39, 191-213, 2001.
- Simpson, I. J., S. Meinardi, D. R. Blake, N. J. Blake, F. S. Rowland, E. Atlas, and F. Flocke, A biomass burning source of C₁-C₄ alkyl nitrates, *Geophys. Res. Lett.*, 29, 10.1029/2002GL016290, 2002.
- Simpson, I. J., N. J. Blake, D. R. Blake, E. Atlas, F. Flocke, J. H. Crawford, H. E. Fuelberg, C. M. Kiley, S. Meinardi, and F. S. Rowland, Production and evolution of selected C₂-C₅ alkyl nitrates in tropospheric air influenced by Asian outflow, *J. Geophys. Res.* 108 (D20), 8808, doi:10.1029/2002JD002830, 2003a.
- Simpson, I. J., O. W. Wingenter, D. J. Westberg, H. E. Fuelberg, C. M. Kiley, J. H. Crawford, S. Meinardi, D. R. Blake, and F. S. Rowland, Airborne measurements of cirrus-activated C₂Cl₄ depletion in the upper troposphere with evidence against Cl reactions, *Geophys. Res. Lett.* 30 (20), 2025, doi:10.1029/2003GL017598, 2003b.
- Tyler, S. C., H. O. Ajie, M. L. Gupta, R. J. Cicerone, D. R. Blake, and E. J. Dlugokencky, Carbon isotopic composition of atmospheric methane: A comparison of surface level and upper tropospheric air, *J. Geophys. Res.*, 104, 13,895-13,910, 1999.

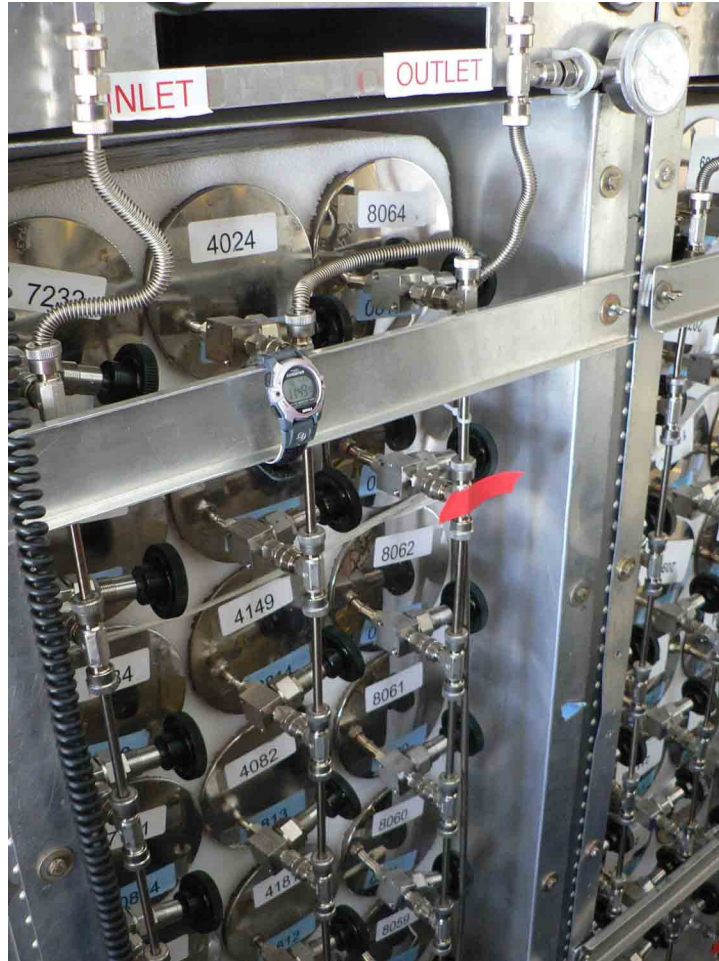


Figure 1. Photo of a UCI foam-embedded set of 24 linked, 2-L stainless steel samplings canisters installed on the NASA DC-8 during TC⁴. Photo by Nicola J. Blake.