



## ACCESS TO RESEARCH INFRASTRUCTURES

The completed and signed form below should be returned by email to [m.oliveri@opgc.univ-bpclermont.fr](mailto:m.oliveri@opgc.univ-bpclermont.fr)

### **Influence of Biosphere-Atmosphere Interactions on the Reactive Nitrogen Budget, IBAIRN**

**John Crowley et al.**

- **Introduction and motivation**

- Investigation and comprehension of the chemical processes that influence the composition of tropospheric air is fundamental to protection of the environmental and human health. Toxic gases and particulate irritants are of environmental concern and are formed in the degradation of primary emit ants both of biogenic and anthropogenic origin. The boreal forest covers a significant fraction of the planet's land mass and is responsible for an important fraction of biogenic emissions. The boreal forest at the SMEAR station in Hyytiälä is an ideal location to investigate the interaction between emissions from the biosphere in the form of biogenic VOCs (such as terpenes, sesquiterpenes and isoprene) and atmospheric pollutants in the form of reactive nitrogen oxides. This site has been extensively characterised for biogenic VOC emissions but to date there have been no concerted measurements of gas-phase organic nitrates at the site, a major focus in IBAIRN.

- **Scientific objectives**

- The main objective of IBAIRN was to investigate the interaction between emissions from the biosphere (in this case from the boreal forest) and anthropogenic pollutants in order to enhance our understanding of the photochemical processes (e.g. O<sub>3</sub> formation) and especially radical termination processes (which limit O<sub>3</sub> formation) in this environment. The more detailed objectives include assessment of the relative importance of daytime versus night time organic nitrate formation via degradation of BVOCS in the boreal forest, establishing the relative importance of photochemical cycle termination via formation of alkyl-nitrates (ANs) and peroxy nitrates (PNs) with formation of organic peroxides (ROOH) and evaluation of the contribution of soil emissions and entrainment from the free-troposphere or nighttime residual layer in providing the canopy level NO<sub>x</sub> necessary to drive the formation of organic nitrates.

- **Methodology and experimental set-up**

- The scientific objectives of the IBAIRN campaign were to be reached by taking extensive instrumentation (in two laboratory-containers) to the SMEAR 2 site at Hyytiälä which broaden the capabilities of the permanent instruments at this site. The instrumentation from MPI-Mainz included reactive nitrogen species, formaldehyde, organic and inorganic peroxides and acids, VOCs, CO and O<sub>3</sub> and also photolysis frequencies for a suite of trace-gases. The permanent instruments at the SMEAR site which are most relevant for this project include gas-phase VOCs and particle composition as well as meteorological data. The instruments deployed by MPI-Mainz, the University of Helsinki and the Finnish meteorological Institute are listed in Table 1.

**Table 1: Parameters, Instruments and operating institute as used in IBAIRN**

Parameter	Operator	Instrument
NO <sub>3</sub> reactivity	MPI	τ-NO <sub>3</sub> (662 nm Cavity-Ring-Down Spectrometer)
O <sub>3</sub>	MPI	2B-205 Ozone monitor
PAN, PAA, HCl, ClNO <sub>2</sub> , SO <sub>2</sub>	MPI	Iodide-CIMS
NO <sub>y</sub>	MPI	2 Channel, 405 nm Thermal Dissociation Cavity-Ring-Down Spectrometer
NO <sub>3</sub> , N <sub>2</sub> O <sub>5</sub> , NO <sub>2</sub> , PNs, ANs	MPI	5C-TD-CRDS (5 Channel, 405 nm and 662 nm Thermal Dissociation Cavity-Ring-Down Spectrometer)
J-values	MPI	Spectral Radiometer
HCHO	MPI	Hantzsch
H <sub>2</sub> O <sub>2</sub> , ROOH	MPI	Enzyme derivatisation and Aerolaser detector
H <sub>2</sub> O <sub>2</sub> , ROOH	MPI	High- Pressure Liquid Chromatography
O <sub>3</sub>	MPI	UV absorption
NO	MPI	Chemiluminescence Detector
CO	MPI	Quantum Cascade laser Absorption Spectroscopy
VOCs	MPI	Gas Chromatograph with Atomic Emission Detector
Particles: 1-2.5 nm	UHEL	PSM (Particle Size magnifier)
Particles: 2-10 nm	UHEL	Half-mini DMPS (Differential Mobility Particle Sizer)
VOCs	FMI	Gas Chromatograph with Mass Spectrometer
OVOCs	FMI	Gas Chromatograph with Mass Spectrometer
Gas and particles composition	FMI	MARGA (Ion Chromatograph)
Aerosol chemical composition	UHEL	L-TOF-AMS (Time of Flight Aerosol Mass Spectrometer)
Ion and particle distributions	UHEL	NAIS14 (Neutral cluster and Air on Spectrometer)
Ion and particle distributions	UHEL	NAIS26 (Neutral cluster and Air on Spectrometer)
Ion size distributions	UHEL	BSMA (Balanced Scanning Mobility Analyser)
Sulphuric acid & HOMs	UHEL	CI-APi-TOF (Chemical Ionisation (NO <sub>3</sub> <sup>-</sup> ) Atmospheric-Pressure Time-of-Flight Mass Spectrometer)
HOMs, H <sub>2</sub> O <sub>2</sub> , Pyruvic acid	UHEL	LTOF-CI-APi-TOF (I-) (Chemical Ionisation (I <sup>-</sup> ) Atmospheric-Pressure Time-of-Flight Mass Spectrometer)
Sulfuric acid & HOMs	UHEL	CI-APi-TOF (NO <sub>3</sub> <sup>-</sup> ) (Chemical Ionisation (NO <sub>3</sub> <sup>-</sup> ) Atmospheric-Pressure Time-of-Flight Mass Spectrometer)
VOCs	UHEL	PTR-QMS (Proton Transfer Quadrupole Mass Spectrometer)
VOCs	UHEL	PTR-TOF-MS (Proton Transfer Time-of-Flight Mass Spectrometer)

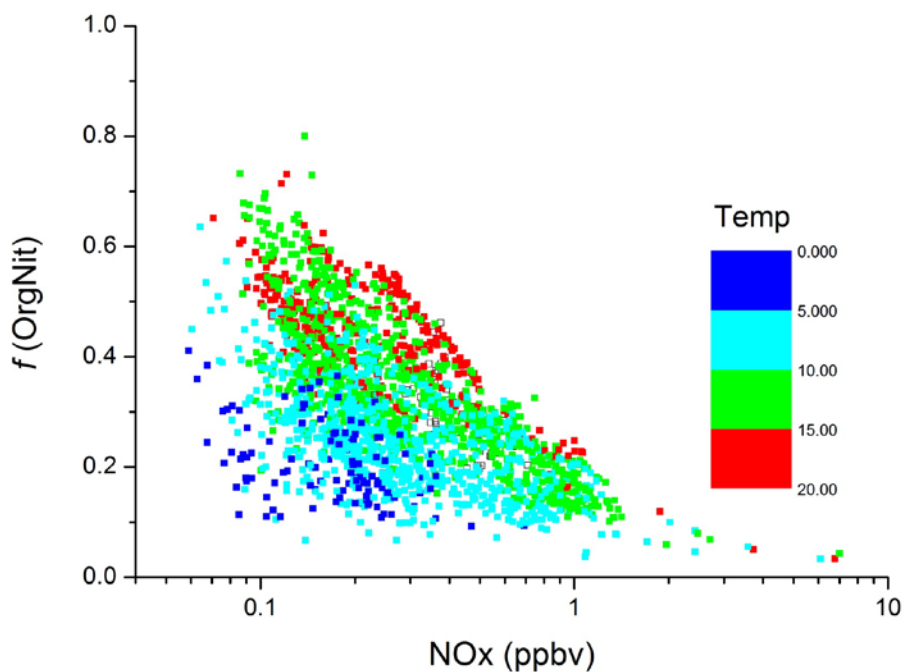
NO<sub>y</sub> = total reactive nitrogen, VOC = Volatile organic compound, OVOC = oxidized VOC, HOMs = Highly oxidized, multifunctional organic compounds.

- **Preliminary results and conclusions**

- The data from the IBairn campaign were discussed in a series of presentations at the recent data-meeting (15/16th February 2017) at the MPI-Mainz. While a limited number of datasets are already available in final format just five months after the campaign, many are still being worked on. The following preliminary results are a small selection from the analyses performed to date and do not cover all aspects of the scientific objectives or of the ongoing analyses.

- *Organic nitrates and NO<sub>x</sub>*

- Organic nitrates as measured by the 5C-TD-CRDS instrument represented an important reservoir / sink of NO<sub>x</sub> during the September campaign. This is illustrated in Figure 1, which shows how the fraction

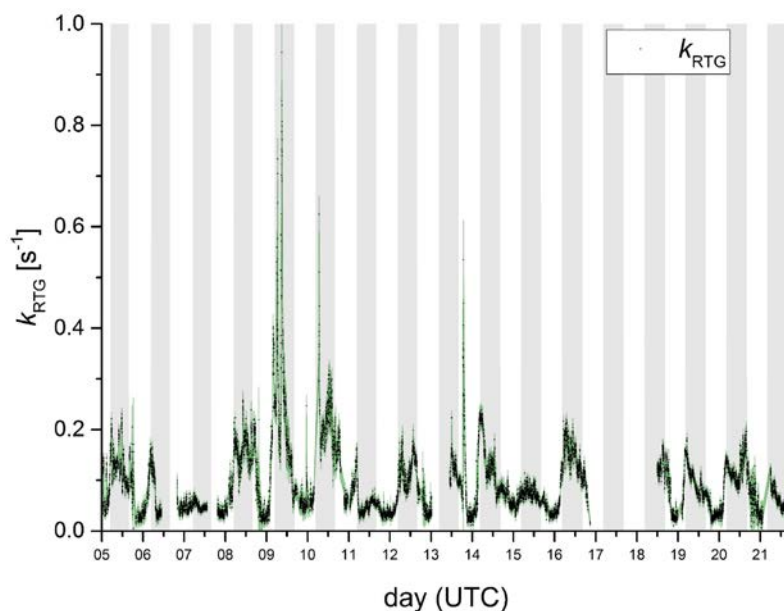


**Figure 1.** The sequestering of NO and NO<sub>2</sub> as organic nitrates.

of NO<sub>x</sub> which is sequestered as organic nitrates  $f(\text{OrgNit}) = (\Sigma\text{PNs} + \Sigma\text{ANs}) / (\Sigma\text{PNs} + \Sigma\text{ANs} + \text{NO} + \text{NO}_2)$  changes as air masses age. Fresh pollutant plumes (high NO<sub>x</sub>) contain little organic nitrate, whereas when NO<sub>x</sub> is low  $f(\text{OrgNit})$  can increase to as high as 0.8 during the daytime (higher temperatures) or about 0.4 during the night (lower temperatures). Averaged over the entire campaign, peroxy nitrates were about 15 % and alkyl nitrates about 10 % of the sum of organic nitrates plus NO<sub>x</sub>.

- *NO<sub>3</sub> and its lifetime in the boreal forest*

- The NO<sub>3</sub> radical concentrations were below the detection limit (< 0.5 pptv) of the 5C-TD-CRDS instrument during the entire campaign, indicating high reactivity (short lifetime). The  $\tau\text{-NO}_3$  instrument provided the first-ever measurement of NO<sub>3</sub> reactivity in the boreal forest, which varied between ~ 0.05 and 1 s<sup>-1</sup> as illustrated in Figure 2.



**Figure 2.** Time series of  $\text{NO}_3$  reactivity ( $\text{s}^{-1}$ ) during IBAIRN. The green-shading indicates total uncertainty.

- When combined with the production rate for  $\text{NO}_3$ , the measurements of its loss rate constant ( $k_{\text{RTG}}$ ) show that  $\text{NO}_3$  levels are expected to be less than 1 pptv. The highest reactivity of  $\sim 1 \text{ s}^{-1}$  (during the night on 09<sup>th</sup> of September) coincides with high concentrations of terpenes coming from the local saw mill (5 km to the south east). Otherwise, the highest reactivities coincided with strong temperature inversions and are the result of a stable, shallow boundary layer in which biogenic emissions accumulate at night. On few nights, vertical gradients (8-25 m) in  $\tau\text{-NO}_3$  were measured, indicating that the highest reactivity was at ground level. No gradient was observed for the turbulently mixed, daytime boundary layer.
- At this early stage, we can already say that the IBAIRN dataset contains some highly interesting observations that, with ongoing detailed analysis, will provide significant insight into gas- and particle-phase chemistry in the boreal forest. At the recent data meeting in Mainz we identified several topics for the Finnish and German scientists involved to collaboratively work on that we expect to result in a series of IBAIRN-related publications and will provide data for PhD students at both institutes.
- **Multidisciplinary approach**
- Combining the instruments and skills available from the Finnish and German institutes involved in IBAIRN has resulted in a very comprehensive dataset that covers many aspects of gas-phase chemistry and particle-composition in the boreal environment. We have found the SMEAR site to be an ideal location for this type of collaboration, which has been very fruitful and which we expect to lead to several joint publications.
-



## *ACCESS TO RESEARCH INFRASTRUCTURES*

- **Outcome and future studies**

- The outcome of the IB AIRN project is a comprehensive dataset covering many aspects of the interaction between the biogenic emissions of the boreal forest and pollutant emissions in this low-NO<sub>x</sub> environment. Although the detailed analysis of the data is in its infancy, we have already identified several interesting topics to pursue as joint publications. Potential future studies with a sub-set of the instruments deploy in IB AIRN have been discussed in order to investigate the seasonality of some of the observations made and to further investigate open questions that arise from further analysis.