

The effect of varying primary emissions on the concentrations of inorganic aerosols predicted by the enhanced UK Photochemical Trajectory Model

Harrison, R.M.; Jones, Alan; Beddows, D.C.S.; Derwent, R.G.

DOI:

[10.1016/j.atmosenv.2012.12.016](https://doi.org/10.1016/j.atmosenv.2012.12.016)

License:

Other (please specify with Rights Statement)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Harrison, RM, Jones, A, Beddows, DCS & Derwent, RG 2013, 'The effect of varying primary emissions on the concentrations of inorganic aerosols predicted by the enhanced UK Photochemical Trajectory Model', *Atmospheric Environment*, vol. 69, pp. 211-218. <https://doi.org/10.1016/j.atmosenv.2012.12.016>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

NOTICE: this is the author's version of a work that was accepted for publication in *Atmospheric Environment*. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in *Atmospheric Environment*, Vol 69, DOI: [10.1016/j.atmosenv.2012.12.016](https://doi.org/10.1016/j.atmosenv.2012.12.016)

Checked September 2015

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

1
2
3
4 **The Effect of Varying Primary Emissions on**
5 **the Concentrations of Inorganic Aerosols**
6 **Predicted by the Enhanced UK Photochemical**
7 **Trajectory Model**
8

9
10 **Roy M. Harrison^{*†}, Alan M. Jones, David Beddows and**
11 **Richard G. Derwent[‡]**
12

13
14 **National Centre for Atmospheric Science**
15 **Division of Environment Health & Risk Management**
16 **School of Geography, Earth & Environmental Sciences**
17 **University of Birmingham**
18 **Edgbaston, Birmingham B15 2TT**
19 **United Kingdom**
20
21
22
23

* To whom correspondence should be addressed (Tel: +44 121 414 3494; Fax: +44 121 414 3709; Email: r.m.harrison@bham.ac.uk)

† Also at: Department of Environmental Sciences / Center of Excellence in Environmental Studies, King Abdulaziz University, PO Box 80203, Jeddah, 21589, Saudi Arabia

‡ Also at: rdscientific, Newbury, Berkshire, RG14 6LH, United Kingdom

24 **ABSTRACT**

25 An enhanced Photochemical Trajectory Model (PTM) has been used to simulate concentrations of
26 secondary inorganic aerosol (for the purposes of this work, sulphate, nitrate, chloride and
27 ammonium) in PM₁₀ over a two-month period at a rural site in central southern England (Harwell).
28 Judged against a base year of 2007, emissions of precursor gases, SO₂, NO_x and NH₃ have been
29 varied over plausible ranges, occurring across the UK only, mainland Europe only, or the whole of
30 Europe. The model is able to reproduce observed non-linearities and shows that abatement is less
31 than proportional in all cases. Additionally, abatement of sulphur dioxide leads to increased nitrate
32 concentrations. The combination of a weak response of nitrate to reductions in NO_x emissions, and
33 the effect of sulphur dioxide reductions in increasing nitrate is consistent with the very small recent
34 observed trends in nitrate concentrations over the UK. A scenario for 2020 in which emissions of
35 SO₂, NO_x and NH₃ fall to 64%, 75% and 96% respectively of their 2007 baseline levels across the
36 whole of Europe shows a reduction of 2 µg m⁻³ in secondary inorganic aerosol which is 13% below
37 the baseline case for a two month period in 2007, due mostly to a fall in sulphate and ammonium.
38 As this was a relatively high pollution period, it is estimated that over a full year, the reduction is
39 more likely to be around 1 µg m⁻³.

40

41 **Keywords:** Secondary inorganic aerosol, sulphate, nitrate, trajectory model

42 **INTRODUCTION**

43 The European Union Limit Values for PM₁₀ and PM_{2.5} and the exposure reduction target for PM_{2.5}
44 (Official Journal, 2008; Harrison et al., 2012a), together with the imperative to protect public
45 health are strong drivers to reduce airborne concentrations of PM₁₀ and PM_{2.5}. As industrial and
46 automotive sources of primary pollutants have steadily reduced in recent years, so the relative
47 importance of secondary components of airborne particulate matter has become more pronounced.
48 Chemical analysis of PM_{2.5} samples collected in Birmingham in 2004-2006 showed that secondary
49 ammonium sulphate and ammonium nitrate contributed 24.0% and 21.2% respectively of measured
50 PM_{2.5} mass (Yin and Harrison, 2008). Additionally, there was an appreciable contribution of
51 secondary organic aerosol (19.4% derived from data in Harrison and Yin (2008)). Yin and Harrison
52 (2008) also showed that on high pollution days when PM₁₀ exceeds the daily limit value of 50 µg
53 m⁻³, ammonium nitrate makes a disproportionately large contribution to the overall particle mass
54 (average 45.8%). Similar influences of secondary components on PM₁₀ and PM_{2.5} are operative
55 also in London (Harrison et al., 2012b).

56
57 In analysing exceedences of the 24 hour PM₁₀ limit value in the southern United Kingdom, Charron
58 et al. (2007) attributed a high importance to regional pollution events associated particularly with
59 elevated concentrations of secondary inorganic aerosol. It is well recognised that a substantial
60 proportion of such particulate matter arises from precursor emissions in the European mainland
61 (Harrison et al., 2012a) and consequently it is important to understand the relative contributions
62 which abatement of UK and continental European precursor emissions respectively can make to
63 reducing airborne concentrations of secondary inorganic particles. An additional factor to take into
64 account is that a careful analysis of the relationship of airborne concentrations of sulphate to those
65 of sulphur dioxide suggests significant non-linearities (Jones and Harrison, 2011), i.e. a reduction in
66 sulphur dioxide emissions is associated with a less than proportionate reduction in sulphate.

67

68 In order to understand the impacts of abatement policies, it is necessary to predict the influences of
69 reductions of precursor emissions upon future secondary pollutant concentrations. This can be done
70 most effectively through use of a chemistry-transport model, but the applicability of many such
71 models is limited by their large computational expense whose implication is that only a small
72 number of scenarios can be run, and consequently the full range of possible future emissions cannot
73 readily be studied. A number of models have been used to predict concentrations of particulate
74 matter components within the European atmosphere. These include Eulerian models such as
75 LOTOS-EUROS (Schaap et al., 2008), CHIMERE (Bessagnet et al., 2009), REM-CALGRID
76 model (RCG) (Beekmann et al., 2007), and the Unified EMEP model (Simpson et al. 2011). The
77 unified EMEP model has been used for policy development in Europe (Aas et al., 2007) and to
78 address regional scale impacts of NO_x and SO₂ emission reductions on PM mass concentrations.
79 More recently, Megaritis et al. (2012) have used the PMCAM_x-2008 model to evaluate the impact
80 of 50% precursor emissions reductions upon PM_{2.5} concentrations in Europe.

81

82 The CityDelta project compared the ability of several models to predict the impact of emissions
83 reductions upon concentrations in European cities (Cuvelier et al., 2007), specifically Berlin, Milan,
84 Paris and Prague (Thunis et al., 2007). A subsequent study (Stern et al., 2008) examined the ability
85 of five chemical transport models to reproduce PM₁₀ episode conditions in central Europe. Model
86 specific studies, such as those with CHIMERE, have sought to simulate particulate matter
87 concentrations in specific parts of Europe, e.g. Portugal (Monteiro et al., 2007) and northern Italy
88 (de Meij et al., 2009). Air quality models used for calculating aerosol species over the UK include
89 the Community Multiscale Air Quality model (CMAQ) (Chemel et al., 2010) and the Hull Acid
90 Rain Model (HARM), (Metcalf et al., 2005). CMAQ over-predicted O₃ and under-predicted
91 aerosol species with the exception of sulphate (Chemel et al., 2010). The HARM and ELMO
92 models (Whyatt et al., 2007) underestimated sulphate, nitrate and ammonium by a large margin, and
93 chloride massively. In the work of Redington and Derwent (2002), the NAME model slightly

94 under-predicted measured sulphate values (average negative bias across three sites was $0.33 \mu\text{g m}^{-3}$)
95 although the annual average values of nitrate compared well.

96
97 This paper is concerned with the application of a Lagrangian trajectory model to provide the results
98 of multiple abatement scenarios upon concentrations of secondary organic aerosol.

99

100 **THE MODEL**

101 The numerical model used in this work is a heavily modified version of the UK Photochemical
102 Trajectory Model (PTM). The PTM has been widely used by Derwent and his collaborators,
103 especially in relation to the modelling of ozone (Derwent et al., 1996; Derwent et al., 2003;
104 Walker et al., 2009; Baker, 2010) and of secondary organic aerosol (Johnson et al., 2006; Derwent
105 et al., 2009; Abdalmogith et al., 2006). For its application to secondary inorganic aerosol, the
106 model has been modified in our group in a number of important aspects. These are described in
107 detail by Beddows et al. (2012) and may be summarised as follows:

- 108 • Enhancements to better describe the boundary layer meteorological processes affecting
109 pollutant concentrations. In particular, data for temperature, relative humidity and mixing
110 depths are derived from the HYSPLIT model and insolation is now a function of Julian Day
111 and subject to attenuation by cloud.
- 112 • A more sophisticated treatment of in-cloud oxidation of sulphur dioxide has been
113 incorporated.
- 114 • Concentrations of sea salt aerosol are estimated from the parameterisation of Gong et al.
115 (2008) and used as inputs to both chloride and sodium for the aerosol thermodynamic model.
- 116 • The partition of reactive gases such as ammonia and nitric acid between vapour and the
117 condensed phase is now described through the thermodynamic model, ISORROPIA II which
118 describes the equilibrium processes within an internally mixed aerosol as a function of
119 temperature and relative humidity (Fountoukis and Nenes, 2007).

120 The model set-up involves the calculation of mean concentrations resulting from back trajectories
121 over a period in 2007, terminating at the Harwell site in southern England. The model has been
122 extensively validated against measured data from Harwell and its performance tested against
123 standard metrics with satisfactory outcomes (Beddows et al., 2012). Concentrations correspond to
124 the PM₁₀ size range.

125

126 Recent decades have seen substantial reductions in the emissions of SO₂ and NO_x (Vestreng et al.,
127 2007; AQEG, 2007) and the range of reductions in emissions modelled allows for a further
128 reduction of 50% in these gases. Reductions in NH₃ are less certain, and it has been predicted that in
129 certain areas (e.g. United States; Pye et al., 2009), there may be future increases in NH₃ emissions.
130 For this reason a wider range including both increases and reductions from the baseline was chosen
131 for the modelled NH₃ emissions than for the modelled NO_x and SO₂ emissions.

132

133 **METHOD**

134 The Photochemical Trajectory Model (PTM) was run over the period 19 March 2007 to 19 May
135 2007 with various assumed emissions of oxides of nitrogen (NO_x), sulphur dioxide (SO₂) and
136 ammonia (NH₃), to predict inorganic particulate matter concentrations at Harwell. This is the same
137 period over which model validation was conducted (Beddows et al., 2012). Emission values were
138 taken from the NAEI on a 10 x 10 km grid for the United Kingdom (UK), and from EMEP on a 50
139 x 50 km grid for the rest of Europe (EU) as described in Beddows et al. (2012), with changes in
140 emissions modelled for these areas both separately and together. Emissions from shipping in local
141 seas were abated in both the UK-only and EU-only scenarios. The variation of emissions was
142 considered over the range of 100% to 40% for NO_x 100% to 50% for SO₂, and 120% to 70% for
143 NH₃, in 10% steps, where 100% is the baseline (2007) rate of emission.

144

145 The 2976 half-hourly calculated concentrations predicted by the PTM for each emission scenario
146 were used to calculate the mean concentration, over the two month period, of particulate nitrate,
147 ammonium, sulphate and chloride. Chloride, although largely primary is affected by the processes
148 determining concentrations of secondary sulphate and nitrate and was therefore included. The mean
149 concentrations of the precursor gases HNO₃ and HCl were also calculated.

150

151 **RESULTS AND DISCUSSION**

152 For the purpose of this study, variations were made to the emissions of three precursor pollutants,
153 i.e. ammonia, NO_x and sulphur dioxide. The model was then used to compute the resultant
154 concentrations of ammonium, nitrate, sulphate and chloride (and coincidentally nitric acid and
155 hydrochloric acid vapours) and the sum of the four particulate components, which for the purpose
156 of this report is described as secondary inorganic aerosol (SIA).

157

$$SIA = \sum SO_4^{2-} + NO_3^- + Cl^- + NH_4^+$$

158

159 Figure 1 shows an example of the effect of abatement policies applied uniformly across the UK and
160 the remainder of Europe. In the three-dimensional plot, one pollutant has been held constant; in
161 this case ammonia emissions have been held constant at 100% of their 2007 value. The plot then
162 shows the concentrations of the species indicated resulting from levels of sulphur dioxide emission
163 between 50% and 100% of 2007 emissions and of abatement of NO_x such that emissions are
164 between 40% and 100% of those in 2007. In Figure 1, it may be seen that nitrate concentrations, as
165 expected, fall with the abatement of NO_x emissions, but that the fall is reduced by the abatement of
166 sulphur dioxide. This confirms that the model is reflecting the atmospheric chemistry well. The
167 reason for this effect is that the abatement of sulphur dioxide reduces the formation of sulphate (as
168 seen in the graph for sulphate), which in turn reduces the irreversible uptake of ammonia into
169 ammonium sulphate. This in turn implies that more ammonia remains in unneutralised form in the

170 atmosphere which then contributes to additional formation of nitrate by reaction with nitric acid.
171 Abatement of sulphur dioxide and NO_x appears to contribute monotonically to a reduction in
172 ammonium in the aerosol, but also leads to modestly increasing concentrations of chloride in the
173 particles. This is a consequence of diminished scavenging of ammonia by sulphuric acid which is
174 then free to react with hydrogen chloride, leading to a reduction in this species, seen in Figure 1,
175 and an increase in particulate chloride. The overall effect of abatement of NO_x to 40% and SO₂ to
176 50% of 2007 emissions at constant ammonia emissions is a reduction of secondary inorganic
177 aerosol to around 11 µg m⁻³ from an initial concentration slightly in excess of 15 µg m⁻³. Figure S1
178 (Supplementary Information) shows the effect of reductions of emissions within the UK only.
179 Taking the 100% ammonia scenario, secondary inorganic aerosol concentrations are reduced by a
180 smaller margin from a little over 15 µg m⁻³ to around 12 µg m⁻³. In Figure S2, the projections of
181 emissions reduction for the European mainland, excluding the UK, show for a 100% ammonia
182 scenario (i.e. 2007 emission levels for ammonia), a maximum reduction of secondary inorganic
183 aerosol to around 13 µg m⁻³ from 15 µg m⁻³.

184

185 Comparative charts of the concentrations of SIA, nitrate, ammonium, sulphate and chloride when
186 emissions of NO_x, SO₂ and NH₃ from UK, EU and both areas together are separately reduced, while
187 the other emissions are held at 2007 values (100%), are presented in Figures S3 to S7
188 (Supplementary Information) respectively. When NO_x or SO₂ emissions are reduced, the reduction
189 of emissions from the United Kingdom (UK) has a greater effect on concentrations of sulphate,
190 nitrate and chloride than the reduction of emissions from the rest of Europe (EU). In the case of
191 ammonium, both appear equally effective. These results appear in tabulated form in Tables S1-3
192 (in Supplementary Information).

193

194 Figure S4 shows a considerable beneficial effect of NO_x abatement upon nitrate concentrations
195 especially if that reduction is across both the UK and mainland Europe. However, the benefits are

196 far less than proportionate. Figure S4 also confirms an increase in nitrate with the abatement of
197 sulphur dioxide as mooted in the earlier text. On the other hand, abatement of ammonia emissions
198 has a decidedly beneficial effect upon nitrate concentrations. The effects of abatement policies for
199 sulphur dioxide, NO_x and ammonia are all beneficial in reducing ammonium concentrations with
200 the greatest benefits coming from reductions across the whole of Europe, including the UK.
201 Reducing ammonia emissions appears to be the most effective measure when comparing the 100%
202 to 70% scenarios, which is consistent with the results of Megaritis et al. (2012). Figure S7 shows
203 that effects on chloride concentrations of reductions in NO_x, SO₂ and ammonia are relatively
204 modest but not zero. When these changes are summed as secondary inorganic aerosol (Figure S3),
205 it is seen that even quite major reductions in emissions of precursor compounds have only a relative
206 modest effect upon the concentration of secondary inorganic aerosol.

207

208 The general trends in concentration with respect to NO_x and SO₂ emissions are consistent across all
209 NH₃ emission levels, and all geographic areas for which emissions were varied. SIA, ammonium
210 and HNO₃ concentrations reduce with reductions in both NO_x and SO₂ emissions. Nitrate falls with
211 reducing NO_x emissions but rises with cuts in SO₂ emissions (Figure S4). Sulphate falls with
212 reducing SO₂ and ammonia emissions but is largely unaffected by reduced NO_x emission (Figure
213 S6). Chloride increases slightly with reductions in SO₂ and NO_x emissions (Figure S7). According
214 to Figure S3, SIA is relatively insensitive to reductions in a single precursor. A much greater
215 reduction in SIA is seen when all three precursors are reduced by the maximum amount.

216

217 **Secondary Pollutant – Precursor Relationships**

218 These appear in Figures 2 to 4. Figure 2 shows the relationship of atmospheric concentrations of
219 sulphate to sulphur dioxide which portrays the non-linearity widely believed to affect this
220 relationship, and which was inferred from measured atmospheric concentrations by Jones and
221 Harrison (2011). This graph also demonstrates the relative ineffectiveness for UK sulphate

222 concentrations of reducing only emissions in mainland Europe, but also that the reduction across
223 both the UK and mainland Europe is more effective than reductions in the UK alone. Figure 3
224 shows the corresponding relationship between nitrate and emissions of NO_x . This portrays a
225 broadly similar pattern of behaviour but the apparent intercept in nitrate at zero NO_x derived from
226 curve fitting seems implausible and there must be a steepening relationship as NO_x is reduced
227 further. The relative shallowness of this curve over the abatement range tested appears consistent
228 with the fact that nitrate concentrations in UK air appear relatively insensitive to NO_x emission
229 reductions in recent years. For example, data from UK rural sites showed a marked decline in NO_2
230 between 1987 and 2007, but no trend in particulate nitrate between 1999 and 2007 (AEA, 2008). It
231 also shows clearly the relative importance of UK emissions in influencing NO_x far more than nitrate
232 concentrations which are quite strongly influenced by European mainland emissions. Figure 4
233 shows the corresponding relationship between ammonium and ammonia emissions. This also
234 shows a non-linearity but a significant beneficial impact of emissions reductions. Figures 5 and S8
235 show the impacts of sulphur dioxide abatement upon nitrate and ammonium respectively. Figure 5
236 shows clearly that nitrate has a tendency to increase as sulphur dioxide is reduced as indicated in the
237 discussion above. On the other hand, reductions in sulphur dioxide emissions have clear benefits in
238 reducing ammonium concentrations (Figure S8) as do reductions in NO_x in reducing ammonium
239 (Figure S9). Figure 6 shows that reductions of NO_x lead to increases in sulphate. The effect is
240 relatively small but it is most marked for reductions in mainland Europe. This is presumably an
241 effect of lesser competition for oxidising agents with a reduction in concentrations of NO_x leading
242 to enhanced oxidation of sulphur dioxide. Substantial benefits arise from the abatement of
243 ammonia. This is seen in respect of sulphate concentrations in Figure 7 and of nitrate concentrations
244 in Figure S10, both of which benefit significantly from ammonia abatement, as do concentrations of
245 ammonium (Figure 4).

246

247

248 **Comparison with the Work of Derwent et al. (2009)**

249 The paper by Derwent et al. (2009) is the only broadly similar study with which to compare our
250 results. It is also based upon a moving air parcel trajectory model but averages over each day of
251 2006 at Harwell, Oxfordshire, rather than focussing on a more limited time period with a minor
252 pollution episode as in this study. In comparison to this study, it investigates a more limited range
253 of abatement scenarios and presents results relating only to 30% reductions in emissions of
254 individual pollutants rather than the mixed abatement cases run in our study. The model of
255 Derwent et al. (2009) uses a “kinetic” approach to simulating formation of aerosol constituents
256 whereas this work uses kinetics to determine the formation of oxidised products and
257 thermodynamics to simulate their incorporation into particles. One difficulty with the
258 thermodynamic approach is selecting an appropriate temperature/humidity condition at which to
259 simulate the particle-vapour equilibria, which can be very sensitive to these variables. Another
260 issue for nitrate is the presence of artefacts (generally negative) in the measurements, which will
261 affect both modelling approaches. Nonetheless, both models perform well in simulating the
262 magnitude of current nitrate concentrations (Beddows et al., 2012; Derwent et al., 2009). Table S4
263 (Supplementary Information) shows the concentrations predicted by the Derwent et al. (2009)
264 model in comparison to those in the current study and Table 1 shows percentage reductions in each
265 case from the base case for the 30% reduction scenarios presented by Derwent and co-workers.

266

267 In the case of sulphur dioxide abatement, it may be seen from Table 1 that the general pattern of
268 behaviour is the same, and within each model a sulphate reduction arising from sulphur dioxide
269 abatement in the UK only and rest of Europe cases and a substantially greater abatement resulting
270 from reductions across the board. The main difference is that Derwent et al. (2009) predicted a
271 70% sulphate concentration from across the board abatement, whereas in the current work, the
272 predicted reduction in sulphate is to a level of 78%. The current work predicts 89% for both the UK
273 only and rest of Europe reductions whereas Derwent et al. (2009) predicted 85%. Once again, a

274 broadly similar pattern of outcomes is seen for abatement of NO_x with greater reductions shown by
275 Derwent et al. (2009) (an 80% nitrate level as compared to 87% in our model), with a greater effect
276 of abatement in the rest of Europe (88% nitrate) in the Derwent et al. (2009) model compared to the
277 UK only case (92% nitrate), comparing with 94% nitrate in both scenarios in our model. In
278 common with our model, the Derwent et al. (2009) model shows an increase in nitrate with sulphur
279 dioxide abatement, although the effect is less in the Derwent et al. (2009) model for across the
280 board abatement but greater for rest of Europe abatement than in our model. In the case of
281 ammonia abatement, Derwent et al. (2009) show a reduction in ammonium to 79% in the across the
282 board case as opposed to 83% in our model. Both models show 90% ammonium in the UK only
283 case and Derwent et al. (2009) show 89% ammonium in the Europe-only case, whereas in our
284 model it is 94%. Both models show ammonia abatement to be beneficial for all measured species.
285 Given the differences both in model formulation, and the scenarios run (annual means versus a two
286 month episode in different years), the agreement is suprisingly close.

287

288 **Predictions for the European 2020 Scenario**

289 AQEG (2012) gives projections of UK precursor emissions in 2020, together with emission for
290 2005 and 2010 in respect of the EU-27 and shipping in European waters. Baseline EU-27 and
291 shipping emissions were estimated by averaging the 2005 and 2010 emissions in the AQEG report.
292 The 2020 emissions (sum of EU-27 and shipping) were estimated as a percentage of baseline as
293 SO₂, 64%; NO_x, 75% and NH₃, 96%.

294

295 The results of this scenario appear in Table 2, which shows the all of Europe, mainland only and
296 UK-only reduction. It shows 2020 concentrations of SIA of 2.0 µg m⁻³ below the baseline case, a
297 reduction of 13%, due mostly to a fall in sulphate and ammonium. The mean PM₁₀ concentration
298 measured at Harwell over the period 19/3/2007 to 19/5/2007 was 28.2 µg m⁻³, while that over the
299 full year of 2007 was 21.5 µg m⁻³. Mean concentrations of chloride, nitrate and sulphate over the 2-

300 month period modelled were 1.18, 6.64 and 3.89 $\mu\text{g m}^{-3}$, somewhat higher than that for the full year
301 of 1.38, 3.06 and 2.40 $\mu\text{g m}^{-3}$ respectively. Thus nitrate and sulphate were 46% and 62%
302 respectively over the full year relative to the modelled period. Consequently, an overall reduction
303 of about 1 $\mu\text{g m}^{-3}$ in PM_{10} might be anticipated over the full year as a result of the estimated 2020
304 emissions reductions relative to 2007.

305

306 **CONCLUSIONS**

307 These results demonstrate that the enhanced PTM is an effective way of investigating complex
308 emission reduction scenarios. The results give a clear view of pollutant interactions and show
309 reductions in some cases, and in others increases in concentrations that are qualitatively the same as
310 Derwent et al. (2009) and quantitatively relatively similar. The differences are probably explained
311 to a large degree by the lower concentrations in the base case in the Derwent et al. (2009) model
312 and the non-linearities accounting for greater percentage reductions in that situation. However, the
313 great benefit of the current work is that it investigates a much wider range of scenarios than those
314 studied by Derwent et al. (2009), therefore allowing an assessment of likely future concentrations
315 over a very wide range of plausible mitigation policies and scenarios. It also gives predictions for
316 specific scenarios, such as that for 2020.

317

318 In the 2020 scenario, despite substantial reductions in both NO_x and SO_2 (by 25% and 36%
319 respectively), the reduction in SIA is almost wholly due to a fall in the sulphate concentration.
320 Nitrate, which already exceeds sulphate in the southern UK, and becomes dominant under episodic
321 conditions (Yin and Harrison, 2008), responds little to the reduction in NO_x , reflecting the low
322 sensitivity of nitrate to NO_x emission reductions seen in Figure S9 and the effect of decreasing SO_2
323 emissions in increasing nitrate (Figure 5). This is reflected in the very small changes in nitrate in
324 the UK in recent years, despite substantial reduction in NO_x emissions.

325

326 **ACKNOWLEDGEMENT**

327 This work was supported by the U.K. Department for Environment, Food and Rural Affairs under
328 contract number CPEA28, and by the National Centre for Atmospheric Science.

329

330

331 **REFERENCES**

332

333 Aas, W., Bruckmann, P., Derwent, R., Poisson, N., Putaud, J.-P., Rouil, L., Vidic, S. and Karl-
334 Espen Yttri, K.-E., 2007. EMEP Particulate Matter Assessment Report, EMEP/CCC-Report
335 8/2007, REF O-7726.

336

337 Abdalmogith, S.S., Harrison, R.M. and Derwent, R.G., 2006. Particulate sulphate and nitrate in
338 southern England and Northern Ireland during 2002/3 and its formation in a photochemical
339 trajectory model, *Sci. Tot. Environ.*, 368, 769-780.

340

341 AEA, 2008. UK Acid Deposition Monitoring Network: Data Summary 2007, Report of the
342 Department for Environment, Food and Rural Affairs and the Devolved Administrations,
343 AEAT/ENV/R/2706, ED48750, Issue 1.

344

345 AQEG, 2007. Trends in Primary Nitrogen Dioxide in the UK. DEFRA
346 [http://archive.defra.gov.uk/environment/quality/air/airquality/publications/primaryno2-](http://archive.defra.gov.uk/environment/quality/air/airquality/publications/primaryno2-trends/documents/primary-no-trends.pdf)
347 [trends/documents/primary-no-trends.pdf](http://archive.defra.gov.uk/environment/quality/air/airquality/publications/primaryno2-trends/documents/primary-no-trends.pdf)

348

349 AQEG, 2012. Fine Particulate Matter (PM_{2.5}) in the United Kingdom, Air Quality Expert Group,
350 Report to Department for Environment, Food and Rural Affairs, [http://uk-](http://uk-air.defra.gov.uk/library/reports?report_id=727)
351 [air.defra.gov.uk/library/reports?report_id=727](http://uk-air.defra.gov.uk/library/reports?report_id=727)

352

353 Baker, J., 2010. A cluster analysis of long range air transport pathways and associated pollutant
354 concentrations with the UK, *Atmos. Environ.*, 44, 563-571.

355

356 Bessagnet, B., Menut, L., Curci, G., Hodzic, B., Guillaume, A., Liousse, C., Moukhtar, S., Pun, B.,
357 Seigneur, C. and Schulz, M., 2009. Regional modeling of carbonaceous aerosols over Europe -
358 Focus on Secondary Organic Aerosols, *J. Atmos. Chem.*, 61, 175-202.

359

360 Beddows, D.C.S., Hayman, G. and Harrison, R.M., 2012. Enhancements to the UK photochemical
361 trajectory model for simulation of secondary inorganic aerosol, *Atmos. Environ.*, *Atmos. Environ.*
362 *57*, 278-288.

363

364 Beekmann, M., Kerschbaumer, A., Reimer, E., Stern, R. and Moller, D., 2007. PM measurement
365 campaign HOVERT in the Greater Berlin area: model evaluation with chemically specified
366 observations for a one year period, *Atmos. Chem. Phys.*, 7, 55-68.

367

368 Charron, A., Harrison, R.M. and Quincey, P., 2007. What are the sources and conditions
369 responsible for exceedences of the 24 h PM₁₀ Limit Value (50 µg m⁻³) at a heavily trafficked
370 London site?, *Atmos. Environ.*, 41, 1960-1975.

371

372 Chemel, C., Sokhi, R.S., Yu, Y., Hayman, G.D., Vincent, K.J., Dore, A.J., Tang, Y.S., Prain, H.D.
373 and Fisher, B.E.A., 2010. Evaluation of a CMAQ simulation at high resolution over the UK for the
374 calendar year 2003, *Atmos. Environ.*, 44, 2927-2939.

375

376 Cuvelier, C., Thunis, P., Vautard, R., Amann, M., Bessagnet, B., Bedogni, M., Berkowicz, R.,
377 Brant, J., Brocheton, F., Builtjes, P., Carnavale, C., Coppalle, A., Denby, B., Douros, J., Graf, A.,
378 Hellmuth, O., Hodzic, A., Honore, C., Jonson, J., Kerschbaumer, A., de Leeuw, F., Minguzzi, E.,
379 Moussiopoulos, N., Pertot, C., Peuch, V.H., Pirovano, G., Rouil, L., Sauter, F., Schaap, M., Stern,
380 R., Tarrasonn, L., Bignati, E., Volta, M., White, L., Wind, P. and Zuber, A., 2007. CityDelta: A
381 model intercomparison study to explore the impact of emission reductions in European cities in
382 2010, *Atmos. Environ.*, 41, 189-207.

383
384 Derwent, R.G., Jenkin, M.E. and Saunders, S.M., 1996. Photochemical ozone creation potentials
385 for a large number of reactive hydrocarbons under European conditions, *Atmos. Environ.*, 30, 181-
386 199.

387
388 Derwent, R.G., Jenkin, M.E., Saunders, S.M., Pilling, M.J., Simmonds, P.G., Passant, N.R.,
389 Dollard, G.J., Dumitrescu, P. and Kent, A., 2003. Photochemical ozone formation in north west
390 Europe and its control., *Atmos. Environ.*, 37, 1983-1991.

391
392 Derwent, R., Witham, C., Redington, A., Jenkin, M., Stedman, J., Yardley, R. and Hayman, G.,
393 2009. Particulate matter at a rural location in southern England during 2006: Model sensitivities to
394 precursor emissions, *Atmos. Environ.*, 43, 689-696.

395
396 Fountoukis, C. and Nenes, A., 2007. ISORROPIA II: A Computationally Efficient Aerosol
397 Thermodynamic Equilibrium Model for K^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , Na^+ , SO_4^{2-} , NO_3^- , Cl^- , H_2O Aerosols,
398 *Atmos. Chem. Phys.*, 7, 4639–4659.

399
400 Gong, S.L., 2003. A parameterisation of sea-salt aerosol source function for sub- and super-micron
401 particles, *Global Biogeochem. Cycles*, 17, 1097.

402
403 Harrison, R.M., Laxen, D., Moorcroft, S. and Laxen, K., 2012a. Processes affecting concentrations
404 of fine particulate matter ($PM_{2.5}$) in the UK atmosphere, *Atmos. Environ.*, 46, 115-124.

405
406 Harrison, R.M., Dall'Osto, M., Beddows, D.C.S., Thorpe, A.J., Bloss, W.J., Allan, J.D., Coe, H.,
407 Dorsey, J.R., Gallagher, M., Martin, C., Whitehead, J., Williams, P.I., Jones, R.L., Langridge, J.M.,
408 Benton, A.K., Ball, S.M., Langford, B., Hewitt, C.N., Davison, B., Martin, D., Petersson, K.,
409 Henshaw, S.J., White, I.R., Shallcross, D.E., Barlow, J.F., Dunbar, T., Davies, F., Nemitz, E.,
410 Phillips, G.J., Helfter, C., Di Marco, C.F. and Smith, S., 2012b. Atmospheric chemistry and
411 physics in the atmosphere of a developed megacity (London): An overview of the REPARTEE
412 experiment and its conclusions, *Atmos. Phys. Chem.*, 12, 3065-3114.

413
414 Harrison, R.M. and Yin J. 2008. Sources and processes affecting carbonaceous aerosol in central
415 England, *Atmos. Environ.*, 42, 1413-1423.

416
417 Johnson, D., Utembe, S.R., Jenkin, M.E., Derwent, R.G., Hayman, G.D., Alfarra, M.R., Coe, H. and
418 McFiggans, G., 2006. Simulating regional scale secondary organic aerosol formation during the
419 TORCH 2003 campaign in the southern UK, *Atmos. Chem. Phys.*, 6, 403-418.

420
421 Jones, A.M. and Harrison, R.M., 2011. Temporal trends in sulphate concentrations at European
422 Sites and relationships to sulphur dioxide, *Atmos. Environ.*, 45, 873-882.

423
424 Megaritis, A.G., Fountoukis, C., Charalampidis, P.E., Pilinis, C. and Pandis, S.N., 2012. Response
425 of fine particulate matter concentrations to changes of emissions and temperature in Europe, *Atmos.*
426 *Chem. Phys. Discuss.*, 12, 8771-8822.

427
428 Meij de, A., Thunis, P., Bessagnet, B. and Cuvelier, C., 2009. The sensitivity of the CHIMERE
429 model to emissions reduction scenarios on air quality in Northern Italy, *Atmos. Environ.*, 43, 1897-
430 1907.

431
432 Metcalfe, S.E., Whyatt, J.D., Nicholson, J.P.G., Derwent, R.G. and Heywood, E., 2005. Issues in
433 model validation: assessing the performance of a regional-scale acid deposition model using
measured and modelled data, *Atmos. Environ.*, 39, 587-598.

434
435 Monteiro, A., Miranda, A.I., Borrego, C., Vautard, R., Ferreira, J. and Perez, A.T., 2007. Long-
436 term assessment of particulate matter using CHIMERE model, *Atmos. Environ.*, 41, 7726-7738.
437
438 Official Journal, 2008. Directive 2008/50/EC of the European Parliament and the Council of 21
439 May 2008 on ambient air quality and cleaner air for Europe, Official Journal of the European
440 Union, 11.6.2008, L152, 1-44, available at: [eur-
441 lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:152:0001:0044:EN:PDF](http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:152:0001:0044:EN:PDF)
442
443 Pye, H.O.T., Liao, H., Wu, S., Mickley, L.J., Jacob, D.J., Henze, D.K. and Seinfeld, J.H., 2009.
444 Effect of changes in climate and emissions on future sulphate-nitrate-ammonium aerosol levels in
445 the United States, *J. Geophys. Res.*, 114 D01205.
446
447 Redington, A.L. and Derwent, R.G., 2002. Calculation of sulphate and nitrate aerosol
448 concentrations over Europe using a Lagrangian dispersion model, *Atmos. Environ.*, 36, 4425-4439.
449
450 Schaap, M., Timmermans, R.M.A., Sauter, F.J., Roemer, M., Velders, G.J.M., C Boersen, G.A.,
451 Beck, J.P. and Builtjes, P.J.H., 2008. The LOTOS-EUROS model: description, validation and latest
452 developments, *Intl. J. Environ. Pollut.*, 32, 270-290.
453
454 Simpson, D., Benedictow, A., Berge, H., Bergstrom, R., Fagerli, H., Gauss, M., Hayman, G.D.,
455 Jenkin, M.W., Jonson, J.E., Nyiri, A., Semeena, V.S., Tsyro, S., Tuovinen, J.P., Valdebenito, A., and
456 Wind, P., 2011. The EMEP MSC-W chemical transport model.
457 https://wiki.met.no/_media/emep/page1/userguide_062011.pdf
458
459 Stern, R., Builtjes, P., Schaap, M., Timmermans, R., Vautard, R., Hodzic, A., Memmesheimer, M.,
460 Feldmann, H., Renner, E., Wolke, R. and Kerschbaumer, A., 2008. A model inter-comparison
461 study focussing on episodes with elevated PM₁₀ concentrations, *Atmos. Environ.*, 42, 4567-4588.
462
463 Thunis, P., Rouil, L., Cuvelier, C., Stern, R., Kerschbaumer, A., Bessagnet, B., Schaap, M.,
464 Builtjes, P., Tarrason, L., Douros, J., Moussiopoulos, N., Pirovano, G. and Bedogni, M., 2007.
465 Analysis of model responses to emission-reduction scenarios within the City Delta project, *Atmos.*
466 *Environ.*, 41, 208-220.
467
468 Vestreng, V., Myhre, G., Fagerli, H., Reis, S. And Tarrason, L., 2007. Twenty-five years of
469 continuous sulphur dioxide emission reduction in Europe, *Atmos. Chem. Phys.*, 7, 3663-3681.
470
471 Walker, H.L., Derwent, R.G., Donovan, R., and Baker, J., 2009. Photochemical trajectory
472 modelling of ozone during the summer PUMA campaign in the UK West Midlands, *Sci. Tot.*
473 *Environ.*, 407, 2012-2023.
474
475 Whyatt, J.D., Metcalfe, S.E., Nicholson, J., Derwent, R.G., Page, T. and Stedman, J.R., 2007.
476 Regional scale modelling of particulate matter in the UK, source attribution and an assessment of
477 uncertainties, *Atmos. Environ.*, 41, 3315-3327.
478
479 Yin J. and Harrison R.M., 2008. Pragmatic mass closure study for PM_{1.0}, PM_{2.5} and PM₁₀ at
480 roadside, urban background and rural sites, *Atmos. Environ.*, 42, 980-988.
481
482

484 **LIST OF TABLES**

485

486 Table 1: Comparison of Derwent et al. (2009) and present work – proportionate reductions

487

488 Table 2: Estimated concentrations ($\mu\text{g m}^{-3}$) resulting from an assumed 2020 scenario (SO_2 , 64%;
489 NO_x , 75%; NH_3 , 96%).

490

491 **LIST OF FIGURES**

492

493 Figure 1: Effect of emission reductions in UK and Europe, for $\text{NH}_3 = 100\%$.

494

495 Figure 2: Predicted sulphate as a function of SO_2 at Harwell (SO_2 emissions varied in UK and
496 Europe)

497

498 Figure 3: Predicted nitrate as a function of NO_x (as NO_2) at Harwell (NO_x emissions varied in UK
499 and Europe)

500

501 Figure 4: Predicted ammonium as a function of NH_3 at Harwell (NH_3 emissions varied in UK and
502 Europe)

503

504 Figure 5: Predicted nitrate as a function of SO_2 at Harwell (SO_2 emissions varied in UK and
505 Europe)

506

507 Figure 6: Predicted sulphate as a function of NO_x (as NO_2) at Harwell (NO_x emissions varied in
508 UK and Europe)

509

510 Figure 7: Predicted sulphate as a function of NH_3 at Harwell (NH_3 emissions varied in UK and
511 Europe)

512

513

Derwent et al., 2009	mean 15.00z values, 2006				Current work	19 March – 19 May 2007			
With respect to base case values	Sulphate	Nitrate	Ammonium	PM _{2.5}	With respect to no emission reduction	sulphate	nitrate	ammonium	SIA
Across the board cases					Reductions in all of Europe				
30% SO ₂ case	70%	105%	94%	93%	30% reduction in SO ₂	78%	108%	87%	94%
30% NO _x case	105%	80%	92%	96%	30% reduction in NO _x	101%	87%	94%	95%
30% NH ₃ case	100%	83%	79%	92%	30% reduction in NH ₃	97%	86%	83%	91%
UK-only cases					Reductions in UK only				
30% SO ₂ case	85%	101%	99%	97%	30% reduction in SO ₂	89%	104%	94%	97%
30% NO _x case	103%	92%	97%	99%	30% reduction in NO _x	100%	94%	98%	97%
30% NH ₃ case	100%	92%	90%	96%	30% reduction in NH ₃	97%	92%	90%	94%
Rest of Europe-only cases					Reductions in rest of Europe only				
30% SO ₂ case	85%	115%	96%	97%	30% reduction in SO ₂	89%	104%	93%	97%
30% NO _x case	101%	88%	94%	97%	30% reduction in NO _x	101%	94%	97%	98%
30% NH ₃ case	100%	91%	89%	96%	30% reduction in NH ₃	100%	94%	94%	97%

Table 1: Comparison of Derwent et al. (2009) and present work – proportionate reductions

Species	No abatement	All area reductions		Mainland only reductions		UK only reduction	
	SO ₂ = 100% NO _x = 100% NH ₃ = 100%	SO ₂ = 64% NO _x = 75% NH ₃ = 96%		SO ₂ = 64% NO _x = 75% NH ₃ = 96%		SO ₂ = 64% NO _x = 75% NH ₃ = 96%	
	concentration	concentration	difference	concentration	difference	concentration	difference
Chloride	1.53	1.58	-0.05	1.56	-0.03	1.54	-0.01
Nitrate	5.98	5.85	0.13	5.97	0.01	5.93	0.05
Ammonium	1.80	1.40	0.41	1.61	0.20	1.62	0.19
Sulphate	5.75	4.24	1.50	5.04	0.70	4.96	0.79
SIA	15.06	13.07	1.99	14.18	0.88	14.04	1.02

Table 2: Estimated concentrations ($\mu\text{g m}^{-3}$) resulting from an assumed 2020 scenario (SO₂, 64%; NO_x, 75%; NH₃, 96%)

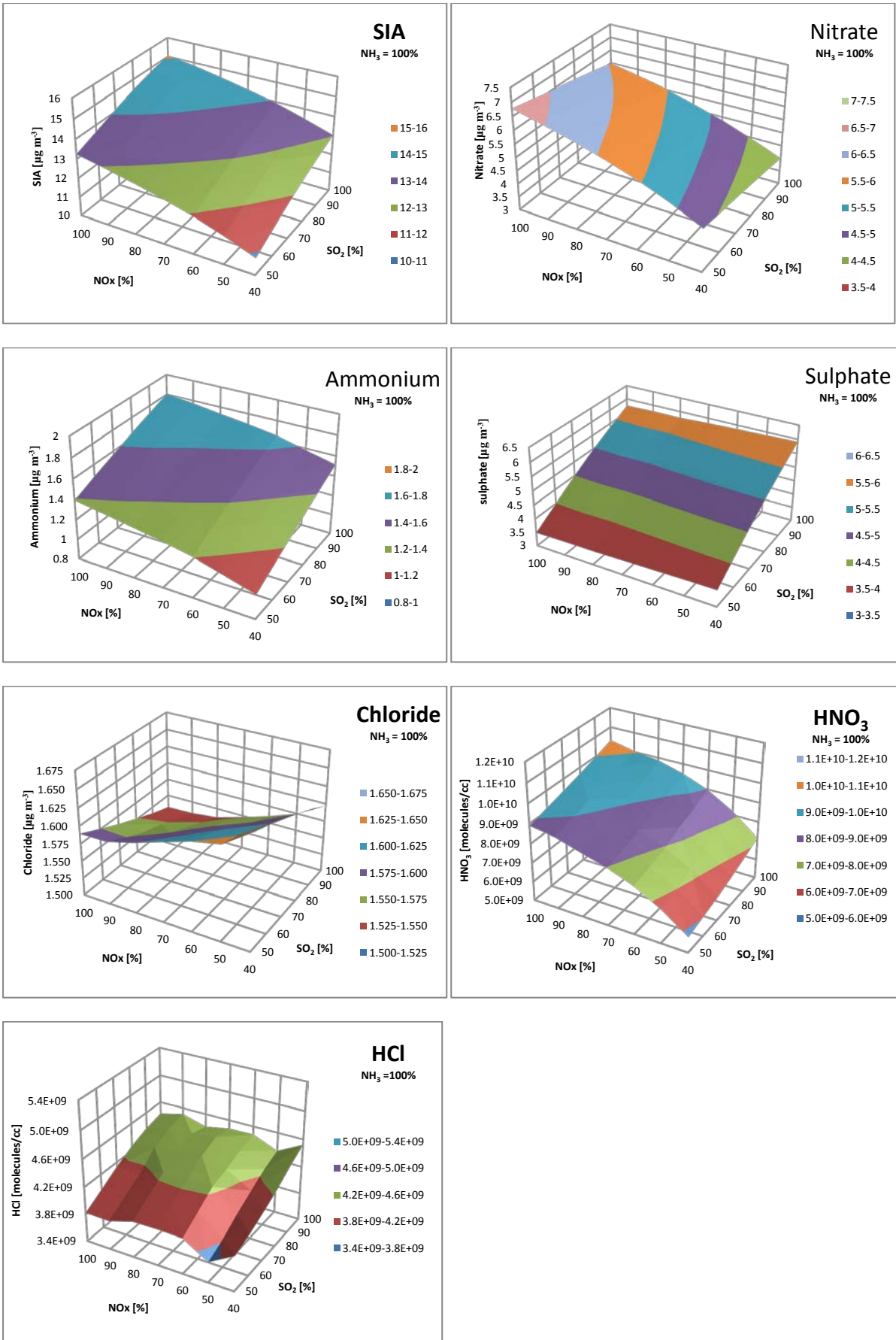


Figure 1: Effect of emission reductions in UK and Europe, for $\text{NH}_3 = 100\%$

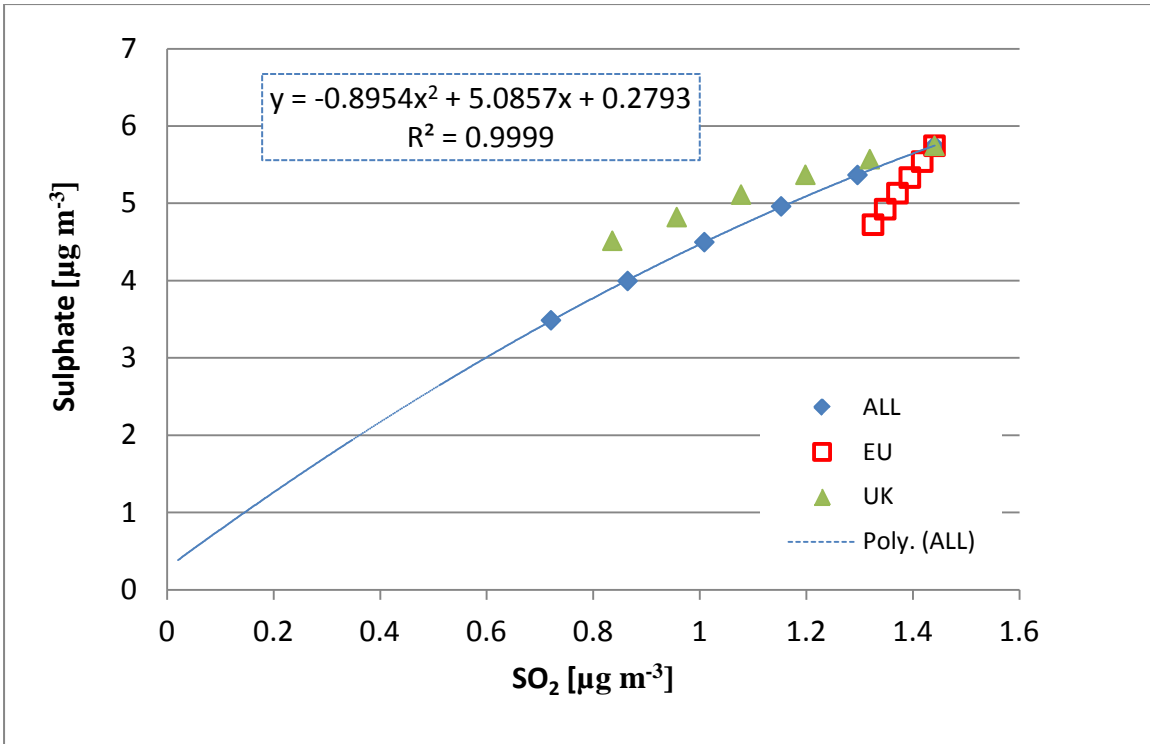


Figure 2: Predicted sulphate as a function of SO_2 at Harwell (SO_2 emissions varied in UK and Europe)

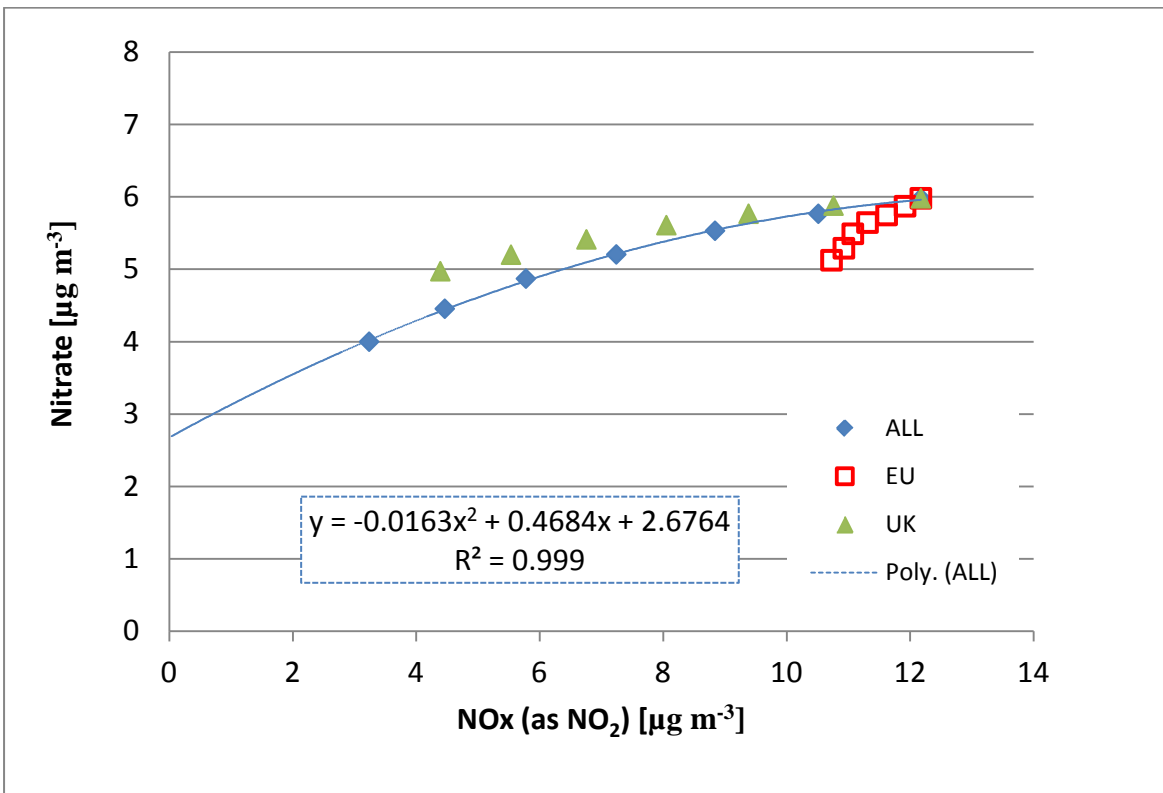


Figure 3: Predicted nitrate as a function of NO_x (as NO_2) at Harwell (NO_x emissions varied in UK and Europe)

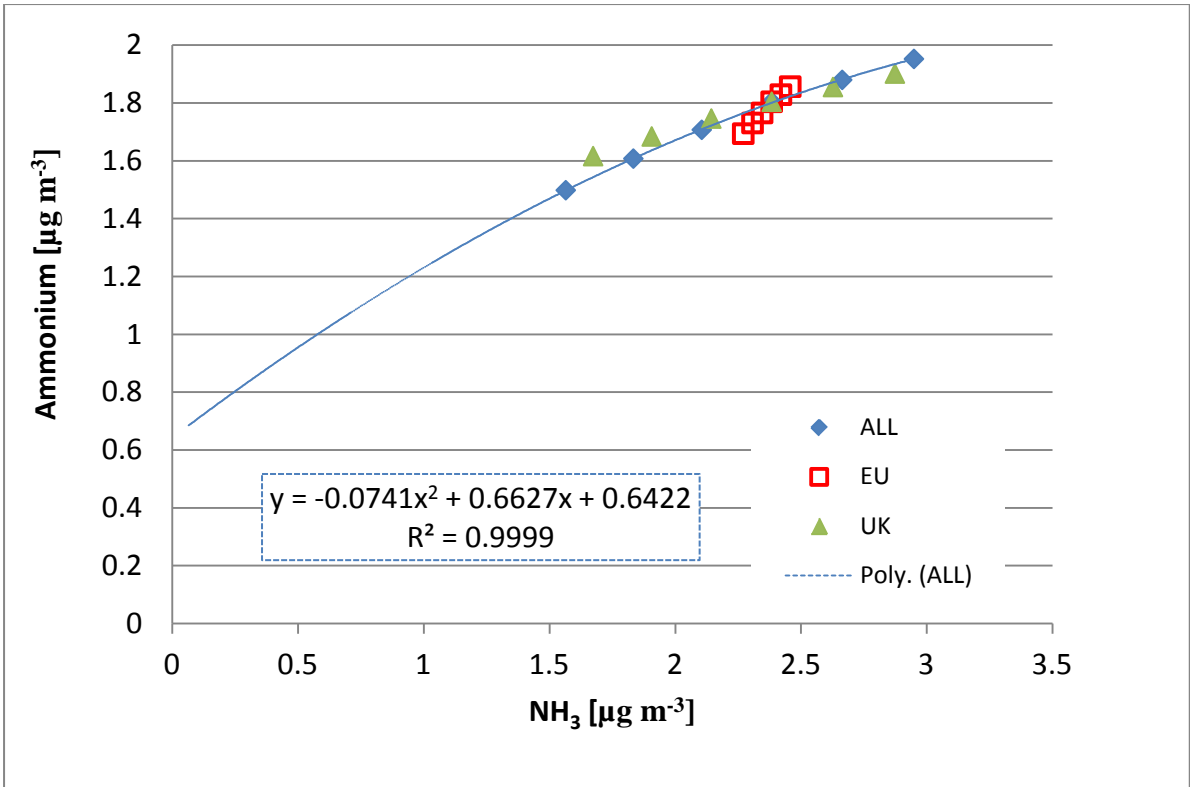


Figure 4: Predicted ammonium as a function of NH_3 at Harwell (NH_3 emissions varied in UK and Europe)

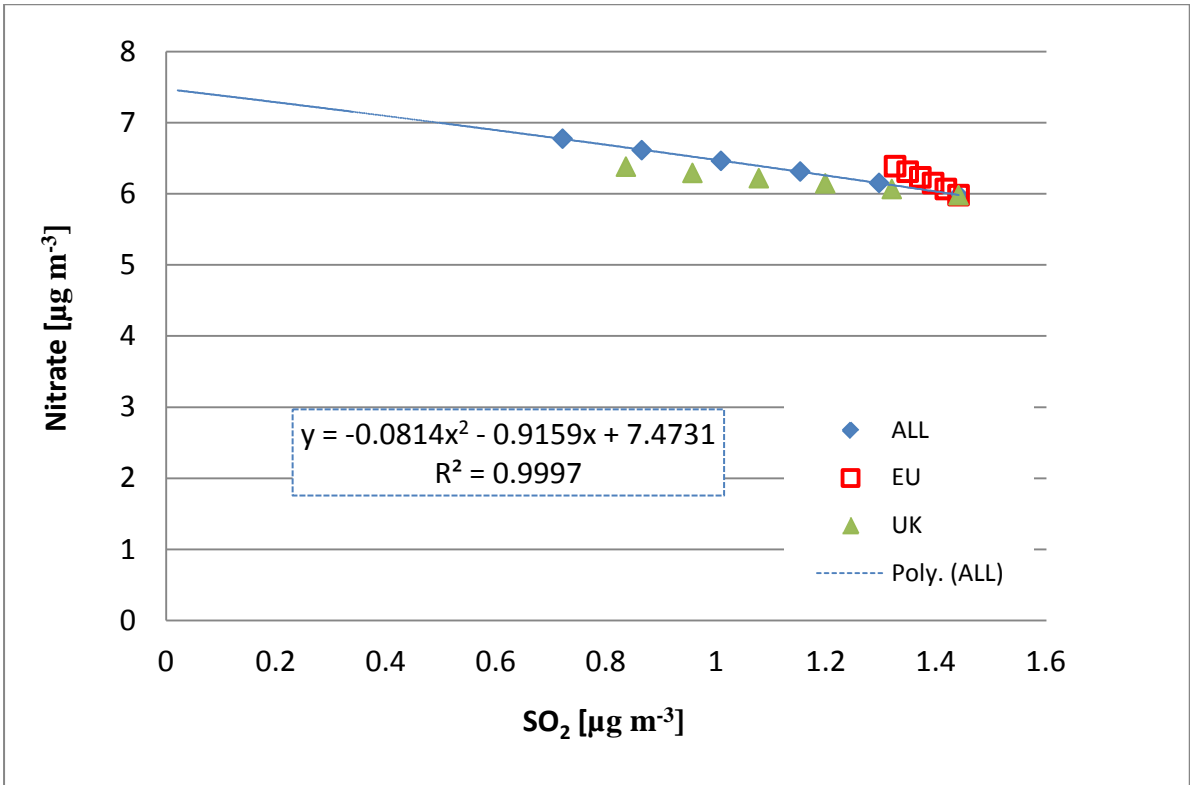


Figure 5: Predicted nitrate as a function of SO_2 at Harwell (SO_2 emissions varied in UK and Europe)

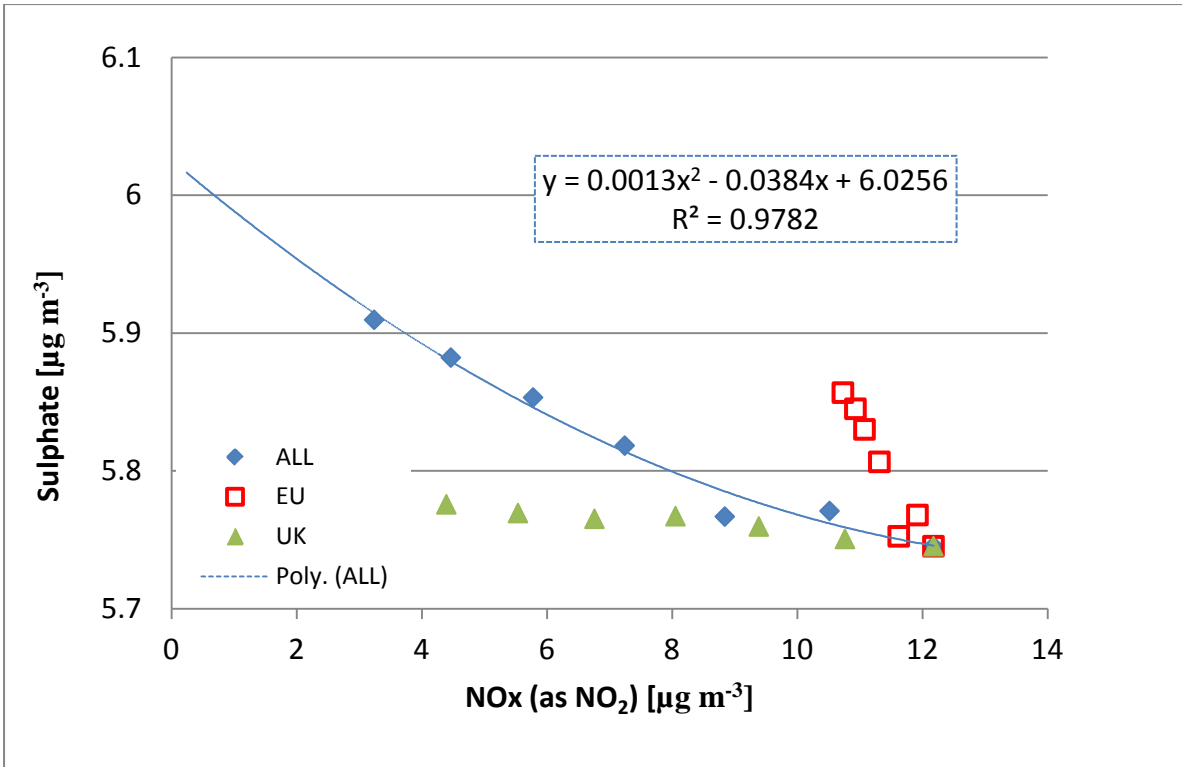


Figure 6: Predicted sulphate as a function of NO_x (as NO₂) at Harwell (NO_x emissions varied in UK and Europe)

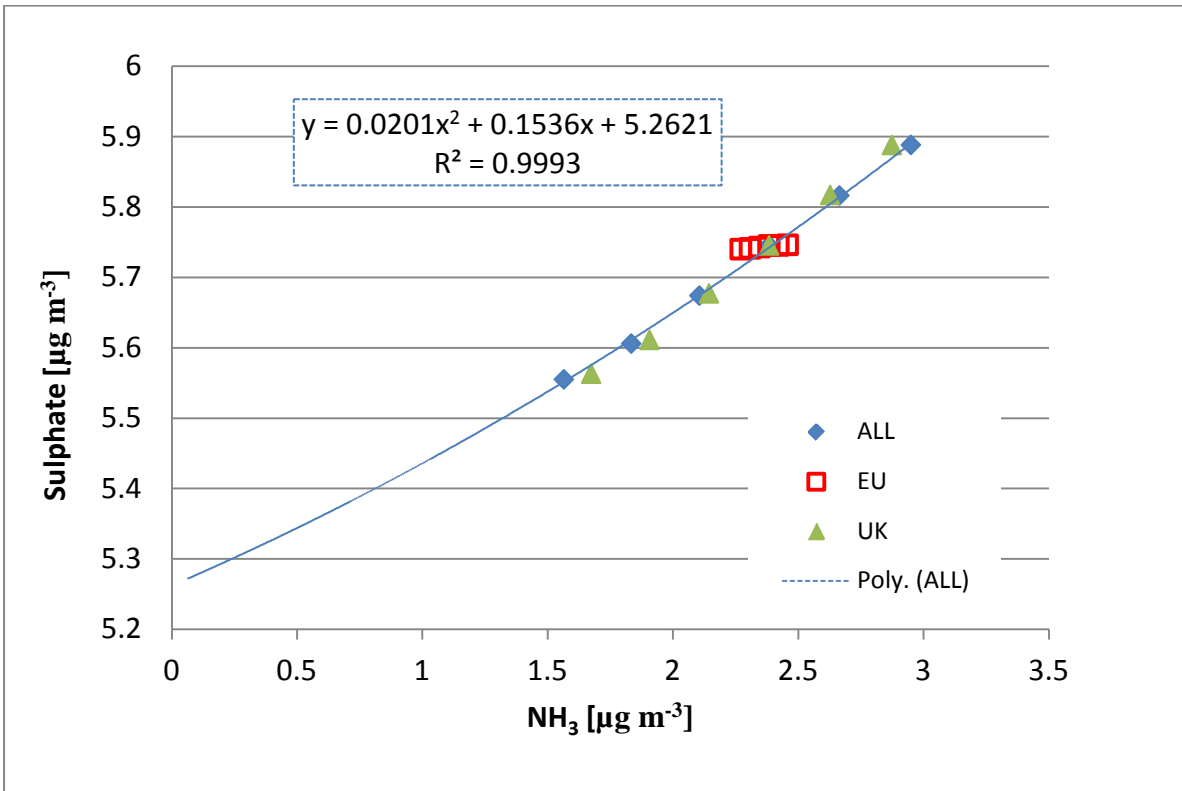


Figure 7: Predicted sulphate as a function of NH₃ at Harwell (NH₃ emissions varied in UK and Europe)