

Annex 1 Progress on recommendations made in the Fourth Report of the Photochemical Oxidants Review Group in 1997

Defra posed the following additional question to AQEG

Of the recommendations made by the Fourth Report of the Photochemical Oxidants Review Group in 1997, which remain to be implemented, to what extent do they remain valid, and which have been superseded by scientific understanding?

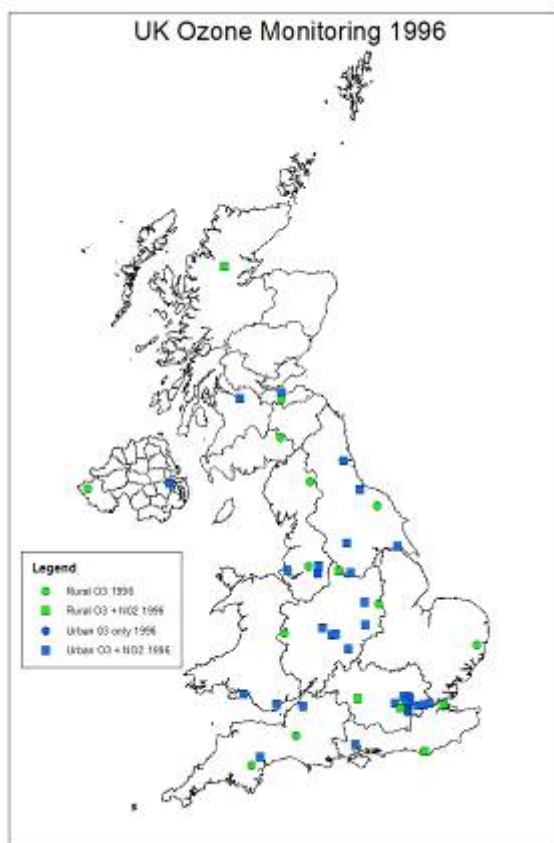
356. Each recommendation from the 1997 PORG report is given in turn in italics. The recommendations in the areas of human health, vegetation and materials are not addressed, because they are not directly discussed in this AQEG report.

A1.1 Ozone monitoring

- **Maintain the rural network to provide the spatial distribution of ozone in the UK and trends with time. Increase the number of monitoring sites to eliminate large areas of uncertain ozone exposure, notably the East Midlands of England, north and west Wales, the Central Highlands of Scotland and inland rural areas of SE England.**

357. Figure A1.1 shows maps with the distribution of ozone sites within the AURN in 1996 and 2007. Sites with co-located NO_2 measurements are indicated.

a)



b)

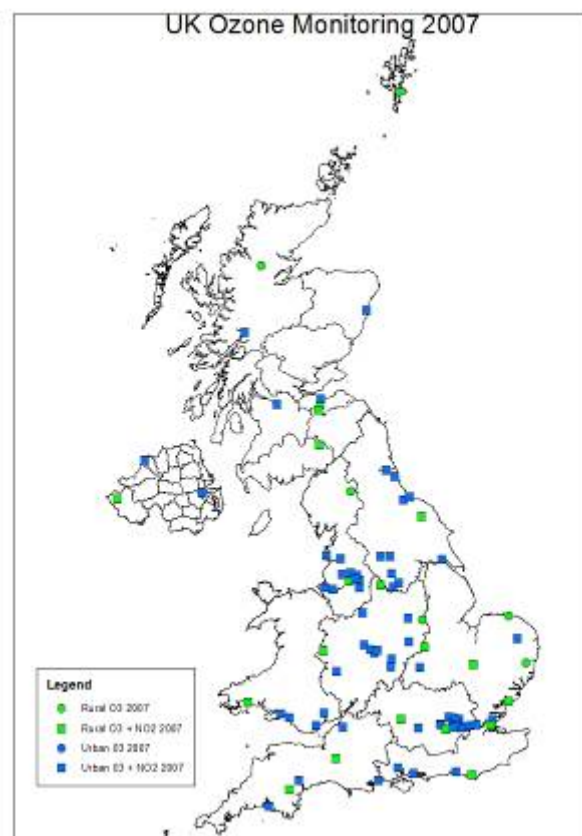


Figure A1.1: The distribution of ozone sites within the AURN in 1996(panel a) and 2007 (panel b). Sites with co-located NO_2 measurements are indicated.

358. Rural site numbers increased from 17 (6 with NO₂) to 24 (16 with NO₂) and urban sites increased from 33 to 66; all except one have co-located NO₂ monitoring. These changes are largely due to the Third Daughter Directive.

359. For the specific areas identified by PORG:

- **East Midlands:** one additional rural site at Market Harborough
- **North and West Wales:** one additional rural site at Narbeth in west Wales (Pembroke)
- **Central Highlands of Scotland:** suburban site in Fort William
- **Inland rural areas of SE England:** one additional rural site at Wicken Fen (East Anglia) and an urban site in Reading.

Status report: Considerable progress has been made.

- **Encourage the development of low-cost ozone monitoring techniques, such as solid state sensors and diffusion tube methods.**

360. Work is in progress on low-cost ozone monitoring techniques, based upon solid state sensors. Market forces for their deployment largely dictate product development. Little work has been done in the UK on diffusion tube methods, which have been developed significantly in other countries. They do, however, have the disadvantage of giving a long-term average and therefore no information on diurnal trends.

Status report: Little progress has been made.

- **Develop further the modelling techniques to quantify the influence of local site factors (land use and shelter).**

361. This recommendation reflected the importance at the time of the preparation of the 4th PORG report of empirical interpolation based maps of various ozone metrics. There was concern that local site factors limited the representativeness of some monitoring sites. The expansion of both rural and urban monitoring networks and the greater availability of process based models means that this is now less of a priority area for further research.

Status report: No longer a priority

- **Increase the number of stations with co-located rural monitoring of O₃, SO₂, NO, NO₂ and PM₁₀ or PM_{2.5}.**

362. Table A1-1 shows the pollutants measured at the 2007 rural AURN sites.

Status report: Progress has been made in the enhancement of the rural network for co-located parameters.

Table A1-1 Pollutants measured at the 2007 rural AURN sites

Sibton	O ₃							
Harwell	O ₃	NO ₂	PM ₁₀	PM _{2.5}	SO ₂	1,3 butadiene	Benzene	Toluene
Bottesford	O ₃	NO ₂						
Bush Estate	O ₃	NO ₂						
Eskdalemuir	O ₃	NO ₂						
Great Dun Fell	O ₃							
Aston Hill	O ₃	NO ₂						
Lullington Heath	O ₃	NO ₂	SO ₂					
Strath Vaich	O ₃							
Lough Navar	O ₃	PM ₁₀						
Yarner Wood	O ₃	NO ₂						
High Muffles	O ₃	NO ₂						
Glazebury	O ₃	NO ₂						
Ladybower	O ₃	NO ₂	SO ₂					
Rochester	O ₃	NO ₂	SO ₂	PM ₁₀	PM _{2.5}			
Somerton	O ₃	NO ₂						
London								
Teddington	O ₃	NO ₂	SO ₂					
Narberth	O ₃	NO ₂	SO ₂	PM ₁₀				
Wicken Fen	O ₃	NO ₂	SO ₂					
Weybourne	O ₃							
St Osyth	O ₃	NO ₂	CO					
Market								
Harborough	O ₃	NO ₂	CO					
Lerwick	O ₃							
Auchencorth								
Moss	O ₃	PM ₁₀	PM _{2.5}	other pollutants				

- **Quantify the effects of urban areas on ozone climatology to improve estimates of materials and human exposure to the potentially damaging ozone concentrations.**

363. The issue of ozone concentration in urban areas, in the context of human health effects has been extensively addressed in this AQEG report.

Status report: Achieved

- **Provide analysis and interpretation of UK ozone monitoring data for effects assessment and to monitor changes in ambient ozone as precursor emissions decline.**

364. Extensive analysis has been reported in this AQEG report and in the 2001 report on Transboundary Air Pollution (NEG-TAP 2001)

Status report: Achieved

- **Develop validated models which describe the small scale spatial variation of ozone within urban and rural areas and its diurnal variation.**

365. This issue has been discussed in the present report, especially in Chapter 8. In 2007, Defra commissioned a review of tools used for modelling ozone formation and assessing impacts on human health and ecosystems (see <http://randd.defra.gov.uk/>). The report concluded with a set of recommendations for further action by Defra which covered improvements to chemical schemes, emissions estimates, quality control processes and recommendations for the review and evaluation of the performance of chosen ozone models. Defra is in process of taking forward the recommendations from this review.

Status report: Progress made, further work in progress.

A1.2 NO_x and chemistry

- **Elucidate in detail the NO_y composition at UK sites ranging from the most polluted urban centres to the least polluted areas.**

366. The detailed composition of NO_y species has rarely been elucidated at UK sites. When and where a reasonably detailed speciation has been measured, this has been limited to campaigns at selected locations. For example Harrison *et al.* (1999) measured concentrations of total NO_y as well as the major individual species comprising NO_y (i.e. NO, NO₂, PAN, HNO₃, HONO and nitrate aerosol), during three NERC campaigns at the rural coastal site at Weybourne, Norfolk in 1993-1995, and were able to draw conclusions about missing species. Measurements of HONO, PAN and more recently alkyl nitrates have also been made at other campaigns (e.g. EU PRIME at Ascot in 1999; NERC TORCH at Writtle in 2003), and concentrations of HONO have been measured at Marylebone Road in 1999 (Martinez-Villa, 2001) and in the Buncefield plume in December 2005 (Mather *et al.*, 2007).

367. Routine measurements of peroxyacetyl nitrate (PAN) up to the early 1990s were reported for Bush and Harwell in PORG (1997), with more recent data (1994-1998) for Bush being published by McFadyen and Cape (2005).

368. Models containing appropriately detailed chemical mechanisms provide a method of simulating NO_y composition for a range of ambient conditions. For example, preliminary box modelling studies using the Master Chemical Mechanism, MCM, have examined the contributions from organic oxidised nitrogen components (e.g. alkyl nitrates, PANs and nitroarenes) in representative urban plumes (Jenkin *et al.*, 2006).

Status report: Only limited information available. Plenty of scope for additional studies.

- **Determine the small scale spatial variations in nitrogen dioxide concentrations within urban areas on a measurement scale of one hour or less.**

369. The density of sites reporting NO₂ concentrations at hourly resolution in urban areas (particularly London) has increased since PORG (1997). As reported in AQEG (2004), there are also some data characterising NO₂ concentrations with distance from roads, at a spatial resolution of a few metres. Measurements at high temporal resolution using portable devices have been carried out in London as part of the NERC DAPPLE project, but have not currently been reported.

Status report: Partially achieved. Plenty of scope for additional studies.

- **Elucidate fully the concentration and formation mechanism of HONO to quantify the role of this compound in the supply of the hydroxyl radical (OH) to the lower atmosphere.**

370. There has been continued national and international effort to elucidate mechanisms which form HONO. It is known that it can be produced from reactions of NO₂ with water on a variety of surfaces (producing HONO and HNO₃), and also from surface reactions with semi-volatile exhaust organics. Recent advances have demonstrated that the conversion of NO₂ to HONO on appropriate surfaces can be enhanced by light, as demonstrated for organic surfaces (George *et al.*, 2005; Stemmler *et al.*, 2006) and recently for titanium dioxide by Cox and co-workers (Gustafsson *et al.*, 2006). The motivation for this latest study was reactions on mineral dust, although the results may also have implications for the impact and effectiveness of de-NO_x paving slabs, which are TiO₂ coated.
371. It has also been shown that o-nitrophenols, products of aromatic hydrocarbon degradation, can form HONO upon photolysis (Bejan *et al.*, 2006). The photosensitised emission of HONO from snowpack has also been observed (e.g. Zhou *et al.*, 2001), and has been interpreted in terms of photolysis of dissolved or surface adsorbed nitrate ions (e.g. Jacobi and Hilker, 2007).

Status report: Substantial progress, but probably still much to be learnt.

- **Assess the extent to which chemical interference in the chemiluminescent method of measurement are influencing the reported concentrations of nitrogen dioxide at UK sites.**

372. A number of older studies have demonstrated that many oxidised nitrogen species can be converted into NO in heated molybdenum converters, and can therefore contribute to the NO₂ signal measured by chemiluminescence NO_x analysers (e.g., Winer *et al.*, 1974; Grosjean and Harrison, 1985; Fehsenfeld *et al.*, 1987). Recently, Dunlea *et al.* (2007) have investigated the level of interference by comparing measurements made by direct spectroscopic techniques (tunable infrared laser differential absorption spectroscopy, TILDAS, and differential optical absorption spectroscopy, DOAS), with those made by chemiluminescence monitors, in Mexico City.
373. Some limited consideration was given in AQEG (2004) to assessing the potential magnitude of interferences from HONO and PAN, based on some of the NO_x speciation measurements referred to above. With the exception of HONO (which can be emitted and therefore interfere close to source), the potential interference of most oxidised nitrogen species increases with air mass age (i.e. as NO_x is progressively converted to other NO_y species).

Status report: Limited progress in the UK.

A1.3 Hydrocarbons

- **To improve understanding of the UK VOC emission it is necessary to attempt closure between the hydrocarbon measurements and emissions inventories at a number of key sites and locations.**
374. Dollard *et al.* (2007) have carried out a comprehensive analysis of concentrations of up to 26 C₂ to C₈ hydrocarbons monitored for varying subsets of the period 1993-2004 at 11 urban background, one rural and one kerbside site within the UK hydrocarbon network. Although these hydrocarbons represent only a fraction of the 660 species in the NAEI speciation (making complete closure effectively unattainable), the observed trends are compatible with the declines in anthropogenic NMVOC emissions from relevant sources, as represented in the NAEI for the same period, and it is reasonable to infer that similar

trends have occurred for other emitted, but unmeasured, NMVOC which contribute to the same source sectors.

375. The measured hydrocarbons include isoprene, and analysis of its concentrations has revealed important contributions from both anthropogenic (vehicle exhaust) and biogenic sources. The inferred biogenic source strength for isoprene, based on the analysis of network measurements and other reported studies (e.g. Lee *et al.*, 2006), cannot be fully reconciled with current biogenic emissions estimates (Stewart *et al.*, 2003; Dore *et al.*, 2003), indicating unidentified or unrepresented sources. The shortfall may indicate a missing biogenic contribution (e.g. emissions from grassland or other vegetation not considered in the inventories), and this requires further investigation. A possible missing anthropogenic contribution, resulting from evaporative emissions, has been considered by AQEG, but this source appears to be minor, by virtue of the low total diene content of gasoline, of which isoprene represents only a small fraction.

Status report: Further work is required to elucidate isoprene sources.

- **Complete an assessment of the contribution made to ozone formation from all emission source categories treated in the NAEI.**

376. This has been considered in some detail in a number of studies using the NAEI speciation in conjunction with the Master Chemical Mechanism, MCM, most recently and comprehensively by Derwent *et al.* (2007a). Reactivity-based strategies for photochemical ozone control in Europe have also been identified (Derwent *et al.*, 2007b).

Status report: Completed for latest NAEI speciation of source categories.

- **Complete spatially disaggregated inventories of the most important individual hydrocarbon emissions, so that we can identify those areas in which photochemical oxidant production is under NO_x or hydrocarbon control and whether regionally differentiated strategies for hydrocarbon and NO_x reductions would be more cost effective.**

377. Spatially disaggregated VOC emissions maps have been compiled by the NAEI, and are routinely reported for total VOC emissions in the UK. They have also been developed for a series of individual VOC source sectors, and this information has been used in UK ozone modelling assessments. Such assessments have included consideration of whether ozone formation is controlled by VOC or NO_x, and how this varies both regionally, and temporally at a given location.

- **Investigate the feasibility of identifying those hydrocarbons which are unreactive and make no significant contribution to ozone formation, so that emissions of these species could be deregulated and so that they could be used as substitutes for more reactive hydrocarbons.**

378. Reactivity-based strategies for photochemical ozone control, based on species substitution, have been identified, using the NAEI speciation in conjunction with the Master Chemical Mechanism, MCM (Derwent *et al.*, 2007b).

Status report: Completed for the latest NAEI speciation.

- **Further research is required to quantify the emissions fluxes of reactive oxygenated VOCs from vegetation in the UK and contiguous areas of continental Europe, and to assess the contribution these compounds of biogenic origin make to ozone formation in the region.**

379. Although flux measurements of biogenic VOC has received continued attention, and new tools to quantify and represent their emissions have been developed, these activities has not been focussed specifically on reactive oxygenated species. More generally, the contribution of biogenic VOC to regional scale ozone formation has been estimated in modelling studies, within the limitations of current representations of emissions source strength and speciation (see also, the first bullet point on “hydrocarbons” above).

Status report: No progress in the specific area of biogenic emissions of oxygenated VOCs and their impact. Improved characterisation of biogenic hydrocarbon sources in general is also required.

A1.4 Synthesis and interpretation

- **The current monitoring of urban and rural photochemical oxidants and volatile organic compounds provides an excellent resource for the UK research community. Mechanisms to analyse and interpret these very expensive measurements should be initiated.**

380. Since the PORG report the monitoring of NO₂ and O₃ has grown significantly, whereas the monitoring of VOCs has reduced in favour of fewer strategic sites and the increased monitoring of specific pollutants such as benzene and 1,3-butadiene. Data from these networks have been extensively analysed through various mechanisms and used to develop an improved understanding of the factors controlling the concentrations of these species. Examples of the use of these data include NEGTA (2001), AQEG (2004, 2007), Clapp and Jenkin (2001), (Coyle *et al.* (2002)) and many other references cited in the current report. These analyses have been supplemented by research council-led field campaigns where a wider range of VOCs and other species have been measured e.g. the 2003 NERC TORCH campaign.

381. The present AQEG report illustrates the extensive analysis and interpretation that has been achieved using these measurements

Status report: Achieved.

- **Specifically, the government’s air quality strategy for ozone recognises the importance of taking further steps on the European scale to reduce ozone exposure levels. PORG therefore recommends that, in three years time, the government commissions an assessment of:**
- **The precursor emissions control actions taken across Europe by the year 2000, and their impact on ambient NO_x and hydrocarbon concentrations,**
- **The resulting change in ozone exposure levels and their likely impact on human health and damage to vegetation,**
- **The requirement for and timing of additional policy actions to control hydrocarbons and NO_x across Europe, and their likely impact over the period up to 2010.**

382. There has been an ongoing commitment since the publication of the PORG report to continuously assess the effects of controls taken at a European level to reduce ozone concentrations. NEGTA (2001) summarises many of the points raised above and additionally considers other pollutants such as SO₂. That report provides a synthesis of research carried out over the 3-year timeframe since PORG and considers human health effects, effects on vegetation and the effects of European-wide initiatives to reduce ozone-precursor emissions. The effects of the complying with the EC National Emissions Ceiling and Ozone Directive were considered in a wide-ranging report (AEAT, 2000).

Exposure to ozone in the UK was assessed using outputs from UK and European modelling studies up to 2010 (Stedman J.R. *et al.* 1999). Other assessments include the analysis urban VOC trends and peak ozone concentrations in the north-west Europe and the effect of controls over motor vehicle emissions of VOCs (Derwent *et al.* 2003).

Status report: Achieved by several means from local to regional assessments, both in the UK and elsewhere in Europe.