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**defra**  
Department for Environment  
Food and Rural Affairs

**SID 4**

## Annual/Interim Project Report for Period **Jun-Aug08**

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### **Project details**

1. Defra Project code	RMP 1906
2. Project title	UK National Ammonia Monitoring Network
3. Defra Project Manager	Sarah Honour
4. Name and address of contractor	Centre for EEcology & Hydrology (CEH) Edinburgh Research Station Bush Estate Penicuik Midlothian  Postcode EH26 0QB
5. Contractor's Project Manager	Sim Tang
6. Project: start date .....	01/05/03
end date .....	31/12/08

## Scientific objectives

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7. Please list the scientific objectives as set out in the contract. If necessary these can be expressed in an abbreviated form. Indicate where amendments have been agreed with the Defra Project Manager, giving the date of amendment.

### **Operate and maintain network of ammonia concentrations across the UK**

The network will be continued on a monthly basis, maintaining the liaison with site operators and visiting sites for equipment servicing. The standard QA/QC procedures for the Ammonia Network developed by CEH would be followed. Analysis of air concentrations would be made at each site in a timely fashion to ensure early identification of problems.

### **Analysis of NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> concentration fields over the UK.**

The UK NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> concentration fields will be analysed at a resolution of 10 km x 10 km, with the data from local and mesoscale variability studies used to assess site representativity and sub-grid variability.

Results will be compared with the FRAME model (link to contract "Modelling the Deposition and Concentration of Long Range Air Pollutants" EPG 1/3/202). Seasonal variability will be examined in relation to the main source sectors in different regions, compensation points and inter-annual variability in relation to weather patterns.

### **Application of the results to provide maps of UK NH<sub>3</sub> concentration and dry deposition.**

The interpolated and modelled estimates incorporating measurement calibration will be applied at a 5 km resolution on an annual basis to investigate UK concentrations fields and dry deposition of NH<sub>3</sub>. Analysis of the results will provide recommendations on the suitability of the approaches for different purposes.

In addition to the objectives noted in the tender, the deposition models will be applied to estimate dry deposition of aerosol NH<sub>4</sub><sup>+</sup> in the UK. The analysis will provide an estimation of the effect of new data on total dry deposition budgets and NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> export from the UK. This will be considered in relation to ongoing work in other contracts ("Acid Deposition Processes" and "Modelling the Deposition and Concentration of Long Range Air Pollutants") on the overall budget of NH<sub>3</sub> for UK.

### **Reporting of monitoring results**

The results will be reported by a) oral and written reports to the Department, b) oral reporting to site operators at site operators meetings (approximately 35-50 people anticipated to attend each meeting, with their travel and subsistence paid by the contract), c) graphs and tables on the website of the NAMN ([www.uk-pollutantdeposition.ceh.ac.uk](http://www.uk-pollutantdeposition.ceh.ac.uk)) and d) publishing of papers in peer review and other international literature.

## Summary of Progress

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8. Please summarise, in layperson's terms, scientific progress since the last report/start of the project and how this relates to the objectives. Please provide information on actual results where possible rather than merely a description of activities.

## UK National Ammonia Monitoring Network

Contributing Authors: Y.S. Tang, N. van Dijk, I. Simmons, M. Anderson, N. Weir & M.A. Sutton

### **Operation of UK NAMN**

- The UK National Ammonia Monitoring Network (NAMN) continues to operate smoothly through the transition into the new extension to the contract (1<sup>st</sup> May – 31<sup>st</sup> December 2008). The new end date of the NAMN contract of 31<sup>st</sup> December 2008 is now synchronised with the end date for the UK Nitric Acid Monitoring network contract.
- Data from the network are available on the website <http://www.uk-pollutantdeposition.ceh.ac.uk/networks>
- Current status of NAMN:
  - Total number of sites in the UK NAMN = 96
  - Sites operating with DELTA system (active denuder method) = 59
  - Sites operating with ALPHA samplers (passive method, NH<sub>3</sub> only) = 50
  - Intercomparison sites with both DELTA & ALPHA operated in parallel = 13 (this allows calibration of NH<sub>3</sub> measurements by ALPHA against the DELTA reference method)
  - Of the DELTA sites:
    - DELTA sites sampling only NH<sub>3</sub> = 13
    - DELTA sites sampling both NH<sub>3</sub> and aerosol NH<sub>4</sub><sup>+</sup> = 46
    - DELTA sites sampling NH<sub>3</sub> / NH<sub>4</sub><sup>+</sup>, which also samples gaseous HNO<sub>3</sub>, SO<sub>2</sub>, HCl & aerosol NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) as part of the UK Nitric Acid Monitoring Network = 30 (The 30 site UK Nitric Acid Monitoring network is operated as a sub-contract to AEA Technology under the defra-funded UK Acid Deposition Monitoring Network contract).
- S15 Llyncllys Common: DELTA sampling (from 1<sup>st</sup> September 1996 to present) and passive sampling (with diffusion tubes from 1<sup>st</sup> November 1996 to 1<sup>st</sup> May 2000, replaced by the high sensitivity ALPHA samplers from 3<sup>rd</sup> May 2000 onwards) are both implemented at this site. Llyncllys Common is one of 13 NAMN intercomparison sites used to calibrate ALPHA samplers against the reference DELTA methodology. The monitoring equipment is located in a private garden at Llyncllys Common. The owners, Mr David Pedlow and his wife (Mrs Jackie Pedlow) have acted as local site operators for the site since the start of the project. Since Spring of this year, the property has been up for sale, but suitable buyers have not been found, and monitoring work at the site has continued in the meantime. Mr and Mrs Pedlow have promised that they will make every effort to persuade the buyer / new owner to continue with the ammonia monitoring work, and will keep CEH informed.
- A new passive ammonia site was set up at the Llydaw ECN Site, close to the S29Dyffryn Mymbyr and S100 Plas Y Brenin site. Monitoring commenced 5<sup>th</sup> June 2008. Monitoring at this site was viewed as useful for examining local-scale variability in the area, as differences in NH<sub>3</sub> concentrations were observed between the long-established S29 Dyffryn Mymbyr site and the new S100 Plas Y Brenin site (established as part of the new expanded Nitric Acid Monitoring network).
- S38 Sheffield: DELTA system is located inside the walled gardens of Tapton Gardens, University of Sheffield. The site has been sold off by the University to developers and is scheduled for closure by end of December 2008. A new research site has been offered by the University for relocation of equipment. Details of the site have not yet been received, but once information has been obtained, then plans will be made to relocate the DELTA equipment before the end of this year, if possible. Long-term monitoring results at this site are shown in Figure 1.
- S38B Weston Park (Sheffield Museum met. enclosure, sk339873). NH<sub>3</sub> measurements with passive (ALPHA samplers) have been implemented at this site (~0.5 km southeast of Tapton Garden location) since May 2004. The samplers are located within the secure met. enclosure on the grounds of the museum. NH<sub>3</sub> measurements were started at this site to check for variability in NH<sub>3</sub> concentrations, since the Tapton garden site is a sheltered location. Monitoring results at this site since May 2004 are shown in Figure 2. Photo of site (met. enclosure) is shown in Figure 3.

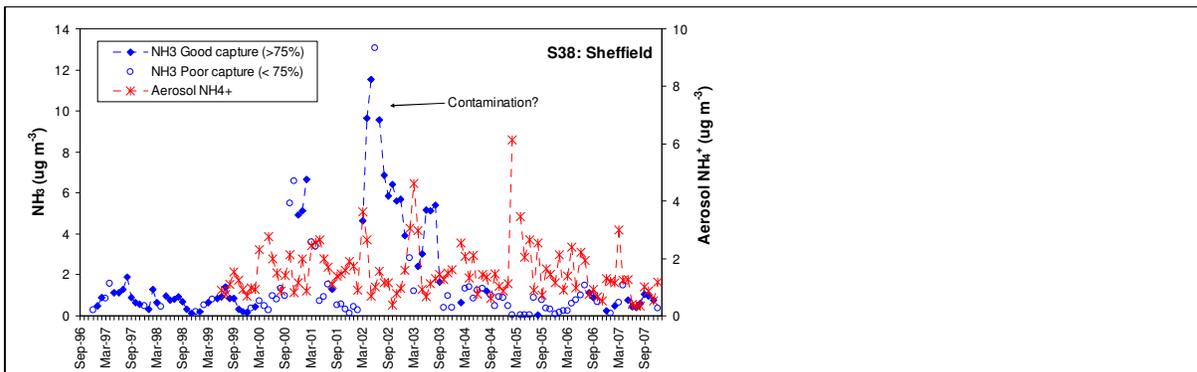


Figure 1. Monitored monthly NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> concentrations from DELTA measurements at S38 Sheffield (Tapton Gardens, University of Sheffield). Mean NH<sub>3</sub> = 1.6 μg NH<sub>3</sub> m<sup>-3</sup>. Mean NH<sub>4</sub><sup>+</sup> = 1.5 μg NH<sub>4</sub><sup>+</sup> m<sup>-3</sup>.

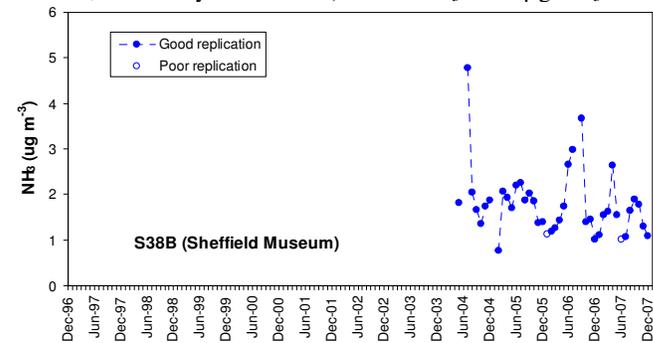


Figure 2. Monitored monthly NH<sub>3</sub> concentrations from ALPHA measurements at S38B Weston Park (Sheffield Museum met. enclosure). Mean NH<sub>3</sub> = 1.7 μg NH<sub>3</sub> m<sup>-3</sup>.



Figure 3. S38B Weston Park (Sheffield Museum sk339873). ALPHA equipment is located within the secure met. enclosure on the grounds of the Museum.

- There are three remote sites in the UK NAMN where mains electricity is not accessible: S21 Glensough (also UK HNO<sub>3</sub> network site), S22 Moorhouse (also UK HNO<sub>3</sub> network site) and S25 Sourhope (monitoring NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>). At these sites, specially built wind/solar powered DELTA systems were deployed which have been operating for over 10 years, and which are beginning to show signs of wear and tear. At S22 Moorhouse, a broken wind turbine was replaced in August 2008. At S25 Sourhope, faults have developed with the solar panels, wind turbines and batteries. Several visits have been made to the site to service / replace faulty parts over the past 2 years, but the plan in the long-term is to replace the entire system with a new one.
- Recognising the need to replace ageing systems, a new solar / wind solar powered DELTA system has been designed and built at CEH, to ensure smooth operation and continuity of measurements.
- The new wind/solar DELTA system (Figure 4, LHS) is currently being tested in the field at CEH. A new design of the DELTA system / enclosure has also been constructed (Figure 4, RHS) and being tested in the field.
- S25 Sourhope is top priority and it is planned that the first new wind/solar powered system will be installed at Sourhope during November 2008.

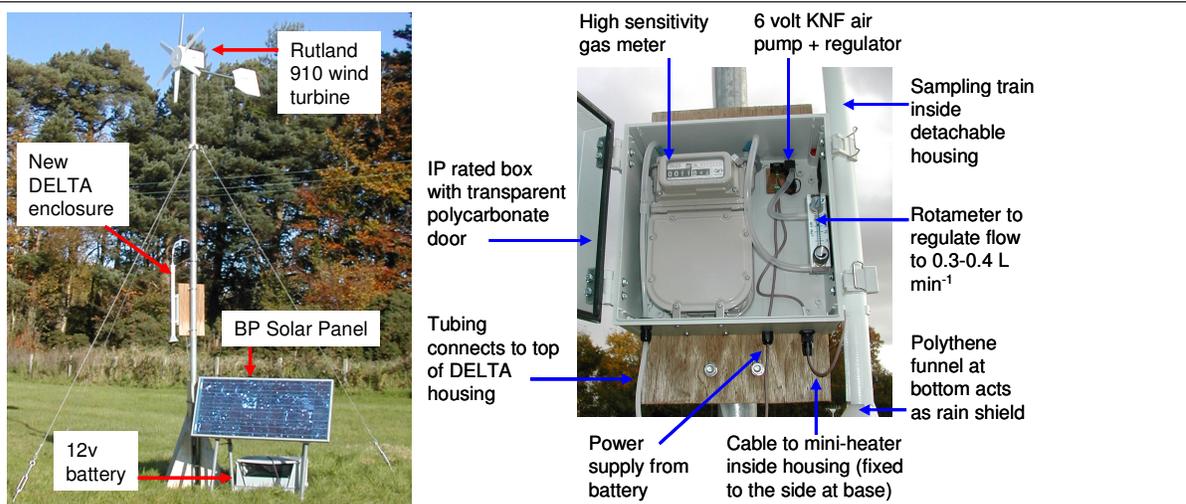


Figure 4. LHS: new wind/solar powered DELTA system. RHS: Front view, with door open, showing detail of components in the new enclosure of the DELTA system.

- The new design DELTA system consists of an IP65 rated enclosure to house the gas meter and a 6 volt KNF air pump (used in conjunction with a rotameter to regulate the air flow between 0.3 – 0.4 / min<sup>-1</sup>). The enclosure has a transparent UV-resistant polycarbonate door, so that gas meter readings can be taken without the need to open the enclosure. There is a separate housing for the DELTA sampling train, which is attached to the side of the enclosure by means of spring clips. The housing consists of a length of PVC tube (3 cm internal diameter) to house the sampling train in a vertical orientation. This is important to minimise any sedimentation of larger aerosol during sampling. At the base is a mini-heater that is fixed to the inside of the sampling train housing. This serves to maintain temperature within the housing a few degrees above ambient. At the top is a screw cap with a hole drilled in the centre. Gland nut fittings providing a water-tight fit connects LDPE tubing to the air pump in the enclosure. A 90mm LDPE funnel, with the stem trimmed to accommodate the inlet of the sampling train is fitted to the bottom. The funnels act as rain shield for the air sampling. The length of the PVC tube can be varied, giving flexibility to accommodate different configuration of sampling trains.
- Work in the local scale variability study in a Southern Scottish Landscape is progressing well. The first years monitoring results on NH<sub>3</sub> was reported in the 2007 annual NAMN report. Monitoring work is scheduled for completion at the end of December 2008.

#### **Other activities**

- CEH continues to contribute to UNECE and EMEP TFMM working groups (Ulrike Dragosits, Mark Sutton).
- CEH continues to contribute to HSE/CAR/WG5 and CEN TC264 WG11 (Sim Tang). The CEN committee is concerned with ambient air monitoring; TC264 covers ambient, indoor and stack monitoring and WG 11 is specifically interested in diffusive sampling methods (Chairman = Dr T.L Hafkenscheid of RIVM, NL). Four standards have been written and published. These are respectively method performance specifications for diffusive sampling methods, and guidance documents on using diffusive sampling in ambient air and in indoor air.  
  - prEN 13528 (*Ambient air quality - Diffusive samplers for the determination of concentration of gases and vapours*) parts 1-3.
  - Part 4, prEN 14412 (*Indoor air quality – Diffusive samplers for the determination of gases and vapours – Guide to selection use and maintenance*) is printed as a CEN document.
- The next CEN TC264 WG11 meeting is scheduled for November 2008, to take place at the Joint Research Centre (JRC) Ispra, Italy.
- JRC has been asked by the Directorate General Environment (DG-ENV) of the European Commission to conduct a pre-normative study to support the development of a CEN standard method for NO<sub>2</sub> monitoring in ambient air using diffusive samplers. At the meeting of the CEN TC 264 WG11, held in Brussels in June 2007, it was decided to include the following diffusive samplers in the pre-normative study: the Radiello sampler, the Ogawa sampler, the Passam sampler and the Palmes tube. Two meetings of experts (to which CEH - Sim Tang, was invited) are organised by JRC in order to review and discuss the draft method for monitoring NO<sub>2</sub> that will be prepared by the project coordinator. The first was held on 2-3 October 2008, and the 2<sup>nd</sup> meeting is scheduled for 27-28<sup>th</sup> November, taking place after the CEN TC264 WG11 meeting on 26<sup>th</sup> November 2008

- Previous proposals for the standardization of diffusive sampling methods for ammonia put to DG Environment were rejected on the basis that “NH<sub>3</sub> is not regulated”. Efforts will continue to be made within the CEN TC264 WG11 to convince European Commission of the need to prepare a similar standard for ammonia.
- NitroEurope IP: NEU Level 1 Inferential N Flux Network (coordinated by Sim Tang, CEH), using the DELTA methodology from the UK ammonia and nitric acid monitoring networks (NEU: [www.nitroeuropa.eu](http://www.nitroeuropa.eu)). Monitoring work is ongoing, and the first years’ data is now available.
- A new network, the ECBN - Environmental Change Biodiversity Network is currently being set up across the UK (Figure 5). There will be around 50 sites, comprising largely of National Nature Reserves, as well as the 12 existing Environmental Change Network (ECN) terrestrial sites ([www.ecn.ac.uk](http://www.ecn.ac.uk)) that form the core of the network. Targeted monitoring of air pollution and climate change are proposed to assess impacts on biodiversity. There are 13 new sites in Wales all based on NNR’s: Coedydd Aber, Newborough, Warren, Cors Erddreiniog, Y Berwyn, Cors Fochno, Cors Caron, Rhos Llaur Cwrt, Tycanol, Stackpole, Skomer, Oxwich, Ogof Ffynnon Dhu and Cwm Cadlan. All the Welsh sites are active. Only 15 English sites are in operation plus one Scottish site.
- All the Welsh sites have automatic weather stations and they have staff that will be visiting the site once a month. Funding has been awarded for the Welsh sites by CCW until 2011. One of the protocols they (CCW) hope to cover is ammonia by passive sampling. CCW has approached CEH to ask, either a) if it would be possible to expand the UK NAMN to include new Targeted Monitoring Sites, since the existing 12 ECN sites are already part of the network, or b) if there is no scientific need / interest to add the new sites to the network, then would it be possible for CCW to contribute to the Network to include these sites in the UK NAMN?
- CCW wants to let a contract to get the ammonia monitoring work started soon. GRADKO offers very low-cost ammonia measurements with diffusion tubes, which is about a third of the cost of ammonia measurements with ALPHA samplers by CEH. However, the higher cost at ALPHA measurements reflects the stringent adherence to protocols that include ongoing calibration and validation of the ALPHA samplers against the reference DELTA methodology, plus advice on siting, deployment and interpretation of data that can be offered by CEH. The ECBN steering committee has apparently acknowledged that the diffusion tube is not as good as the ALPHA samplers, but ammonia measurements with GRADKO diffusion tube were proposed and accepted nonetheless on the basis of cost.
- The following cautions were communicated by CEH to CCW: “The diffusion tubes sample air very slowly, and over the course of a month, collects about 0.15 m<sup>3</sup> of air only! Typically, the coated grids (which collect NH<sub>3</sub>) on the diffusion tubes are then extracted into 1.5 ml deionised water. This means that the limit of detection for the diffusion tubes is around 2 ug NH<sub>3</sub> m<sup>-3</sup> for monthly sampling (depending on quality of blanks. If blanks are poor /variable, then the detection limit will be even worse). For the ECBN sites (NNRs), the monthly mean concentrations will probably be less than 2 ug NH<sub>3</sub> m<sup>-3</sup> (especially over the winter months). Which means that CCW will be wasting money (even if gradko is offering very cheap prices) if the monthly NH<sub>3</sub> concentrations are < 2 ug NH<sub>3</sub> m<sup>-3</sup>. If you do go down the gradko route, please make sure that you ask gradko to provide an extra cap to go over the membrane - its a long story, but briefly, gradko supply prepared diffusion tubes to their customers with the membrane uncovered. When the membrane is not covered up, the diffusion tube is already sampling air from the time of preparation, before they even reach their intended sampling location, leading to potential contamination due to storage and transit (which has been demonstrated, and which is particularly important when you're monitoring at low concentration sites). When the membrane is covered up, sampling begins only when the cap is removed, and sampling stops when the membrane is covered up again. “

#### References

- Tang Y.S., Cape J.N., Sutton M.A. (2001) Development and types of passive samplers for monitoring atmospheric NO<sub>2</sub> and NH<sub>3</sub> concentrations. In Proceedings of the International Symposium on Passive Sampling of Gaseous Pollutants in Ecological Research. The Scientific World, 1, 513-529.
- Tang, Y.S & Sutton M.A. (2003) A new passive sampler for long-term ambient monitoring of atmospheric ammonia. The Diffusive Monitor Newsletter: Dec 2003 issue 14 (<http://www.hsl.gov.uk/publications/diffuse-monitor.htm>).

- Following the above communications, CCW is presently reconsidering their options for ammonia monitoring. However, they have indicated that they will go ahead with the GRADKO diffusion tubes for an initial trial.

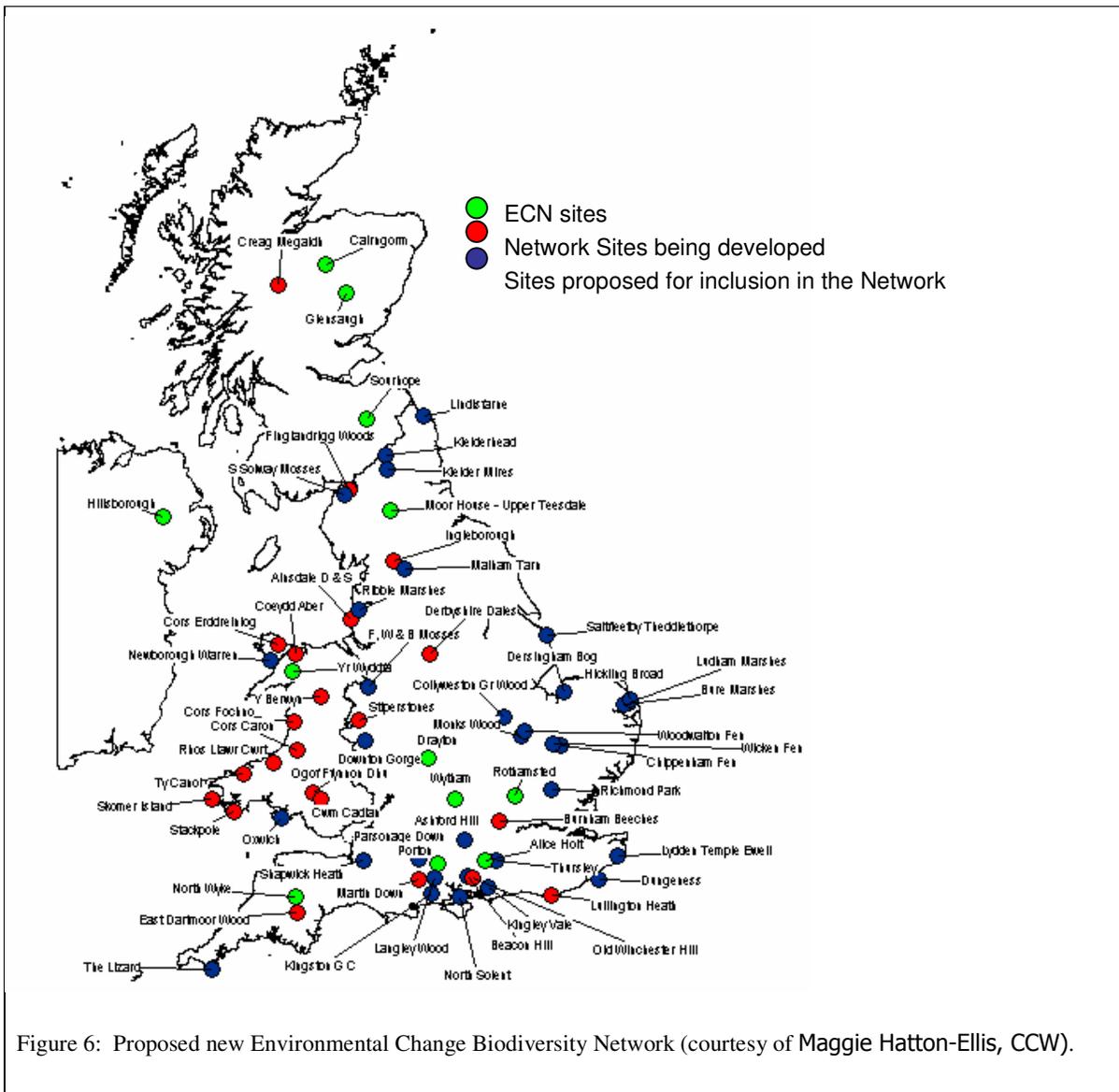


Figure 6: Proposed new Environmental Change Biodiversity Network (courtesy of Maggie Hatton-Ellis, CCW).

### Amendments to project

9. Are the current scientific objectives appropriate for the remainder of the project? ..... YES  NO

If NO, explain the reasons for any change giving the financial, staff and time implications.

**Contractors cannot alter scientific objectives without the agreement of the Defra Project Manager.**

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## Progress in relation to targets

10. (a) List the agreed milestones for the year/period under report as set out in the contract or any agreed contract variation.

It is the responsibility of the contractor to **check fully that all milestones have been met** and to provide a detailed explanation when they have not been achieved.

Milestone		Target date	Milestones met	
Number	Title		In full	On time
1	Annual report: Analysis of spatial and temporal patterns of NH <sub>3</sub> and NH <sub>4</sub> <sup>+</sup> over the UK, and reporting on other monitoring activities.	30/05/2008	Yes	No Delivered 21/08/08
2	Quarterly progress report: Continuation of NH <sub>3</sub> and NH <sub>4</sub> <sup>+</sup> monitoring in network between contracts, incorporating any agreed revisions.	31/08/2008	Yes	No Submitted 17/10/08. Resubmitted 24/10/08 on SID4 form
3	Quarterly progress report: Monitoring data, contributions to NitroEurope project, UNECE AEG and TFMM, and GEN TC264/WG11 on passive sampling with respect to NH <sub>3</sub> and initial results from local variability study at Auchencorth.	30/11/2008		
4	Final report: Analysis of long-term trends in spatial and temporal patterns of NH <sub>3</sub> and NH <sub>4</sub> <sup>+</sup> over the UK, including results from local scale variability study.	28/02/2009		

(b) Do the remaining milestones look realistic? ..... **YES**  **NO**

If you have answered **NO**, please provide an explanation.

## Publications and other outputs

11. (a) Please give details of any outputs, e.g. published papers/presentations, meetings attended during this reporting period.

Book chapter. Dragosits U, Dore A.J, Sheppard L.J, Vieno M, Tang Y.S, Theobald M.R. & Sutton M.A (2008) Chapter 11: Sources, Dispersion and Fate of Atmospheric Ammonia in "Nitrogen in the Environment: Sources, Problems, and Management" Second Edition of Nitrogen in the Environment (Elsevier). J.L. Hatfield and R.F. Follett (Eds.) Published 2008.

Jan Willem Erisman, Mark A. Sutton, James Galloway, Zbigniew Klimont and Wilfried Winiwarter (2008) How a century of ammonia synthesis changed the world. Nature Geoscience VOL 1. 636-639.

Hellsten, S., Dragosits, U., Place, C.J., Vieno, M., Dore, A.J., Misselbrook, T.H. Tang, Y.S. and Sutton, M.A. (2008): Modelling the spatial distribution of ammonia emissions in the UK, Environmental Pollution 154, 370-379.

- (b) Have opportunities for exploiting Intellectual Property arising out of this work been identified? ..... YES  NO   
If YES, please give details.

(c) Has any other action been taken to initiate Knowledge Transfer?..... YES  NO

If YES, please give details.

Dissemination of DELTA and ALPHA sampling methodologies to improve Europe-wide monitoring of  $\text{NH}_3$  and  $\text{NH}_4^+$ ,  $\text{HNO}_3$  and related species.

- 1) Implementation of the DELTA system in a European Level 1 Inferential Flux Network (56 sites) under the NitroEurope IP project. Monitoring work commenced in January 2006, to provide monthly speciated measurements of atmospheric  $\text{NH}_3$ ,  $\text{HNO}_3$ ,  $\text{SO}_2$ ,  $\text{HCl}$  and gaseous  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , plus  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (same as UK Nitric acid monitoring network)
- 2) Implementation of the CEH ALPHA samplers in NitroEurope Landscape studies in France, Poland, Denmark, as well as at the Scottish Southern Landscape study site.

Supply of CEH ALPHA samplers as implemented in the UK NAMN to USA (EPA, University of Illinois), Canada (Environment Canada) and Denmark (National Environmental Research Institute) for ammonia monitoring work.

## Future work

12. Please comment briefly on any new scientific opportunities which may arise from the project.

### Estimate contribution of $\text{NH}_4^+$ , $\text{NO}_3^-$ and $\text{SO}_4^{2-}$ to PM

The DELTA methodology provides accurate measurements of trace gas and aerosols (under both the UK NAMN and the integrated UK Nitric acid monitoring network), but does not provide information on aerosol mass concentrations (i.e. PM). A proposal was made under the Defra-funded "NH<sub>4</sub><sup>+</sup> in Agriculture" project to modify / improve the DELTA methodology to provide additional information on PM concentrations and thereby estimate the contribution of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  to PM.

Under the proposal, the existing DELTA technology will be modified to provide a measure of total aerosol mass, in addition to the speciated gas and aerosol concentrations. This involves the addition of a third (Teflon) filter, which will be weighed before and after exposure under controlled conditions. The modified sampling trains are currently being validated against the existing DELTA methodology at three sites of the UK Ammonia / Nitric Acid Monitoring Network, in environments of contrasting aerosol loading (large, medium, low). The sites are S36 London Cromwell Rd, S98 Harwell and S18 Auchencorth Moss, respectively.

Work started in June 2008, and will continue for six 1-month sampling periods. Based on the results, further modifications may need to be implemented that allow PM concentrations to be established without compromising the chemical data.

Once a validated measurement technology has been established, a local transect will be established across an agricultural area with considerable  $\text{HNO}_3$  background concentration for a test period.

## Declaration

13. I declare that the information I have given is correct to the best of my knowledge and belief.

Name

Sim Tang

Date

24/10/08

Position held

Higher Scientific Officer