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Atmospheric behaviour of particulate oxalate at UK urban background and rural sites

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5 **ATMOSPHERIC BEHAVIOUR OF**
6 **PARTICULATE OXALATE AT UK URBAN**
7 **BACKGROUND AND RURAL SITES**
8

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23 **ABSTRACT**

24 Oxalic acid is widely reported in the literature as one of the major components of organic aerosol.
25 It has been reported as both a product of primary emissions from combustion processes and as a
26 secondary product of atmospheric chemistry. Concentrations of particulate oxalate have been
27 measured at a UK urban site (500 daily samples) and for a more limited period simultaneously at a
28 rural site (100 samples) in the fine (less than 2.5 μm) and coarse (2.5-10 μm) size fractions. Full
29 size distributions have also been measured by sampling with a MOUDI cascade impactor. Average
30 concentrations of oxalate sampled over different intervals in PM_{10} are $0.04 \pm 0.03 \mu\text{g m}^{-3}$ at the
31 rural site and $0.06 \pm 0.05 \mu\text{g m}^{-3}$ at the urban background site, broadly comparable with
32 measurements from other European locations. During the period of simultaneous sampling at the
33 urban and rural site, concentrations were very similar and the inter-site correlation in the $\text{PM}_{2.5}$
34 fraction for oxalate ($r = 0.45$; $p < 0.001$) was appreciably weaker than that for sulphate and nitrate
35 ($r = 0.82$ and 0.84 , respectively). Nonetheless, the data clearly point to a predominantly secondary
36 source of oxalate at these sites. Possible contributions from road traffic and woodsmoke appear to
37 be very small. In the larger urban dataset, oxalate in $\text{PM}_{2.5}$ was correlated significantly ($p < 0.01$)
38 with sulphate ($r = 0.60$), nitrate ($r = 0.48$) and secondary organic carbon ($r = 0.25$). Clustering of
39 air mass back trajectories demonstrates the importance of advection from mainland Europe. The
40 size distribution of oxalate at the urban site showed a major mode at around 0.55 μm and a minor
41 mode at around 1.5 μm in the mass distribution. The former mode is similar to that for sulphate
42 suggesting either a similar in-cloud formation mechanism, or cloud processing of oxalate and
43 sulphate after formation in homogeneous reaction processes.

44

45 **Keywords:** Oxalate; secondary organic aerosol; regional pollution

46 1. **INTRODUCTION**

47 Organic compounds, including both water-soluble and insoluble species, account for a significant
48 fraction of the fine particulate matter mass in the atmosphere (Jacobson, et al., 2000; Zhang et al.,
49 2007; Harrison and Yin, 2008). Among the different types of water-soluble organic carbon
50 (WSOC), monocarboxylic acids (MCA) and dicarboxylic acids (DCA) are groups of significant
51 interest in the chemical characterisation of PM (Chebbi and Carlier, 1996; Cecinato et al., 1999;
52 Dabek-Zlotorzynska and McGrath, 2000; Limbeck et al., 2001; Falkovich et al., 2004; Karthikeyan
53 and Balasubramanian, 2005; Wang et al., 2007).

54

55 Oxalic acid is the dominant dicarboxylic acid (DCA) followed by malonic and succinic acids
56 (Kawamura and Ikushima, 1993; Kawamura and Usukura, 1993; Yao et al., 2002a,b), and it
57 constitutes up to 50-70% of total atmospheric DCA (Sempere and Kawamura, 1994; 1996). The
58 occurrence of oxalate in aerosols and precipitation was demonstrated using ion chromatography by
59 Norton et al. (1983). Thereafter, Kawamura and Kaplan (1987) found that the diacids (C₂-C₁₀) were
60 mainly associated with particles but a minor fraction of these compounds was present in the vapour
61 phase. They suggested the possibility that low molecular weight diacids (i.e. oxalic) were present in
62 the vapour phase under elevated temperature conditions. Oxalic acid is mostly present in the
63 particulate phase in the ambient atmosphere and is of lower volatility compared with formic and
64 acetic acids, which are the main monocarboxylic acids present in the gas phase (Chebbi and Carlier,
65 1996).

66

67 The sources of oxalate in the atmosphere comprise both primary biogenic and anthropogenic
68 emissions (Kawamura and Kaplan, 1987; Kawamura and Ikushima, 1993) and transformations of
69 precursors in the gaseous and condensed phases (Dabek-Zlotorzynska and McGrath, 2000; Chebbi
70 and Carlier, 1996; Kawamura et al., 1996; Myriokefalitakis et al., 2011). Knowledge of the size
71 distribution of oxalate can provide valuable insights into its sources, formation and growth

72 mechanism. Oxalate is predominantly found in size distributions in the large droplet mode, while
73 the condensation mode and the coarse mode are both relatively less abundant (Kerminen et al., 2000;
74 Yao et al., 2003; Huang et al., 2006).

75
76 In this paper, we aim to gain a better understanding of the sources and atmospheric behaviour of
77 particulate oxalate by analysis of a dataset of oxalate concentrations from two UK sites in
78 comparison with other, major chemical components i.e. sulphate, nitrate, chloride, primary and
79 secondary organic carbon (OC) and elemental carbon (EC) in ambient air.

80

81 2. **METHODOLOGY**

82 2.1 **Sampling Locations**

83 2.1.1 *Elms Road Observatory Site (EROS) (N 52:27:13; W 1:55:41)*

84 EROS is located within the “green space” of the University of Birmingham campus. This is an
85 urban background site located in an open field within the University. The site is about 3.5 km
86 southwest of the centre of Birmingham, which has a population of over one million and is part of a
87 conurbation of 2.5 million population. The nearest anthropogenic sources are a nearby railway
88 (predominantly electric), some moderately trafficked B roads at about 500 metres and other
89 activities of the university and local residents. Figure S1 in Supplementary Information shows the
90 locations of the two sites.

91

92 2.1.2 *Harwell (N 51:34:16; W 1:19:31)*

93 This rural site is located within the grounds of the Harwell Science Centre, Didcot, Oxfordshire.
94 The air sampler was installed outside the main monitoring station. The surrounding area is generally
95 open with agricultural fields. There is limited activity in the area and the nearest road about 400
96 metres from the monitoring site is used only for access to buildings within the Science Park. The
97 nearest trees are at a distance of 200 - 300 metres from the monitoring station. Distant sources

98 include the busy A34 dual carriageway about 2 km to the east and the Didcot Power Station about 5
99 km to the north-east. The Harwell site is located 115 km from the EROS site, both in central
100 England.

101

102 2.2 Air Sampling

103 Airborne particulate matter in both fine ($PM_{2.5}$) and coarse ($PM_{2.5-10}$) fractions was collected daily
104 by Partisol samplers with filter changing taking place at 1200 noon local time over the period from
105 November 2008 to April 2011 at EROS and from July to December 2010 at Harwell. A
106 Dichotomous Partisol Plus model 2025D sequential air sampler fitted with a PM_{10} inlet and
107 containing a virtual impactor and downstream flow controllers which separate the flow into fine and
108 coarse fractions, at flow rates of 15.0 L min^{-1} and 1.7 L min^{-1} , respectively was utilised. The
109 calculation of coarse PM is achieved by the correction of fine particles in the carrier flow using the
110 formula, $C_c = M_c/V_t - V_c/V_t \cdot C_f$ (where C_c is the mass concentration of the coarse particle fraction,
111 M_c the mass collection on coarse particle fraction filter, V_c and V_t are the volumes of air samples
112 through the coarse fraction filters and the sum of coarse and fine fraction filters, respectively, and C_f
113 is mass concentration of the fine particle fraction). The Partisol sampler was equipped with a 47
114 mm quartz fibre filter (Whatman QMA) substrate. Filters were pre-heated at 500°C in air using a
115 furnace for 4 hours in order to minimize their carbon content and stored sealed in a freezer prior to
116 air sampling. The exposed filters were stored in filter cassettes within the storage magazines inside
117 of the instrument. After the sampling was completed, the exposed filters were stored in a metal
118 container at about -18°C in a freezer until analysis to prevent loss of volatile compounds. This
119 sampling method is subject to the usual artefacts of adsorption and volatilisation which occur when
120 sampling semi-volatile materials on filters.

121

122 Samples were also collected at the EROS site using a MOUDI cascade impactor run at 30 L min^{-1} ,
123 giving cut points at 10, 5.6, 3.2, 1.8, 1.0, 0.56, 0.32 and $0.18 \mu\text{m}$. Impaction substrates were 47 mm

124 Teflon with a 37 mm Teflon back-up. Because of its reduced pressure the MOUDI is liable to
125 under-sample semi-volatile particulate substances including nitrate (Huang et al., 2004) and oxalate.
126

127 2.3 Analysis of Samples

128 2.3.1 OC, EC and TC

129 For the determination of OC, EC and TC concentration, a Sunset Laboratory Thermal-Optical
130 Carbon Aerosol Analyser was used in this study. It uses thermal desorption in combination with
131 optical transmission of laser light through the sample to speciate carbon collected on a quartz fibre
132 filter (Sunset Laboratory Inc., 2004). Organic carbon is removed during an initial non-oxidizing
133 temperature ramp from about 75°C to 650°C under a helium atmosphere, and then passes to a
134 manganese dioxide oxidizing oven where it is converted to carbon dioxide, which is mixed with
135 hydrogen and converted to methane over a heated nickel catalyst. The methane is subsequently
136 measured using a flame ionization detector (FID). A second temperature ramp from 500°C to 850°C
137 is then initialized with the carrier gas switched to a helium/oxygen mixture, under which elemental
138 carbon and pyrolysis products are oxidized and carried through the system and measured in the
139 same manner as the organic carbon. A laser is used to monitor the light transmission through the
140 filter during the analysis, which determines a split point which separates the elemental carbon
141 formed by charring during the initial non-oxidising temperature ramp from the elemental carbon
142 that was originally in the sample. The split point is the point in time when the laser signal measured
143 during the oxidizing stage equals the initial laser signal. The temperature programme used a
144 protocol recently developed for the European Super-sites for Atmospheric Aerosol Research project
145 (EUSAAR 2), which is He at 200°C (120 s); 300°C (150 s); 450°C (180 s); 650°C (180 s) following
146 by He/O₂ 500°C (120 s); 550°C (120 s); 700°C (70 s) and 850°C (80 s) (Cavalli et al., 2010). A filter
147 punch 1.5 cm² in size was removed from the 47-mm QMA filter and loaded into the carbon aerosol
148 analyser. The results of OC/EC analysis were corrected for the blank.

149

150 Organic carbon concentrations were sub-divided into primary and secondary OC using the
151 elemental carbon tracer method (Castro et al., 1999), as reinterpreted by Pio et al. (2011). This
152 involved estimating primary OC as equal to 0.35 EC and secondary OC by difference from the total.

153

154 2.3.2 *Ionic species*

155 The exposed QMA filters remaining from carbon analysis and PTFE filters were transferred from
156 their bags to a narrow neck 15 ml HDPE bottle. Distilled deionised water (10 mL) was added and
157 the bottles were extracted in an ultrasonic bath for 30 min at room temperature. After
158 ultrasonication, the filter extracts were filtered through a syringe filter (0.2 µm) and then kept in a
159 cold room until analysis. For particulate matter collected onto PTFE filters in size-segregated
160 samples, the filters were wetted with propan-2-ol (0.5 mL) to eliminate the natural hydrophobicity
161 of the filters. Then, 15 mL of ddw were added and ultrasonication performed for 30 min. The
162 leachate was filtered and kept refrigerated until being analysed.

163

164 Anion concentrations (sulphate, nitrate, chloride and oxalate) were determined using ion
165 chromatography (Dionex model ICS-2000). The ICS-2000 is an integrated ion chromatography
166 system containing an analytical column (IonPac AS11HC with 2 × 250 mm) with a guard column
167 (IonPac AG11HC with 2 × 50 mm). The eluent for these samples was potassium hydroxide
168 (gradient) and its flow rate during the analyses was 0.38 mL min⁻¹. The injection sample volume of
169 200 µl was loaded into the eluent stream and 5 mL sample vials were used with the auto sampler.
170 The ICS-2000 was controlled by Chromeleon software which also provided data acquisition and
171 data processing functions. The IC system was calibrated using a series of mixed anion standards of
172 known concentration (0.2 – 20 ppm) before running a sample. The mixed standard solutions
173 containing SO₄²⁻, NO₃⁻, Cl⁻ and C₂O₄²⁻ were prepared and kept in the cold room.

174

175

176 2.3.3 *Quality Assurance*

177 The quality of chemical analysis was investigated and detailed in the Supplementary Information.
178 After completion of the work, it was learned that oxalate is susceptible to degradation in aqueous
179 solutions (Dabek-Zlotorzynska and McGrath, 2000). As our samples had been stored for periods
180 between 2 and 28 days as aqueous extracts at 4°C prior to analysis, statistical tests were applied to
181 evaluate oxalate losses. Application of the Mann-Whitney test showed no significant difference
182 between samples stored for 7 days and 25 days, and for < 7 days and > 7 days, and we conclude that
183 degradation losses were negligible.

184

185 2.4 **Air Mass Trajectories Calculation**

186 In order to investigate the potential source regions of oxalate, backward air mass trajectories were
187 calculated for the period of study. The Hybrid Single Particle Lagrangian Integrated Trajectory
188 (HYSPLIT_4) model available on the NOAA Laboratory website was used for calculation of the
189 trajectories. The meteorological data used (the Global Data Assimilation System; GDAS) were
190 obtained at the NOAA Air Resource Laboratory (ARL) archives. Each of the trajectories
191 corresponded to a 72h back trajectory ending at 500 metres altitude at each site. A cluster analysis
192 was applied to minimise the uncertainty of individual trajectories associated with the resolution and
193 accuracy of the meteorological data and by any simplifying assumptions used in the trajectory
194 model (Stohl, 1998).

195

196 3. **RESULTS AND DISCUSSION**

197 3.1 **Oxalate Concentration Level and Major Chemical Composition in PM**

198 Table 1 shows the concentrations of oxalate in PM in comparison with published data from other
199 sites from Europe and Asia. The differences in oxalate concentration depend on the local sources as
200 well as on the variability in meteorological and atmospheric chemical conditions in the area at the

201 time of sampling. In our dataset, oxalate exhibited higher concentrations in fine particulate matter
202 than in the coarse fraction especially for aerosol samples taken at the urban site.

203

204 The major anion components of the aerosol samples were also measured in order to investigate
205 relationships of oxalate with those constituents, and their concentration data appear in Table S1 in
206 the Supplementary Information.

207

208 3.1.1 *Effect of the Local Factors upon Oxalate Concentration*

209 Regression analysis of ionic species in PM_{2.5} obtained from simultaneously collected EROS and
210 Harwell samples was conducted using reduced major axis (RMA) regression. The relationships of
211 concentrations of oxalate and other chemical components between the two sites are summarized in
212 Table 2. In these data, the correlation coefficients (*r*) of sulphate and nitrate in fine particles show
213 quite high values of 0.82 and 0.84, respectively. On the other hand, lower values of correlation
214 coefficient for chloride, oxalate, WSOC and OC_{sec} between the sites were observed in the range
215 from 0.45 to 0.57.

216

217 The plot for sulphate in the fine mode showed a zero intercept with a gradient close to 1.0,
218 indicating that the regional contribution of long-range transport in the atmosphere plays a dominant
219 role in determining its concentration. For nitrate in PM_{2.5}, the regression intercept in Table 2
220 indicates a small local increment of 0.11 µg m⁻³ consistent with the local fine nitrate contribution of
221 0.17 µg m⁻³ estimated from the difference in mean concentrations of data from simultaneously
222 collected samples from the two sites (Table 3). This finding suggests a small nitrate urban
223 increment, as was concluded for London by Abdalmogith and Harrison (2005), although the
224 observation of a similar increment of SO₄²⁻ at EROS indicates that it may simply reflect slightly
225 greater regional formation at EROS. With regard to chloride, oxalate and WSOC, the intercept
226 values in the fine fraction were low (0.05 µg m⁻³, 0.01 µg m⁻³ and 0.01 µg m⁻³, respectively)

227 suggesting regional sources and no significant urban effect. The Mann-Whitney U test was applied
228 to assess whether any significant concentration difference for aerosol components existed between
229 the two sites. This test is a nonparametric test that can be used to analyse data from two independent
230 groups. Test results indicated that SO_4^{2-} , NO_3^- , $\text{C}_2\text{O}_4^{2-}$ and OC_{sec} concentrations measured in $\text{PM}_{2.5}$
231 simultaneously at EROS and Harwell were not significantly different, with $p > 0.05$. There were
232 differences for Cl^- , EC, OC_{prim} , OC and WSOC concentrations in fine particles between the two
233 sites ($p < 0.05$). The estimation of an urban contribution to atmospheric aerosol was quantified by
234 subtraction of Harwell concentrations representing the rural site from EROS concentrations
235 representing an urban background site. The results for the local contribution can be inferred from
236 Table 3. As expected, EC shows a strong local contribution ($0.6 \mu\text{g m}^{-3}$) in $\text{PM}_{2.5}$ reflecting local
237 urban emissions at the EROS site. OC_{sec} and OC_{prim} in fine particles show a lower local contribution
238 ($0.4 \mu\text{g m}^{-3}$ and $0.3 \mu\text{g m}^{-3}$). Small local contributions were observed in fine sulphate, nitrate and
239 chloride in this study ($0.13 \mu\text{g m}^{-3}$, $0.17 \mu\text{g m}^{-3}$ and $0.08 \mu\text{g m}^{-3}$, respectively). There is no
240 difference in mean concentrations of oxalate in $\text{PM}_{2.5}$ between the two sites although concentrations
241 are low and less precise than for the other analytes. This finding is strongly supportive of the
242 formation of oxalate by regional-scale atmospheric chemical processes and atmospheric transport
243 and its presence as a long-lived species. Backward air mass trajectories arriving at both sites are
244 reported in a subsequent section in order to investigate further the origins of the regional
245 contribution.

246

247 3.2 Seasonal Variation of Oxalate

248 The time series of oxalate measured daily in the fine fraction at the EROS and Harwell sites is
249 shown in Figure 1. It is clear that the within-site temporal variation of oxalate was greater than the
250 spatial variation. In order to evaluate seasonal variations, monthly concentration data for major
251 components are presented in Figure 2. The air sampling period was split into four seasons as
252 follows: summer (JJA); autumn (SON); winter (DJF) and spring (MAM). The significance of

253 differences in ionic concentrations between the seasons was determined for EROS data by applying
254 a Kruskal-Wallis test. The number of data in the whole, summer, autumn, winter and spring periods
255 were 500, 116, 165, 101 and 118 samples, respectively. In these data, test results indicated
256 significant differences for each of sulphate, nitrate, chloride and oxalate concentrations between the
257 four seasons ($p < 0.05$). It is clear that sulphate, nitrate and chloride in the fine fraction were lower
258 in the summer months (Figure 2), but the dataset is too small to draw firm conclusions. For chloride,
259 the mean concentration in $PM_{2.5}$ and PM_{10} is higher in the winter and lower in the summer as
260 expected due to generally much higher wind speeds in winter leading to greater generation of
261 marine aerosol. A seasonal trend for particulate oxalate does not show through so clearly but the
262 average concentration level is highest in spring. This may be the result of strong sunshine levels
263 and plant growth favouring secondary formation, with lower temperatures than in summer reducing
264 the partitioning into vapour. Kerminen et al. (2000) saw a clear summer maximum and winter
265 minimum at sites in Finland.

266

267 3.3 Sources and Formation Pathways of Oxalate by Correlation Analysis

268 An intra-site correlation analysis of measured components at EROS was conducted in order to
269 investigate the origin of particles (Table S3). Oxalate in $PM_{2.5}$ and PM_{10} shows a slightly higher
270 correlation (r value) with sulphate ($r = 0.60$ and $r = 0.59$, respectively) than with nitrate ($r = 0.48$
271 and $r = 0.49$, respectively) for the entire period. These results suggest that oxalate originates from
272 similar atmospheric processes as sulphate i.e., from secondary formation. The close relationship of
273 oxalate with sulphate is consistent with results reported by Kerminen et al. (2000), Yao et al. (2003)
274 and Yu et al. (2005). Strong relationships of oxalate with sulphate and nitrate are observed
275 particularly in summer (for $PM_{2.5}$, $r = 0.70$ and $r = 0.79$, respectively; for PM_{10} , $r = 0.69$ and $r =$
276 0.78 , respectively). The correlations between oxalate and nitrate suggest that temperature may
277 influence the oxalate concentration as it does for nitrate through the ammonium nitrate dissociation.
278 This has recently been confirmed in field observations by Bao et al. (2012), although laboratory

279 studies of the atmospheric gas-particle partitioning of oxalic acid/oxalate do not give unequivocal
280 predictions (Soonsin et al., 2010).

281

282 The mean oxalate concentration in the whole dataset had a very weak correlations with EC in PM_{2.5},
283 PM_{2.5-10} and PM₁₀ ($r = 0.07$, $r = -0.09$ and $r = 0.04$, respectively). This was anticipated from its
284 regional distribution and reflects an insignificant contribution to oxalate from primary combustion
285 sources. A similar observation was reported by Yao et al. (2004) and Yu et al. (2005), which clearly
286 indicated little contribution of vehicular emissions to ambient oxalic acid. EC is strongly related to
287 road traffic emissions at our site (Yin and Harrison, 2008; Yin et al., 2010). Moreover, a poor
288 correlation between oxalate and potassium, a tracer for biomass burning, was observed in the fine
289 fraction at EROS ($r = 0.18$) suggesting that primary biomass burning or rapid formation in biomass
290 burning plumes was also not a major source of the oxalate. This is contrary to the measurements of
291 Legrand et al. (2007) using data from K-Pusztta (Hungary) and Aveiro (Portugal) who infer a major
292 contribution of wood burning to oxalate concentrations in winter. In order to investigate secondary
293 sources of oxalate aerosol, the relationship between oxalate and secondary OC was determined and
294 the plots of oxalate versus OC_{sec} in PM_{2.5} at EROS are shown in Figure S2 (Supplemental
295 Information). This figure shows that when all data ($n = 500$) are pooled, the two variables are
296 weakly correlated ($r = 0.24$), but when sub-divided by season, show stronger correlations in spring
297 ($r = 0.35$), and especially summer ($r = 0.55$). The high correlation coefficient found during summer
298 suggests a photochemical and/or biogenic contribution to both secondary OC formation and to
299 oxalate. This is in agreement with the results reported by Kawamura and Ikushima (1993) and
300 Sempere and Kawamura (1994). The relatively low correlation between oxalate and SOC indicates
301 that oxalate makes up a very variable proportion of secondary organic aerosol, but is typically 1-3%
302 of SOA (after conversion of SOC to SOA mass), or 0.5-1.5% expressed as oxalate carbon/organic
303 carbon.

304

305 Oxalate in coarse particles showed a modest correlation with nitrate and sulphate in summer ($r =$
306 0.49 and $r = 0.45$, respectively). Coarse oxalate may arise from gas-phase oxalic acid reacting with
307 pre-existing particles, by particle coagulation or by heterogeneous reactions within large droplets.
308 However, for the full dataset, oxalate in the coarse mode correlated weakly with the other ionic
309 species. The general assumption is that oxalate in ambient air is formed in the aqueous phase and
310 therefore coarse mode oxalate can be produced by aqueous phase processes. Russell and Seinfeld
311 (1998) have proposed that supermicron particles can be formed by in-cloud processes. Earlier
312 studies by Dutton and Evans (1996) and Gadd (1999) have reported that oxalate was a by-product
313 of the hydrolysis of oxaloacetate from citric acid and glyoxylate via the metabolic action of fungi in
314 soil. Wind-blow soil might then be a source of oxalate in coarse airborne particles, but this seems
315 unlikely to be a large contributor to airborne concentrations.

316

317 3.4 Size Distribution of Oxalate

318 The size distribution of oxalate was studied in comparison with major anionic and cationic species
319 in ambient aerosol. Earlier studies have highlighted the strong similarities of the oxalate size
320 distribution with that of sulphate (Kerminen et al., 2000; Huang et al., 2006).

321

322 In most of our samples, the mass size distributions of oxalate were bimodal consisting of one
323 submicron mode and one supermicron mode. Some samples appeared to exhibit a more complex
324 structure (Figure 3). The dominant mode of oxalate peaked at $0.4 \mu\text{m} - 0.5 \mu\text{m}$ with a more
325 variable coarse mode around $1-2 \mu\text{m}$. The finer mode was very similar to that of sulphate, seen in
326 simultaneously collected material in Figure S3 (Supplementary Information). This reflects the
327 significant relationship between $\text{C}_2\text{O}_4^{2-}$ and SO_4^{2-} in $\text{PM}_{2.5}$ ($r = 0.60$) found at this site for the
328 samples collected by Partisol Plus air samplers (500 samples). The similarity in size distributions
329 suggests that oxalate and sulphate may have similar formation pathways. Yao et al. (2002a)
330 concluded that oxalate in the $0.32 \mu\text{m} - 0.54 \mu\text{m}$ size range was produced by in-cloud processes and

331 other studies have attributed sulphate in the droplet mode to in-cloud processes (Meng and Seinfeld,
332 1994; Kerminen and Wexler, 1995; Yu et al., 2005).

333

334 Oxalate has previously been attributed to a range of sources including primary emissions from
335 vehicular transportation (Kawamura and Kaplan, 1987), biomass burning (Narukawa et al., 1999;
336 Legrand et al., 2007), biogenic activity (Kawamura, et al. 1996; Jones, 1998) and as a secondary
337 product of the oxidation of both anthropogenic and biogenic precursors (Kalberer et al., 2001; Lim
338 et al., 2005). Kawamura et al., (1996) and Kalberer et al., (2001) concluded that the condensation
339 mode oxalate was from the photochemical formation in the gas phase by the reaction of organic
340 compounds with photochemical oxidants such as OH free radicals and O₃ to form gaseous oxalic
341 acid, followed by its condensation onto existing particles. If gas-particle condensation were the
342 main process to form oxalate, the highest concentrations should be found in the condensation mode
343 (0.175 μm – 0.325 μm). On the contrary, the results showed the highest concentration of oxalate in
344 the droplet mode, suggesting that condensation mode oxalate-containing particles were activated
345 and became droplet mode particles due to cloud processing. A further proposed mechanism of
346 formation of oxalic acid is from isoprene by in-cloud oxidation processes (Lim et al. 2005).

347

348 Oxalate in the coarse mode accounted for 12% to 15% of total oxalate for the samples collected by
349 cascade impactor. There were no significant correlations observed between cationic species and
350 oxalate in the coarse mode. Similarities in coarse mode size distribution with sodium (1.8 μm – 9.9
351 μm), suggest the possibility of formation within, or uptake of gaseous oxalate by sea salt particles.
352 Alternatively, Russell and Seinfeld (1998) have proposed that supermicron particles can be formed
353 by in-cloud processes.

354

355

356

357 3.5 **Air Mass Trajectories**

358 3.5.1 *Full Dataset at EROS*

359 The 500 daily midday back trajectories arriving at EROS during the sampling period between
360 November 2008 to April 2011 were generated by the HYSPLIT_4 model. The result of the cluster
361 analysis of the 3-day trajectories is presented in Figure 4. There were five main back trajectory
362 clusters arriving at this site; cluster 1 – the fast south westerly accounted for 22% of the total
363 trajectories, cluster 2 – the north westerly accounted for 21% of the total trajectories, cluster 3 – the
364 slow southerly accounted for 19% of the total trajectories, cluster 4 – the fast westerly accounted for
365 9% of the total trajectories, cluster 5 – the slow easterly accounted for 29% of the total trajectories.
366 Cluster 5 occurred more frequently during autumn and spring. The fast maritime trajectory
367 represented in cluster 4 occurred predominantly both in the winter and autumn months and less
368 during the summer. Many of the trajectories during the summer grouped in the slow southerly
369 airflow (cluster 3) whilst many of winter time trajectories appeared significantly both in cluster 2
370 and cluster 5. Table 4 contains the average concentration of oxalate and major components in the
371 fine fraction for all trajectory clusters. The highest concentration of all species in PM except
372 chloride are associated with the slow easterly (cluster 5) airflows. This result indicates that for the
373 urban background site (EROS), the concentration of major secondary aerosol species would be
374 expected to be associated with the long range transport of pollutants emitted from European
375 mainland sources, consistent with the studies reported by Baker (2010), Abdalmogith and Harrison
376 (2005) and Buchanan et al. (2002). As anticipated, the fast maritime cluster 4 originating from the
377 Atlantic Ocean carries the highest chloride concentration of $1.12 \mu\text{g m}^{-3}$. Salvador et al. (2010)
378 observed the source of oxalic and other diacids from central Europe, consistent with our trajectory
379 observations.

380

381 A significant source of biogenic emissions from vegetation especially isoprene, could be a potential
382 precursor associated with continental trajectories as stated by Legrand et al. (2007). Their study

383 confirmed the role of isoprene as a precursor of oxalic acid associated with the high estimated
384 isoprene emissions in Europe especially in the east flank of France (Simpson et al., 1995). This
385 seems unlikely to be the main source, however, as this would produce a pronounced seasonality
386 which is not observed.

387

388 **4. CONCLUSIONS**

389 Previous work on atmospheric oxalate has highlighted both primary and secondary sources. The
390 former have included both road traffic and biomass burning. However, in our dataset oxalate does
391 not show a positive urban increment analogous to that of elemental carbon and does not correlate
392 with EC and for this reason we discount road traffic as a significant source. The concentrations
393 measured in our work, although comparable with many contemporary data (see Table 1) are
394 generally lower than in older studies, suggesting that the road traffic source may have decreased
395 with the advent of exhaust after-treatment devices. Additionally, we see no correlation between
396 oxalate and fine potassium, a woodsmoke tracer, and we think it unlikely that biomass burning is
397 contributing significantly to concentrations of oxalate.

398

399 A number of features of the behaviour of oxalate are consistent with a secondary, regional source.
400 Mean concentrations are very similar at the urban and rural sites, and at the rural site oxalate is
401 significantly correlated with the secondary inorganic components sulphate and nitrate. After
402 clustering of air mass back trajectories, the highest concentrations of oxalate were found to be
403 associated with air masses originating over the European mainland consistent with the behaviour of
404 sulphate, nitrate and secondary organic carbon. It should, however, be noted that the elevation of
405 oxalate in the continental trajectory is less than that for sulphate, nitrate or secondary organic
406 carbon and the inter-site correlation between the urban EROS and rural Harwell sites is less strong
407 for oxalate than for sulphate and nitrate. This is interpreted as oxalate having a number of
408 secondary sources through different reaction pathways, depending upon different precursors which

409 react at different rates, consequently leading to less spatial homogeneity than for sulphate and
410 nitrate which have predominantly single precursor compounds. Biogenic precursors may play a
411 role, but the lack of a substantial summer maximum suggests that this is not dominant.

412

413 The size distribution of oxalate sampled at the urban site bears strong similarities to that of sulphate
414 suggesting common pathways in their formation either through aqueous phase formation processes
415 or cloud processing subsequent to formation.

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660 Table 1. Average concentrations ($\mu\text{g m}^{-3}$) of oxalic acid in airborne particulate matter in some
 661 previous studies
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Site	Period	Size fraction	Oxalic acid concentration	References
Urban background*, UK	Nov 08 – Apr 11	PM _{2.5}	0.05 ± 0.05	This work
		PM _{2.5-10}	0.02 ± 0.01	
		PM ₁₀	0.06 ± 0.05	
Rural, UK*	Jul – Dec 10	PM _{2.5}	0.02 ± 0.03	This work
		PM _{2.5-10}	0.02 ± 0.01	
		PM ₁₀	0.04 ± 0.03	
Mountain, Austria	Apr 99	—	0.052 ± 0.029	Limbeck et al., 2005
Urban background, Austria	Feb 99	—	0.068 ± 0.023	
Urban, Italy	1997	PM ₁₀	0.019	Cecinato et al., 1999
Semi-rural, Italy	1994	PM ₁₀	0.008	
Forest, Italy	1994	PM ₁₀	0.007	
Coastal rural, Germany	Feb – Mar 98	TSP	0.021-0.432	Rohrl and Lammel, 2001
Rural, Germany	Nov – Dec 99; Jul – Aug 98	TSP	0.004 – 0.157	
Urban, Germany	Jul – Aug 98	TSP	0.064 – 0.497	
Urban, Finland*	Apr – May 06; Jul – Sep 06	PM _{2.5}	0.050 ± 0.37	Saarnio et al., 2010
		PM ₁	0.140 ± 0.024	
Urban background, Romania	Jan 07 – Mar 08	PM _{1.5}	0.035 ± 0.023	Arsene et al., 2011
		PM _{>1.5}	0.049 ± 0.032	
Urban, China	Dec 06 – Jan 08 July – Aug 07	PM _{2.5}	0.182 ± 0.106	Ho et al., 2011
		PM _{2.5}	0.216 ± 0.097	
Urban, India	Jan 07 – May 07	PM ₁₀	0.114 ± 0.696	Pavuluri et al., 2010

663 * Reported as concentration of oxalate

664

665 Table 2. Results of regression analyses of EROS (urban background) and Harwell (rural)
 666 concentrations of ionic components in PM_{2.5}
 667

Analyte	RMA regression ^a
Sulphate	$y = 1.09x$ ($r = 0.82$)
Nitrate	$y = 1.05x + 0.11$ ($r = 0.84$)
Chloride	$y = 1.13x + 0.05$ ($r = 0.52$)
Oxalate	$y = 0.67x + 0.01$ ($r = 0.45$)
WSOC	$y = 1.25x + 0.01$ ($r = 0.52$)
OC _{sec} ^b	$y = 1.62x - 0.67$ ($r = 0.57$)

668 ^a y represents urban background (EROS) concentration of analyte in $\mu\text{g m}^{-3}$; x represents rural (Harwell)
 669 concentration of analyte in $\mu\text{g m}^{-3}$

670 ^b Secondary organic carbon calculated based on the ratio of $(\text{OC}/\text{EC})_{\text{min}} = 0.35$

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Table 3. Statistical data on the concentrations ($\mu\text{g m}^{-3}$) at EROS and Harwell sites during the simultaneous period ($n = 100$)

	PM _{2.5}		PM _{2.5-10}		PM ₁₀	
	Mean	Range	Mean	Range	Mean	Range
EROS						
SO ₄ ²⁻	1.60 ± 1.35	0.32 – 6.48	0.25 ± 0.17	<dl – 0.89	1.85 ± 1.47	0.55 – 7.37
NO ₃ ⁻	1.61 ± 2.11	<dl – 10.88	0.63 ± 0.64	<dl – 3.29	2.25 ± 2.50	<dl – 12.49
Cl ⁻	0.35 ± 0.27	<dl – 1.29	0.61 ± 0.51	0.08 – 2.79	0.96 ± 0.67	0.16 – 3.38
C ₂ O ₄ ²⁻	0.02 ± 0.02	<dl – 0.10	0.01 ± 0.01	<dl – 0.05	0.03 ± 0.02	<dl – 0.12
EC	1.0 ± 1.1	0.2 – 8.2	0.04 ± 0.1	<dl – 0.5	1.0 ± 1.1	0.2 – 8.3
OC	2.3 ± 1.6	0.9 – 12.1	1.2 ± 0.6	0.5 – 5.3	3.5 ± 1.8	1.6 – 13.7
OC _{prim}	0.4 ± 0.4	0.1 – 2.9	n.a	n.a	0.4 ± 0.4	0.1 – 2.9
OC _{sec} *	2.0 ± 1.3	0.7 – 9.2	n.a	n.a	3.1 ± 1.5	1.4 – 10.8
WSOC	1.7 ± 1.0	0.1 – 6.7	n.a	n.a	n.a	n.a
WSOC/OC _{sec}	0.9 ± 0.2	0.1 – 1.2	n.a	n.a	n.a	n.a
HAR						
SO ₄ ²⁻	1.47 ± 1.24	0.05 – 6.76	0.35 ± 0.40	<dl – 2.36	1.82 ± 1.40	0.36 – 7.53
NO ₃ ⁻	1.44 ± 2.02	0.03 – 11.65	0.71 ± 0.68	<dl – 3.40	2.16 ± 2.50	0.19 – 14.75
Cl ⁻	0.27 ± 0.23	<dl – 1.22	0.66 ± 0.60	0.04 – 3.17	0.93 ± 0.80	0.09 – 4.39
C ₂ O ₄ ²⁻	0.02 ± 0.03	<dl – 0.18	0.02 ± 0.02	<dl – 0.05	0.04 ± 0.03	<dl – 0.19
EC	0.4 ± 0.4	<dl – 1.9	0.03 ± 0.1	<dl – 0.5	0.4 ± 0.4	<dl – 2.2
OC	1.8 ± 0.9	0.5 – 4.8	1.0 ± 0.5	0.4 – 3.3	2.8 ± 1.1	1.0 – 7.0
OC _{prim}	0.1 ± 0.1	<dl – 0.7	n.a	n.a	0.1 ± 0.2	<dl – 0.8
OC _{sec} *	1.6 ± 0.8	0.5 – 4.5	n.a	n.a	2.7 ± 1.0	0.9 – 6.6
WSOC	1.3 ± 0.8	0.1 – 4.0	n.a	n.a	n.a	n.a
WSOC/OC _{sec}	0.8 ± 0.2	0.2 – 1.1	n.a	n.a	n.a	n.a

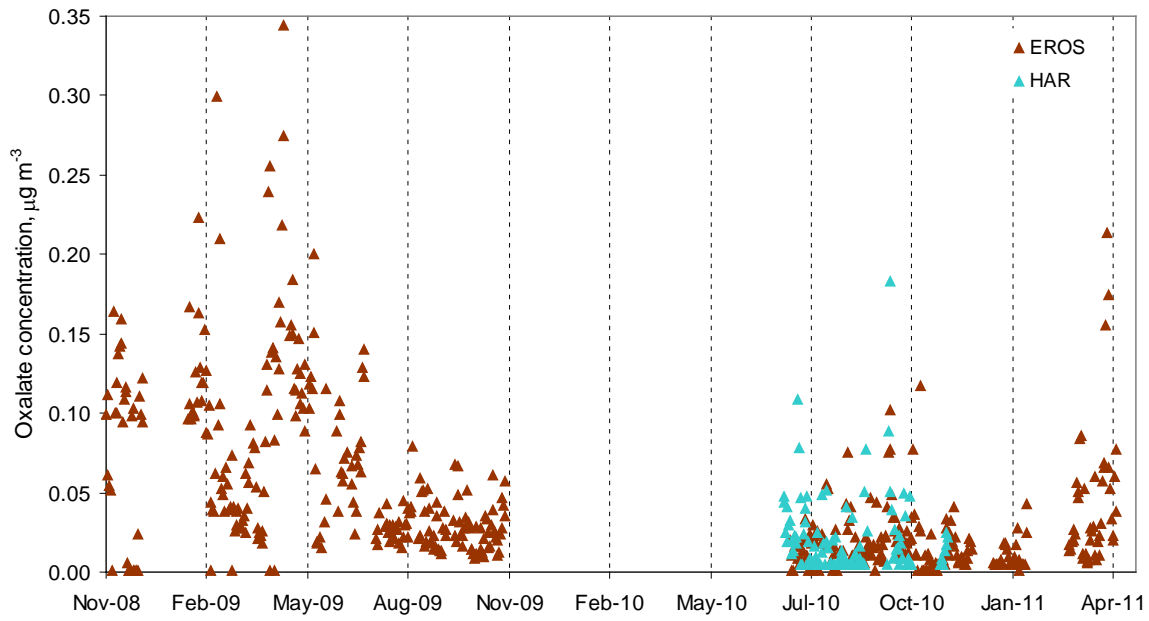
676 * OC_{prim} and OC_{sec} calculated using an assumed OC_{prim}/EC ratio = 0.35

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Table 4. Average concentrations of major chemical components in PM_{2.5} including mean temperature by trajectory clusters at EROS for the entire dataset

PM _{2.5}	n	Concentration, $\mu\text{g m}^{-3}$								T (°C)
		SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	C ₂ O ₄ ²⁻	OC	EC	OC _{prim}	OC _{sec}	
Cluster 1	108	1.30	1.18	0.79	0.03	2.3	0.8	0.3	2.0	11
Cluster 2	105	1.59	2.04	0.69	0.04	3.3	1.3	0.4	2.8	9
Cluster 3	95	1.63	2.08	0.52	0.05	2.5	0.9	0.3	2.2	12
Cluster 4	45	1.49	1.40	1.12	0.05	2.6	0.9	0.3	2.3	8
Cluster 5	147	2.71	5.16	0.74	0.06	3.9	1.5	0.5	3.4	8

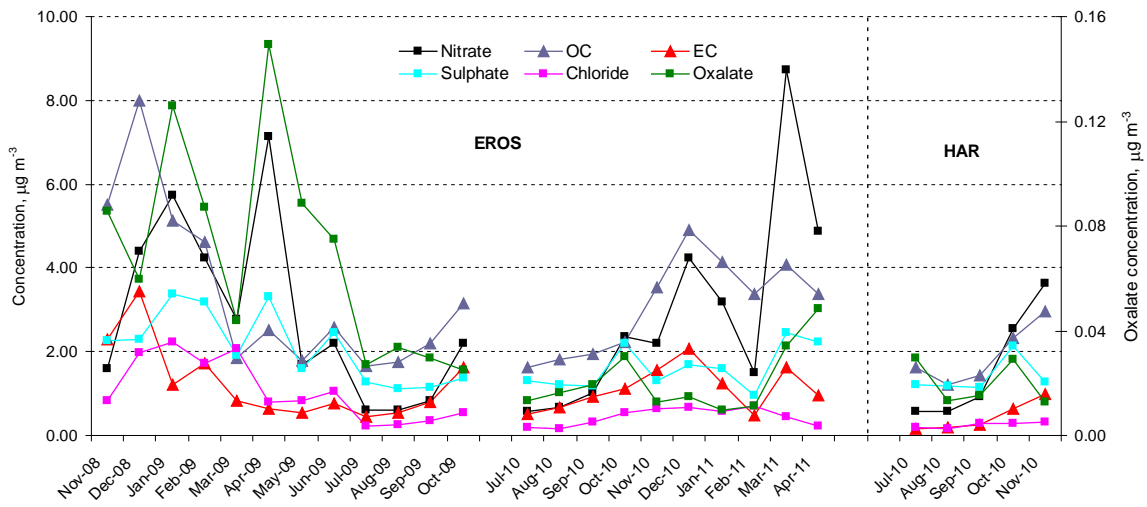
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685 Figure 1. Time series of oxalate concentrations in PM_{2.5} measured at EROS and Harwell sites

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688 Figure 2. Monthly average concentrations of major chemical components in PM_{2.5} at EROS and
689 Harwell sites

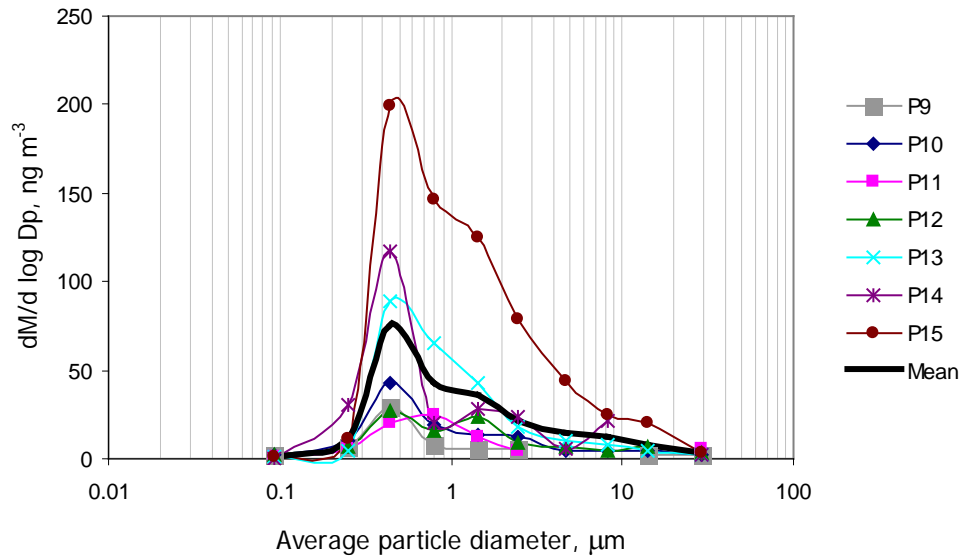
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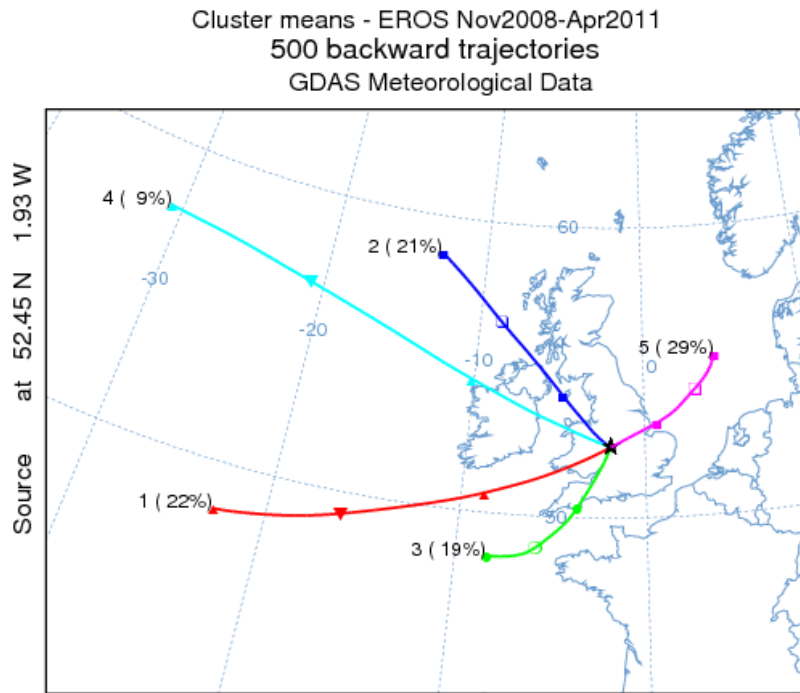


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696 Figure 3. Size distributions of oxalate in aerosol samples collected by MOUDI impactor

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700 Figure 4. Results of trajectory clustering for full EROS dataset

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