

Project Number 282910

ÉCLAIRE

**Effects of Climate Change on Air Pollution Impacts and Response
Strategies for European Ecosystems**

Seventh Framework Programme

Theme: Environment

**D1.3 – 2 x 6 weeks of campaign-based fluxes of VOCs, NH₃ and NO_x at
selected sites**

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Start Date of Project: **01/10/2011**

Duration: **48 months**

Organisation name of lead contractor for this deliverable : **NERC**

Project co-funded by the European Commission within the Seventh Framework Programme		
Dissemination Level		
PU	Public	<input type="checkbox"/>
PP	Restricted to other programme participants (including the Commission Services)	<input checked="" type="checkbox"/>
RE	Restricted to a group specified by the consortium (including the Commission Services)	<input type="checkbox"/>
CO	Confidential, only for members of the consortium (including the Commission Services)	<input type="checkbox"/>

1. Executive Summary

This delivery encompasses the generation of additional campaign-based measurements at the 9-site ECLAIRE flux network, depending on the capability and instrument availability at the individual sites.

Objectives:

This Deliverable is associated with the objective to deliver campaign-based measurements of fluxes of volatile organic compounds (VOCs), reactive nitrogen compounds other than NO (e.g. NH₃) and aerosol components of a quality suitable for the development and improvement of surface exchange parameterisations.

2. Activities:

At the kick-off meeting it was decided not to impose common time windows for these measurements, but to enable the different groups to make the most of their instrumentation when available and to target periods of particular interest for the particular field site.

Highlights of the measurements that were realised were:

VOCs. Fluxes of volatile organic compounds were measured at Auchencorth (by PTR-MS), Hyttiala (by PTR-MS), Ispra (by PTR-ToF-MS and with a fast isoprene sensor) and Castelporziano (by PTR-MS; measurements were not funded by ECLAIRE). In addition, information on VOC fluxes at Bosco Fontana were obtained during the Integrated Campaign (Deliverable 1.5). VOC flux measurements at Speuld were analysed and published.

Ammonia. Fluxes of ammonia were made at Grignon, Posieux, Auchencorth, Speuld and at Bosco Fontana during the Integrated Campaign. Flux measurements were planned and prepared for Petrodolinkoye, but eventually could not be realised because the flux measurement site was first hit by a tornado reducing the amount of electrical power available at the site and later the political situation in the Ukraine made it impossible to import/export instrumentation.

Oxidised nitrogen compounds. Detailed eddy-covariance flux measurements of NO were made at Posieux and Grignon. NO₂ eddy-covariance flux measurements by LIF were made at Auchencorth Moss and by photolytic converter coupled to a fast chemiluminescence NO analyser at Posieux. At Posieux a fast NO analyser was coupled to three inlets, operated at different temperatures, to iteratively measure fluxes of NO, NO₂, NO_y and NH₃. In addition, HONO and HNO₃ gradient were measured at Auchencorth and at Bosco Fontana during the integrated campaign. Measurements of HONO gradients by LOPAP were analysed for Grignon.

Fluxes of aerosol chemical components were measured by Aerosol Mass Spectrometer eddy-covariance and wet-chemical gradient system at Auchencorth and Bosco Fontana.

Table 1. Overview of the campaign-based flux measurements across the project.

Eco-system	Site	VOCs	NH ₃	NO _y	Aerosol
Forest	Hyytiala (FI)	Various (PTR-MS)			Total number
	Speuld (NL)	Analysis of NitroEurope measurements	Wet chemistry (GRAHAM gradient)		
	Bosco Fontana (IT)*	Various (PTR-MS; PTR-ToF-MS)	Wet chemistry (GRAEGOR gradient)	HNO ₃ , HONO (GRAEGOR gradient)	Water-soluble (GRAEGOR) and non-refractory (AMS EC)
	Ispra Forest (IT)	Various (PTR-ToF-MS); isoprene (FIS)			
	Castelporziano Forest [#]	Various (PTR-MS)			
Grassland	Bugac (HU)				
	Auchencorth Moss (UK) [§]		Wet chemistry (GRAEGOR gradient)	HNO ₃ , HONO (GRAEGOR gradient); NO ₂ EC (LIF)	Water-soluble (GRAEGOR) and non-refractory (AMS EC)
	Posieux (CH)		By total N analyser EC	NO/NO ₂ /NO _y EC	
Arable	Grignon (FR)		Wet chemistry (ROSASA gradient)	Analysis of HONO gradient measurements (LOPAP)	
	Potrodolinskoye (UE)		Unsuccessful		

* Realised as part of the integrated campaign; [#] associated site; measurements not funded by ECLAIRE; [§] Final intensive measurements still ongoing.

3. Results:

The deliverable is the data themselves, not a full report about the data. Here we outline a few highlights from the database:

- a) *High isoprene fluxes over moorland.* The first measurement period at Auchencorth Moss included some for Scotland atypically warm days, during which surprisingly high emissions of isoprene were detected (Figure 1). The fluxes imply an average emission factor (at reference conditions of $T=30^{\circ}\text{C}$ and $\text{PAR} = 1500 \mu\text{mol m}^{-2} \text{s}^{-1}$), in the region of $1.3 \text{ mg m}^{-2} \text{ hr}^{-1}$, which is much larger than previously reported for this type of ecosystem. The only plant species at the site known to emit isoprene are sphagnum mosses. Further investigations are needed whether it is indeed these mosses that dominate the flux or whether some other, so far unidentified, species make a major contribution to the flux.

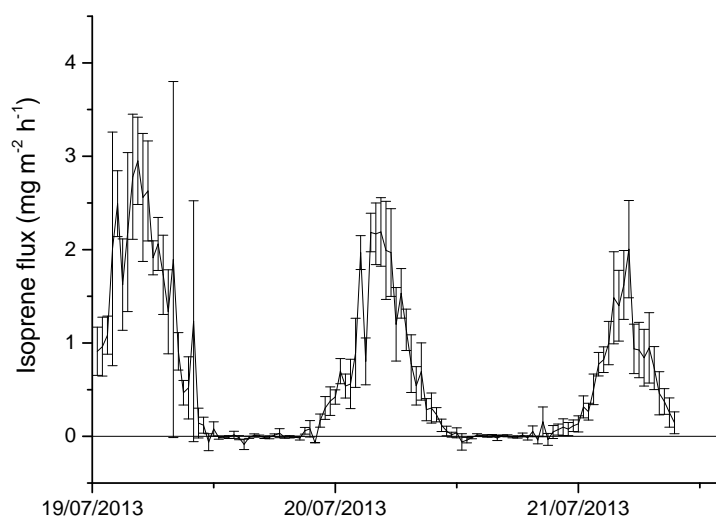


Figure 1. Example of Isoprene fluxes above the grassland/moorland site at Auchencorth Moss during a warm summer period.

- b) *Total reactive nitrogen measurement.* Good closure was achieved when comparing the total reactive nitrogen measurement at Posieux with the sum of the individual gaseous components NO, NO₂ and NH₃ (Figure 2). This agreement validates the Nr converter, but also suggests that other nitrogen components including PAN, HONO as well as aerosol nitrate and ammonium are minor contributor to the N budget at this site during the measurement period.

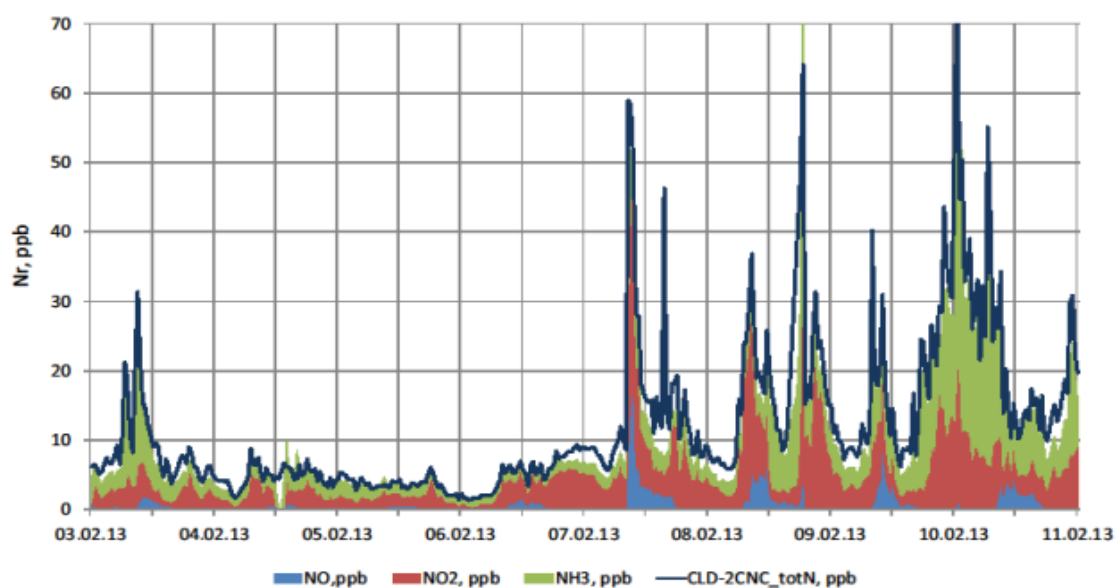


Figure 2. Comparison of the total reactive nitrogen measurement at Posieux with the sum of the major gaseous components.

- c) *Isoprene flux measurements over a mixed oak forest.* Oak forests are estimated to be the largest single biogenic contributor to European isoprene emissions, but the emission factor database consists of only three measurements. ECLAIRE is improving greatly over the situation, providing new measurements of isoprene fluxes over two Italian and, through a collaboration at a French site, also a French site.

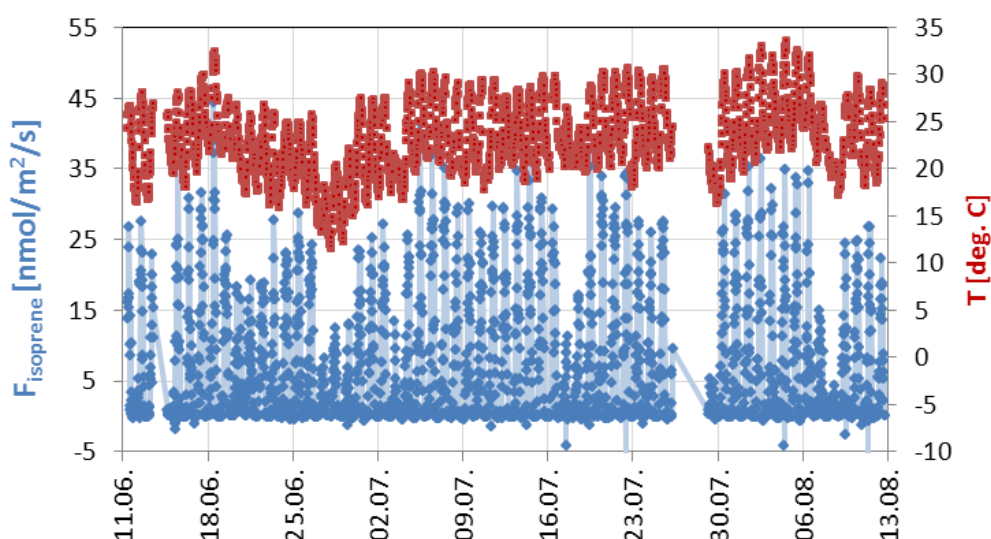


Figure 3. Time-series of isoprene fluxes measured at the Ispra mixed oak forest in relation to temperature.

4. Milestones achieved:

The associated milestones MS 3 and 4 have been mainly achieved in that most data have been submitted to the database. Some fluxes are still being processed due to the complexity of the data and the development status of the approach (e.g. PTR-ToF-MS at Ispra) and some last measurements are still ongoing (e.g. aerosol and 2nd VOC fluxes at Auchencorth Moss) as these got delayed due to instrument problems.

5. Deviations and reasons:

These measurements relied on state-of-the-art equipment, some of it still being developed, typically shared with many other projects. Thus the measurements had to be scheduled with other commitments in mind and some were delayed due to instrument problems. In particular, instrument problems led to a delay of the second campaigns at Auchencorth and Posieux.

Two anticipated NH₃ flux measurements could not be realised: at Bugac ammonia flux measurements turned out to be impossible because the power supply could not be upgraded due to the fact of this site being situated within a National Park. At Petrodolinskoye, ammonia flux measurements could not be initiated because first a tornado destroyed the power supply and later the political situation in Ukraine made the import / export of equipment from other countries impossible.

While some of the measurements were compromised, additional opportunities also arose since the DoW was developed. For example, the opportunity arose to measure VOC fluxes at Ispra Forest not only with a fast isoprene sensor, but also by PTR-ToF-MS, through a collaboration between JRC Ispra and the University of Innsbruck. At Auchencorth, measurements of the NO₂ flux by laser induced fluorescence was realised by collaboration between NERC/CEH and the University of l'Aquila, with additional TNA support through the ACTRIS project.

Further refinements of the TRANC total nitrogen converter developed in collaboration between Agroscope, the Max Planck Institute Mainz and Ecophys enable flux measurements of NO, NO₂, reduced nitrogen and NO_y with the same instrument.

6. Publications:

Analysis of the measurement results is only just starting properly, now that the full dataset is becoming available. Many publications are planned on site-specific reporting of results, site-specific model applications as well as cross-site analyses.

7. Meetings:

Meetings to prepare the measurements, review measurement status and to identify problems happened during the first three ECLAIRE annual meetings (kick-off in Brescia, 24-27 Oct 2011; 2nd annual meeting in Edinburgh, 15-18 Oct 2012; 3rd annual meeting in Zagreb, 22-24 Oct 2013).

In addition, representatives from the flux sites met at NERC / CEH Edinburgh 26-28 May 2014 to discuss further harmonisation of ozone flux measurements and reporting and to make a start on the data analysis.

8. List of Documents/Annexes:

Most of the data is still being analysed and written up.

Copeland, N.; Cape, J.N.; Nemitz, E.; Heal, M.: Volatile organic compound speciation above and within a Douglas fir forest. *Atmos. Environ.* 94, 86-95, 2014.

Kalogridis, C.; Gros, V.; Sarda-Esteve, R.; Langford, B.; Loubet, B.; Bonsang, B.; Bonnaire, N., Nemitz, E., Genard, A.-C., Boissard, C., Fernandez, C., Ormeno, E., Baisnee, D., Reiter, I., Lathiere, J.: Concentrations and fluxes of isoprene and oxygenated VOCs at a French Mediterranean oak forest. *Atmos. Chem. Phys. Discuss.*, 14, 871-917, 2014 (accepted for publication in ACP subject to minor revisions).