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6 **Sulphur isotopes as tracers of the influence of a coal-fired power plant**
7 **in a Scots pine forest in Catalonia (north-eastern Spain)**
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26 **Abstract**

27

28 Stable sulphur isotopes and the major ionic composition were
29 analyzed in precipitation and throughfall samples from a Scots pine (*Pinus*
30 *sylvestris*, L.) forest near the Cercs coal-fired power plant (Catalonia, NE
31 Spain). The study aimed at determining the sources of the sulphur
32 deposition in this pine forest. Sulphur isotopes were also analyzed from the
33 SO₂ power plant stack emissions to identify the isotopic signature of this
34 source.

35

36 Net throughfall fluxes of sulphur (26.1 kgS/ha/yr) and nitrogen (16.3
37 kgN/ha/yr) were higher at this site than in other forests in Catalonia, by
38 factors ranging 5-25 for S and 5-15 for N. By means of the S isotope
39 analysis we confirmed that the S net throughfall fluxes were originated
40 from dry deposition of the power plant emissions. Two potential sulphur
41 atmospheric contributing end-members were identified: (1) natural
42 background rainwater ($\delta^{34}\text{S}_{\text{SO}_4} = 7\text{‰}$, 40 $\mu\text{eq/L SO}_4^{2-}$ concentration) and (2)
43 SO₂ stack emissions ($\delta^{34}\text{S}_{\text{SO}_4} = -1.1\text{‰}$, 1188 $\mu\text{eq/L SO}_4^{2-}$ concentration). By
44 applying a two end-member mixing model, we found that during periods
45 of low power plant activity, 3-55% of the throughfall sulphate
46 concentrations could be attributed to the power plant emissions. For high
47 intensity working periods, this contribution arose to 12-97%. The
48 contribution of the power plant to bulk deposition was much lower (up to
49 8%).

50

51 Thus, increased understanding of the relation between emission
52 sources and atmospheric deposition will improve the ability of land
53 managers to protect sensitive ecosystems from atmospheric pollution.

54

55 *Keywords:* Sulphur isotopes, Sulphate, Throughfall, Power plant emissions

56

57 **1. Introduction**

58

59 The deposition of atmospheric coal-derived sulphur has been found
60 to cause environmental impacts in forested ecosystems around the globe,
61 its main effects being the incorporation of sulphates into rainwater causing
62 acid rain and the increase of S deposition to vegetation surfaces and soils
63 (Novák et al., 1995).

64

65 The forest canopy constitutes an important sink for airborne material
66 due to its large surface area (Lovett, 1994). Exposed leaves provide a
67 surface for the deposition of particles and for gas absorption through the
68 stomata. In particular, SO₂ can be absorbed, oxidized inside plant tissues,
69 and the resulting sulphate can be removed in a process similar to leaching
70 (Lindberg, 1992). Sulphur dioxide, apart from contributing to acidification,
71 can yield biochemical and physiological effects on vegetation, such as the
72 degradation of chlorophyll in leaves, damage to biological membranes and
73 chloroplasts and reduced photosynthesis (Legge and Krupa, 2002).

74

75 Near the coal-fired power plant of Cercs (Berguedà, Catalonia) the
76 impact of S emissions had previously been evaluated in various Scots pine
77 (*Pinus sylvestris* L.) stands at increasing distances from the emission point
78 through the measurements of the S content in the pine needles. These
79 studies concluded that S emissions from the power plant were responsible
80 for tree deterioration and death in areas upwind from the power plant stack
81 (Ferrés, 1986; Àvila, 1989).

82

83 The Cercs power station (EnelViesgo, 160 MW) started to work in
84 1971. In 1985-1986 a trial, the first in Spain for environmental causes was
85 sued against the plant administration because of the strongly negative
86 impact of the plant emissions on forests upwind from the stack. Since then,
87 the plant emissions have been subjected to a closer control: SO₂ emissions
88 have been reduced by 50% and emitted particle material has been cut down
89 by 70%. This has been achieved by means of the installation of
90 electrostatic filters and using coal of lower S content (a mix of 60% of
91 lignite of the zone, with S content of 3.1%, and 40% of coal from South
92 Africa, with S content of 0.44%). However, **despite these abatement**
93 **strategies, the surroundings of the power plant are still affected by a**
94 **major SO₂ impact, as can be seen from the Catalan Government Air**
95 **Quality monitoring program: the average SO₂ concentration in 4**
96 **stations around the Cercs plant (St. Corneli, St. Jordi, Vallcebre and**
97 **La Nou de Berguedà) was 40,5 µg/m³, compared to 6,3 µg/m³ (n=33)**
98 **in the rest of the monitoring stations around Catalonia (Data for**
99 **2002-03; Anon. 2004).**

100

101 **Because of this SO₂ rich climate in the area, a study was**
102 **necessary to document the effects of the power plant SO₂ emissions on**
103 **the sulphur deposition and cycling in the surrounding forests.**

104

105 It is not easy to describe the mechanisms responsible for the sulphur
106 impact to forests, since there are various sources of sulphur to the
107 atmosphere. Natural sources include sea-salt-spray, biogenic emissions in
108 the form of H₂S or dimethylsulfide (DMS) and gypsiferous soil derived
109 sulphate (**Schlesinger, 1987**). Anthropogenic sources are mainly due to the
110 combustion of fossil gas and fuels in the form of oil or coal (Kellogg et al.,

111 1972). The amount of sulphur in any of the fuels depends on where and
112 how it was formed and it may vary between a few tenths percent to 5-10%
113 of S.

114

115 In the last decades sulphur isotopes have been widely used as a tool
116 for distinguishing sources of sulphur in atmospheric gases and
117 precipitation, and for gaining a better understanding of the fate of sulphur
118 in the environment (Krouse and Grinenko, 1991; McArdle and Liss, 1995;
119 Alewell et al., 2000). If the sulphur isotopic compositions of natural and
120 anthropogenic sources are different and reduction-oxidation does not
121 occur, these signatures can be used to trace the origin of sulphate.
122 Moreover, isotopic signatures can tell us about mixing processes and so,
123 the proportional contribution of the different sources (Adorni-Braccesi, A.
124 et al., 1998; Soler et al., 2002; Otero and Soler, 2002). In particular, this
125 methodology has been successfully used to identify the sources of natural
126 and anthropogenic sulphur around coal-fired power plants (Newman and
127 Forrest, 1991; Querol et al. 2000, Novák et al., 1995, 2000).

128

129 Here we use the ionic composition and the stable sulphur isotopic
130 ratios of dissolved sulphate in bulk precipitation and throughfall collected
131 at a Scots pine stand near the Cercs power plant in order to: (1) quantify
132 the S dry deposition fluxes, and (2) identify its sources **and asses the**
133 **contribution of the Cercs power plant to the forest inputs.**

134

135 *1.1 The study area*

136

137 The study area is located in north-eastern Spain, in the Cadí massif,
138 eastern Pyrenees, about 150 km north of Barcelona. This massif is
139 enclosed within the Cadí thrust sheet and is composed of Cenozoic and

140 Mesozoic sedimentary materials (limestone, sandstone, mudstone and
141 evaporites) (Domingo et al., 1988). The climate is humid Mediterranean
142 with a mean annual precipitation of 925 mm. Mean annual temperature is
143 7.3°C with a maximum daily temperature of 35°C in July and a minimum
144 daily temperature of –10°C in January. The area is mostly forested and the
145 main human activity is in the sylvo-agricultural sector. Agriculture has
146 sharply declined since the second half of the twentieth century and forest is
147 occupying the abandoned fields (Gallart et al., 1998). The power plant is
148 the main industrial activity of the zone and is supported by a residual coal
149 mining industry at the region. **The stack is 122m high and 6 m wide.**

150

151 -----Figure 1-----

152

153 The Scots pine plot is at 1500 m.a.s.l in Vallcebre township, in the
154 Llobregat river basin near its sources in the Pre-Pyrenean region. The
155 200m² plot is located in the Cal Parisa catchment (42° 12'N, 1° 48'E), 6.2
156 km to the NW of the Cercs power plant. Predominant wind direction in the
157 area is from the S-SW, following the Llobregat river course (Fig. 1).
158 Therefore, the study plot, albeit susceptible of contamination due to its
159 proximity to the power plant, does not fully lie under the main direction of
160 the plume. The forest consisted of Scots pine with sparse underlying
161 vegetation of *Corylus avellana*, *Amelanchier ovalis*, *Juniperus communis*,
162 *Buxus sempervirens*, and *Sorbus aria*. The Scots pine density was 2359
163 trees ha⁻¹, mean DBH (diameter breast height) was 18 cm, mean tree height
164 was 10.4 m, mean canopy area was 9.8 m² and mean canopy depth was 5.0
165 m. Mean tree age was 39 years (Oliveras and Llorens, 2001).

166

167 **2. Methodology**

168

169 *2.1 Sampling*

170

171 Rainwater samples were collected with 3 replicate continuously
172 open collectors placed 1.5m above the ground, collecting, therefore, bulk
173 deposition. The collectors consisted of a polyethylene funnel of 19 cm
174 diameter connected **through a** tygon tubing to a 10L polyethylene bottle.
175 The bottles stood inside a box to avoid light induced alteration of the
176 collected water. A nylon sieve was placed in the funnel outlet to exclude
177 insects and large debris from the sample. Plastic-grid extensions were
178 attached to the funnel borders to oust birds. The bulk collector site was
179 about 200 m apart from the pine stand.

180

181 Throughfall samples were collected with 10 throughfall collectors
182 randomly placed inside the pine plot. The throughfall collectors consisted
183 of a polyethylene funnel of 9 cm diameter directly attached to a 2L
184 polyethylene bottle, both supported by a PVC tube at 1m above the
185 ground. The collection schedule for bulk deposition and throughfall was
186 weekly from 22 March 2000 to 31 January 2001 and monthly from 31
187 January 2001 to 24 August 2001.

188

189 SO₂ emissions were sampled **on** the 21st June 2001 from the power
190 plant stack, by means of an isocynetic probe. **This probe is specially**
191 **designed so as to sample the gas flux at the same velocity as it flows**
192 **from the stack.** Two replicate samples were obtained consisting each of a
193 composite of 4 orthogonal samples at a height of 90 m in the chimney. The
194 gas was bubbled in a H₂O₂ 3% solution kept at pH 4-5 with 0.01 M HClO₄

195 to oxidize SO₂ to SO₄²⁻. A Teflon pre-weighted filter was deployed at the
196 **probe inlet** to collect the emitted particles.

197

198 For isotopic analysis, in order to prevent sulphate reduction
199 processes during sample collection, 10 mL of a solution with excess of
200 BaCl₂·2H₂O was added in the field **to** one of the 3 bulk deposition
201 collectors and five of the 10 throughfall collectors, **in n episodes. In the**
202 **rest of samples, BaCl₂·2H₂O was added in the laboratory. A Student t**
203 **test of paired samples comparing the δ³⁴S ratio in samples precipitated**
204 **in the field and in the laboratory indicated non significant differences**
205 **between methods (Table 1).**

206 **Taula 1 Repassar les dades, (tota la numeració de les demes**
207 **taules va correguda)**

208

209 *2.2 Analyses*

210

211 The day of collection, samples were taken to the CREAM laboratory.
212 The pH, conductivity and alkalinity were determined in unfiltered samples.
213 pH was measured with a combined Ross electrode for low ionic strength
214 solutions in an ORION EA 960 meter. Alkalinity was measured by a
215 conductometric method (Golterman et al., 1978) and, when negative, by
216 Gran titration. Before major elements analysis, bulk deposition and
217 throughfall samples were filtered with a Millipore[®] filter of 0.45 μm pore
218 size. Major anions (Cl⁻, NO₃⁻ and SO₄²⁻) were analysed by ionic
219 chromatography and NH₄⁺ by continuous flow injection analysis at
220 CREAM. Na⁺ and K⁺ were analysed by flame emission and Ca²⁺ and Mg²⁺

221 by atomic absorption spectrometry at the Serveis Científico-Tècnics
222 (Universitat de Barcelona).

223

224 The analytical quality of the data was checked with: (1) the
225 cation/anion balance, and (2) the conductivity balance (comparing the
226 measured conductivity with a calculated one from the concentration of all
227 measured ions and their specific conductivity). Only 5% of bulk deposition
228 and 11% of throughfall samples were outside an accepted 20% margin of
229 error for the ionic balance. For the conductivity balance, the outliers were
230 11% of bulk deposition and 6% of throughfall samples for the same
231 tolerance range. For the calculation of annual means, the **ionic**
232 **concentrations** have been weighted by precipitation volume. **The**
233 **accuracy of the analysis was assessed by routinely participating in the**
234 **European intercalibration program Aquacon-Medbas for acid rain**
235 **analysis (Mosello et al., 90, Marchetto et al., 1996) with results within**
236 **10% of the expected value.**

237

238 *Isotopic analyses*

239

240 Bulk deposition and throughfall samples, with sulphate precipitated
241 as BaSO₄ during field sampling **or at the laboratory (Table XX)**, were
242 filtered with Millipore[®] filter of 3 µm pore size. Since the BaSO₄ could not
243 be removed from the particulate material, the isotopic analyses were
244 carried out with filter portions. Unused filters and filters with **throughfall**
245 **particulate material collected from samples without the BaSO₄**
246 **precipitate** were analyzed as blanks.

247

248 The sulphate-rich solutions obtained from the SO₂ emissions
249 sampling were treated in order to precipitate the sulphate as BaSO₄ for δ³⁴S
250 determinations. According to the method of Coleman and Moore (1978), 2
251 mL of H₂O₂ were added to 100 mL of sample solution, then they were
252 acidified with 2 mL of HCl 6M and reacted with excess of BaCl₂·2H₂O 6%
253 at 90°C. Once BaSO₄ was precipitated, the solutions were filtered with
254 Millipore® filter of 3 μm pore size and the collected BaSO₄ was cleaned
255 with MilliQ grade water in order to remove all the chlorides. The sulphur
256 isotope analyses were prepared at the “Mineralogia Aplicada i Medi
257 Ambient” laboratory and performed using on-line elemental analyser (EA)-
258 continuous flow-isotope ratio mass spectrometer (IRMS) at the Serveis
259 Científico-Tècnics (Universitat de Barcelona). The EA-IRMS consists of a
260 Carlo Erba 1108 elemental analyser coupled by a continuous flow interface
261 to the Finnigan Matt Delta C IRMS. The EA oxidizes all the sample
262 compounds under a stream of helium and oxygen by flash combustion in a
263 single oxidation-reduction quartz tube filled with oxidizing (tungsten
264 trioxide) and reducing (elemental copper) agents at 1030 °C. Water is
265 removed using anhydrous magnesium perchlorate and the gases enter a
266 chromatographic column (poropak QS) for separation of SO₂, which is
267 isotopically analyzed by IRMS (Giesemann et al., 1994). The isotope ratios
268 were calculated using the NBS-127, IAEA-S1, IAEA-S2, IAEA-S3 and
269 internal laboratory standards. Notation is expressed in terms of δ³⁴S per mil
270 relative to the Vienna Canyon Diablo Troilite (VCDT) standard.

271

272 **3. Results and discussion**

273

274 *3.1 Throughfall fluxes*

275

276

277 The forest canopy modifies the chemistry of rainfall by absorbing or
278 releasing nutrients. To describe the net effect of the canopy, the term Net
279 Throughfall (defined as Net Throughfall = Throughfall – Bulk Deposition)
280 is generally employed (Parker, 1983). Thus, negative net throughfall fluxes
281 indicate retention at the canopy, while positive values indicate nutrient
282 enrichment as precipitation crosses the forest canopy. This enrichment can
283 be produced either by: (1) leaching of intracellular solutes from leaves or
284 epiphytic vegetation, or (2) washing of dry deposition from the canopy
285 (Parker, 1983).

286

287 At Vallcebre, the net throughfall fluxes for all elements (except for
288 alkalinity) were positive (Table 2). When compared to net throughfall
289 fluxes from other forests in Catalonia, Vallcebre fluxes were higher than
290 **those reported for** other sites. **Because** Montseny and Prades study sites
291 are in evergreen oak (*Quercus ilex* L) forests, we also include throughfall
292 data from a coniferous forest (*Pinus nigra* and *Pinus pinaster*) in southern
293 Spain (Filabres, Almeria) to compare the Scots pine throughfall with that
294 of other coniferous tree species. In either case, Vallcebre showed much
295 higher positive N fluxes (16.3 kg N/ha/yr). In some of the other sites, N
296 fluxes were negative indicating uptake at the canopy (Table 2). This
297 **retention** is probably due to the limiting role of nitrogen in Mediterranean
298 forests (Serrasolsas et al., 1999). We attribute the high net NO₃-N and
299 NH₄-N fluxes at Vallcebre to the deposition of the NO_x from power plant
300 emissions and to the NH₃ emissions from the local cattle grazing activity
301 respectively, but more research is needed to confirm this topic. For
302 sulphate, net throughfall value at Vallcebre (26.1 kg/ha/yr) was also very
303 high compared to that of the other sites (Table 2). At Montseny, surrogate
304 surface experiments suggested that sulphate in throughfall was mostly due
305 to dry deposition (Rodrigo and Àvila, 2002). Similar conclusions have

306 been reported in the literature, both for broad-leaved or coniferous trees
307 (Johnson and Lindberg, 1992; Lindberg et al., 1986; Mayer and Ulrich,
308 1977). In North America, a study of sulphur circulation in pine trees
309 injected with ³⁵S showed that leaching only accounted for 3% of the
310 sulphate flux in net throughfall (Garten, 1990), the main contribution being
311 dry deposition. Furthermore, dry deposited SO₂ can penetrate rapidly
312 through stomata, be oxidized inside the leaves and the resulting sulphate be
313 released during rain events by means of a mechanism similar to leaching
314 (Lindberg, 1992).

315

316 -----Table 2-----

317

318 Dry deposition is important at sites close to pollution sources and
319 has been shown to decrease with distance to the source (Poikolainen and
320 Lippo, 1995; Rodrigo et al., 2003). **At Vallcebre, the power plant is**
321 **probably responsible of the observed high dry deposition input of**
322 **sulphate. To fully assess this assumption we investigated the sulphur**
323 **isotopic signal in the stack emissions, bulk deposition and throughfall.**

324

325 It has to be noticed that, despite these high anionic throughfall
326 fluxes, at Vallcebre the net throughfall was only moderately acidic (Table
327 2). This was due to the simultaneous high deposition of base cations (Ca
328 and Mg) from Saharan dust, resuspension of the calcareous soils of the
329 surroundings, and to ammonia deposition. In terms of concentrations (in
330 meq/L), the throughfall anionic sum (SO₄ = 0.28 plus NO₃ = 0.10) was
331 nearly compensated by the sum of Ca (0.23) and NH₄ (0.12). Therefore,
332 the high input fluxes of SO₄ and NO₃ at this forest did not cause soil
333 acidification, **and tree damage was not observed. However, more work**

334 **is needed to determine the effect of the pollution climate around Cercs**
335 **on the assimilation of S by the pine forests.**

336

337 *3.2 Sulphur isotopes*

338

339 At Vallcebre, the bulk deposition and throughfall $\delta^{34}\text{S}$ values
340 depended on: (1) the isotopic signal of the Cercs power plant emissions,
341 (2) the isotopic signal of the rest of the potential sources, mostly
342 background rainwater, and (3) the isotopic fractionation due to chemical
343 reactions during S atmospheric transport.

344

345 *Power plant SO₂ emissions*

346

347 The $\delta^{34}\text{S}_{\text{SO}_2}$ value of the gas emitted was -2.75 ± 0.05 ‰.
348 Determining this value is important because of the wide range of the
349 carbon $\delta^{34}\text{S}$ signatures: -30 to +30 ‰ (Newman et al., 1991).

350

351 -----Table 2-----

352

353 *Bulk deposition and throughfall dissolved sulphate*

354

355 The mean $\delta^{34}\text{S}$ values in bulk deposition and throughfall (+3.3 and
356 +0.2‰ respectively, Table 2) were within the range given for precipitation
357 in nature (between -2.5 and +19.4 ‰; Herut et al., 1995). The range of
358 bulk deposition $\delta^{34}\text{S}$ values at Vallcebre was similar to ranges registered at
359 remote non-perturbed sites (Mast et al., 2001). However, its $\delta^{34}\text{S}$ volume-
360 weighted mean value was closer to values for polluted sites: e.g. in the
361 surroundings of the Andorra power plant, $\delta^{34}\text{S}$ values in precipitation
362 varied between +1.2 and +3.0 ‰ (Querol et al., 2000). Panettiere et al.

363 (2000) reported a $\delta^{34}\text{S}$ mean value of +3.2 ‰ (range +0.4 to +6.2 ‰) for
364 the polluted atmosphere in Bologna In heavily industrialized areas in
365 Japan, Nakai et al. (1991) found a $\delta^{34}\text{S}$ mean value of +2.5 ‰ (range +0.5
366 to +5.5 ‰).

367

368 $\delta^{34}\text{S}$ values in bulk deposition at Vallcebre were higher than in
369 throughfall (Table 2), similarly as in polluted sites elsewhere (Groscheová
370 et al., 1998; Novák et al., 1995, 2000). At sites without significant sources
371 of S pollution in the surroundings, little $\delta^{34}\text{S}$ differences between
372 precipitation and throughfall have been found (Heaton et al., 1997; **Van**
373 **Stempvoort, et al 1991**, Zhang et al., 1998). The decrease of $\delta^{34}\text{S}$ in
374 throughfall relative to bulk deposition is consistent with the hypothesis of
375 washing dry deposited S from the power plant emissions impacted at the
376 canopy, as the emissions signal (-2.8 ‰) was lower than that of bulk
377 deposition (+3.3 ‰).

378

379 **At Vallcebre, the decrease of S values tending towards those of**
380 **the power plant emission and the fact that this trend was accelerated**
381 **with the plant work intensity indicated that the plant SO₂ emissions**
382 **had a major role in the S throughfall inputs.**

383

384 **Natural sources (e.g. sea-salt sulphate, marine DMS, and crustal**
385 **evaporites and gypsum) can also influence S ratios in the atmosphere,**
386 **eventually affecting those of the precipitation and throughfall.**
387 **Vallcebre is 82 km distant from the Mediterranean Sea and receives**
388 **little marine influence as seen by the small Na input in bulk (2,2**
389 **kg/ha/yr) and dry deposition (represented by net throughfall, 1**
390 **kg/ha/yr). Further evidence of the little marine influence at Vallcebre**

391 is given in Fig. 3 where the rainwater $\delta^{34}\text{S}$ signal shows independence
392 with respect to the Cl/SO₄ ratio. By contrast, throughfall has a
393 positive correlation with Cl/SO₄ ratio ($r= 0,60, p<0,001$). The values
394 to the left of the graph correspond to throughfall samples more
395 influenced by the power plant while those at the right tend to the
396 rainwater signal, representing a convergence towards wet deposition
397 when dry deposition is small.

398

399 As for the contribution of biological S, even at sites near the sea,
400 the phytoplankton derived DMS has been found to be a very small
401 component of rainwater (McArdle and Liss, 1995, Wadleigh et al
402 1996). Terrestrial biological emissions at the Vallcebre are probably
403 very low as its environment is formed by steep slopes on calcareous
404 forested land providing little opportunity for microbial emissions.

405

406 Furthermore, the natural sources of S that could be invoked have
407 very different $\delta^{34}\text{S}$ signatures: biogenic S emissions from DMS are
408 characterized in continental zones by a $\delta^{34}\text{S}$ value around +10 ‰ (Mitchell
409 et al., 1998). The $\delta^{34}\text{S}$ value of sulphate derived from marine aerosols is
410 +20 ‰ (Newman et al., 1991). As for the crustal component, in the study
411 zone, Garumnian facies limestones have a low S content, represented by
412 pyrite and organic sulphur related to coal with $\delta^{34}\text{S}$ values lower than -10
413 ‰ (Querol et al., 2000). There are also some outcrops of Keuper facies
414 Triassic gypsum-rich materials that are characterized by values of $\delta^{34}\text{S}$
415 between +10 ‰ and +14 ‰.

416

417 -----Figure 2-----

418

419 From the natural processes that can produce isotopic fractionation,
420 only the $\text{SO}_2\text{-SO}_4^{2-}$ oxidation took place during either atmospheric
421 transport or within canopy leaves. Taking into account that processes as
422 dilution or canopy interaction do not affect sulphur isotopic composition
423 (Alewell and Gehre, 1999; Heaton et al., 1997) and that the power plant
424 was the main sulphur source, the $\delta^{34}\text{S}$ difference between throughfall and
425 power plant emissions should approach sulphur isotopic fractionation due
426 to oxidation. This difference $\Delta^{34}\text{S}_{\text{SO}_4^{2-}\text{-SO}_2} = +3\text{‰}$ ($\alpha = 1.003$) agrees with
427 the isotopic fractionation reported by various authors (Table 3).

428

429 -----Table 3-----

430

431 In Fig. 3, we present the variation in $\delta^{34}\text{S}$ vs sulphate concentration
432 of the precipitation and throughfall samples. In this diagram, bulk
433 deposition samples show high isotopic variability with little changes in
434 sulphate concentration, whereas throughfall samples show low isotopic
435 variability with big changes in sulphate concentration. Data delineate an L-
436 shaped distribution compatible with a mixing process between two end-
437 member sources. The large isotopic shift could be explained as a mixing
438 between a regional background sulphur source and the local SO_2 emissions
439 of the Cercs power plant. The background isotopic signature (bulk
440 precipitation) around 6‰ approaches values reported by different authors
441 for an external input of sulphate by long-range transport events (Otero and
442 Soler, 2002; Querol et al., 2000).

443

444 *3.3 Two end-member mixing model*

445

446 A two end-member mixing model between the Cercs power plant
447 (CPP) and the regional background (RB) is proposed based on the mass
448 balance equation:

449

$$450 \delta^{34}\text{SSO}_4 (\text{mixing}) = \delta^{34}\text{SSO}_4 (\text{CPP}) \cdot [\text{SO}_4^{2-}] (\text{CPP}) + \delta^{34}\text{SSO}_4 (\text{RB}) \cdot [\text{SO}_4^{2-}] (\text{RB}) \quad (1)$$

451

452 where $\delta^{34}\text{SSO}_4 (\text{CPP})$ and $\delta^{34}\text{SSO}_4 (\text{RB})$ are the sulphur isotopic compositions of
453 the CPP SO₂ emissions and the regional background, respectively, and
454 $[\text{SO}_4^{2-}] (\text{CPP})$ and $[\text{SO}_4^{2-}] (\text{RB})$ are the sulphate concentrations associated to
455 them. The mixing model calculation requires a starting value for every
456 parameter and a sensitivity analysis depending on parameter variations.

457

458 Bulk deposition data from a site located 70 km to the SE of CPP was
459 taken as the regional background values, i.e. $[\text{SO}_4^{2-}] (\text{RB}) = 40.0 \mu\text{eq/L}$ and
460 $\delta^{34}\text{SSO}_4 (\text{RB}) = +7.2\text{‰}$ (Otero and Soler, 2002). Since sulphur isotopic
461 composition and concentration measured in the CPP stack refer to SO₂,
462 $\delta^{34}\text{SSO}_4 (\text{CPP})$ and $[\text{SO}_4^{2-}] (\text{CPP})$ were calculated from these empirical values
463 (Tables 2 and 4), and taking in account the parameters that can influence
464 sulphur transport from the CPP to the studied site. $[\text{SO}_4^{2-}] (\text{CPP})$ is defined as
465 the part of the emitted SO₂ concentration that reaches the studied site in the
466 form of sulphate:

467

$$468 [\text{SO}_4^{2-}] (\text{CPP}) = [\text{SO}_4^{2-}]_{\text{stack}} \cdot \omega \cdot E \cdot [P + (1 - P) \cdot B \cdot C] \quad (2)$$

469 where:

470 - $[\text{SO}_4^{2-}]_{\text{stack}}$ is the sulphate concentration corresponding to $[\text{SO}_2]$ measured
471 in the stack (Table 4).

472 - ω is the southeast-easterly wind fraction that took place during the
473 studied period. According to data from the meteorological station of Sant
474 Jordi de Cercs, $\omega = 0.23$.

475 - E is the scavenging ratio during rain events. From Galloway et al. (1993),
476 this atmosphere washout factor in contaminated areas is $E = 1500$.

477 - P is the SO_2 - SO_4^{2-} oxidation rate, according to the travel time in the
478 atmosphere and hours of sunshine. The distance between the CPP and the
479 studied area is around 6 km, the mean wind speed is 6 km h^{-1} and SO_2 -
480 SO_4^{2-} oxidation rate is between 1 and 6% h^{-1} , depending on the exposure
481 time (Querol et al., 2000), thus we have considered that SO_2 is transformed
482 into SO_4^{2-} at a rate of $P = 0.04$.

483 - B is the non-oxidized SO_2 fraction ($1 - P = 0.96$) that can reach the studied
484 area and be dry deposited onto the canopy. A first approach is obtained by
485 the ratio of the linear dimension of the plot by the distance to the CPP, so

486 that $B = \frac{\sqrt{200m^2}}{6000m} = 0.0023$.

487 - C is the fraction of deposited SO_2 onto canopy that is oxidized inside
488 stomata. According to Lindberg (1992), $C = 0.6$.

489

490 -----Table 4-----

491

492 The $\delta^{34}\text{SSO}_4$ (CPP) value was estimated from the $\delta^{34}\text{SSO}_2$ value
493 measured in the stack, plus the isotopic fractionation shift due to SO_2
494 oxidation in the stack and during atmospheric transport. Taking the
495 measured isotopic compositions $\delta^{34}\text{SSO}_2$ (CPP) (g) = -2.8‰ , $\delta^{34}\text{SSO}_4$ (CPP) (particle)
496 = -2.0‰ and $\delta^{34}\text{SSO}_4$ (TR) = $+0.2\text{‰}$ (Table 4), the isotopic differences can be
497 calculated:

498 $(\Delta^{34}\text{SSO}_4\text{-SO}_2)_{\text{stack}} = \delta^{34}\text{SSO}_4_{\text{(CPP) (particle)}} - \delta^{34}\text{SSO}_2_{\text{(CPP) (g)}} = +0.8\text{‰}$

499 $(\Delta^{34}\text{SSO}_4\text{-SO}_2)_{\text{atmosphere}} = \delta^{34}\text{SSO}_4_{\text{(TR)}} - \delta^{34}\text{SSO}_2_{\text{(CPP) (g)}} = +3.0\text{‰}$

500 $(\Delta^{34}\text{SSO}_4\text{-SO}_2)_{\text{stack + atmosphere}} = \frac{[(+0.8\text{‰}) + (+3.0\text{‰})]}{2} = +1.9\text{‰}$

501 so that

502

503 $\delta^{34}\text{SSO}_4_{\text{(CPP) (g)}} = \delta^{34}\text{SSO}_2_{\text{(CPP) (g)}} + (\Delta^{34}\text{SSO}_4\text{-SO}_2)_{\text{stack + atmosphere}} = -0.9\text{‰}$

504

505 Weighted by both gas and particulate material sulphur contribution,
506 the total sulphur isotopic signature of sulphate from the CPP is:

507

508 $\delta^{34}\text{SSO}_4_{\text{(CPP) (particle)}} = \left(\frac{82.6}{82.6+13.7}\right) \cdot \delta^{34}\text{SSO}_4_{\text{(CPP) (g)}} + \left(\frac{13.7}{82.6+13.7}\right) \cdot \delta^{34}\text{SSO}_4_{\text{(CPP) (g)}} + (\Delta^{34}\text{SSO}_4\text{-SO}_2)_{\text{stack + atmosphere}}$
509 $= -1.1\text{‰}$

510

511 The starting values of the mixing model thus obtained are summarized in
512 Table 5.

513

514 -----Table 5-----

515

516 The mixing model fits well with experimental data (Fig. 3), showing
517 that throughfall samples are mainly controlled by CPP emissions, whereas
518 bulk deposition samples are more influenced by the regional background.
519 The sulphate contribution from the emissions of the power plant to the
520 sulphur input in the studied site was up to 8% in bulk precipitation,
521 whereas in throughfall samples it oscillated from 3 to 55% for low

522 intensity working periods, and from 12 to 97% for high intensity working
523 periods.

524

525 -----Figure 3-----

526

527 Different mixing curves between the two end-members have been
528 calculated and plotted in order to analyze the sensitivity of the parameters
529 of equation (2). The mixing model response to parameter variations was as
530 follows:

531 - $[\text{SO}_4^{2-}]_{\text{stack}}$ and ω values were well enclosed, because both come from
532 empirical measurements, but any variation of these parameters changed the
533 mixing model, due to the linear dependence of the $[\text{SO}_4^{2-}]_{\text{(CPP)}}$ on them
534 (equation 2). With a wind fraction of 0.5, the CPP sulphate contribution
535 was reduced to the half (Fig. 4a).

536 - the mixing model was also very sensitive to the P parameter variations
537 because SO_4^{2-} availability is directly affected by the SO_2 oxidation rate. For
538 instance, P values lower than 4% gave aberrant results, producing CPP
539 contributions higher than 100%. Inversely, P values next to 6% notably
540 reduced the percentages of the CPP contributions on throughfall samples
541 (Fig. 4b, 4c).

542 - the atmosphere washout enrichment factor (E) can produce important
543 changes of the mixing model: if $E > 1500$, which means higher
544 contamination levels, then the CPP influence decreases; on the other hand,
545 if $E < 1500$ (while $[\text{SO}_4]_{\text{stack}}$ and ω take the empirical values), then P must
546 be higher than 4% in order to obtain reasonable estimations of the mixing
547 model (Fig. 4d).

548 - the mixing model was sensitive to B variations only considering distances
549 lower than the distance between the CPP and the experimental plot, but
550 this case makes nonsense. On the other hand, for distances higher than the
551 distance between the CPP and the experimental plot, the mixing model
552 hardly changed.

553 - C variations were not reflected on the mixing model as this parameter is
554 minimized by the B parameter.

555

556 -----Figure 4-----

557

558 **Conclusions**

559

560 This study shows the usefulness of combining elemental and
561 isotopic geochemistry to trace the origin of sulphur in a rural forested area
562 near a coal-fired power plant. The net throughfall fluxes for N and S were
563 very high, although they did not cause net throughfall acidification because
564 of the neutralizing effect of base cations and ammonia deposition. Sulphur
565 and nitrogen net fluxes were attributed to dry deposition. The role of the
566 power plant in this deposition was evaluated with the analysis of $\delta^{34}\text{S}$ of
567 precipitaton and throughfall. This analysis identified two main sources of
568 dissolved sulphate: the power plant SO_2 emissions ($\delta^{34}\text{S} = -2.8\text{‰}$) and a
569 regional background sulphur source ($\delta^{34}\text{S}$ around $+6\text{-}7\text{‰}$).

570

571 According to the calculated mixing model, the sulphate contribution
572 from the power plant emissions was more important in throughfall than in
573 bulk deposition samples: only accounted for a maximum 8% in bulk
574 precipitation, while for throughfall samples it oscillated from 3 to 55% for

575 low intensity power plant working periods, and from 12 to 97% for high
576 intensity working periods. The mixing model was very sensitive to
577 parameters directly related to the amount of sulphate such as $[\text{SO}_4^{2-}]_{\text{(CPP)}}$
578 and ω (SE-E wind fraction), whose values were well determined. E
579 (scavenging ratio) and P (SO_2 - SO_4^{2-} oxidation rate) parameter values
580 showed some uncertainty and the mixing model was very sensitive to their
581 variations. Thus, semiquantifying the contribution of the SO_2 emissions is
582 mainly subjected to the characterization of atmospheric conditions. Finally,
583 the mixing model was hardly dependant on B (non-oxidized SO_2 fraction
584 that can reach the studied area and be dry deposited onto the canopy) and C
585 (fraction of deposited SO_2 onto canopy that is oxidized inside stomata)
586 parameter variations.

587

588 *Acknowledgements*

589 This study was partially financed by the CICYT projects of the Spanish
590 government CGL2005-08019-C04-01, CGL2005-07543/CLI, and
591 SGR2005-933. The contribution of the Direcció General de Qualitat
592 Ambiental del Departament de Medi Ambient de la Generalitat de
593 Catalunya is fully acknowledged. We would like to express our gratitude
594 to Dr. Andrés Alastuey and Dr. Xavier Querol from Institut de Ciències de
595 la Terra Jaume Almera (CSIC) for their technical support and helpful
596 advices. Special thanks are due to Mercè Gonzàlez and Txema Mancheño
597 for the power plant stack sampling and to technical personnel in CREAF
598 and Dpt. Cristal·lografia, Mineralogia i Dipòsits Minerals of the
599 Universitat de Barcelona for laboratory help.

600

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816

817 **Tables**

818

819 Table 1. Comparison of the S precipitation methods. $\delta^{34}\text{S}$ mean values
820 (S.E) when precipitating with BaCl added in the field or at the CREAM
821 laboratory

822

	mean $\delta^{34}\text{S}$ (‰)	S.E.	n.
Bulk deposition-Field	+3.67	+0.87	4
Bulk deposition-Lab	+4.3	+0.79	4
Throughfall-Field	+0.47	+0.30	11
Throughfall-Lab	+0.66	+0.28	11

823

824

825

826

827 Table 2. Bulk deposition at Vallcebre and net throughfall (Net throughfall
 828 = Throughfall – Bulk Deposition) at various rural forested sites in eastern
 829 and north-eastern Spain. Units in kg ha⁻¹ year⁻¹, except for alkalinity (meq
 830 m⁻² year⁻¹) and rainfall (mm year⁻¹). Period of study at Vallcebre: from 22
 831 March 2000 to 24 August 2001, at Montseny from 6 June 1995 to 25 June
 832 1996, and at Prades, from November 1991 to November 1992. Filabres,
 833 from April 1988 to September 1989. Main tree species: Vallcebre, *Pinus*
 834 *sylvestris*, Prades and Montseny, *Quercus ilex*, and Filabres, *Pinus nigra*
 835 *and Pinus pinaster*.

836

837

	Rainfall	Alk.	H+	Na+	K+	Ca ²⁺	Mg ²⁺	NH ₄ ⁺ -N	NO ₃ ⁻ -N	SO ₄ ²⁻ -S	Cl ⁻
Bulk deposition											
Vallcebre	975	35.3	0.01	2.2	1.8	12.8	0.8	3.6	3.0	7.3	3.5
Net Throughfall											
Vallcebre	222*	-7.2	0.09	1.4	21.8	21.7	3.6	8.7	7.6	26.1	7.3
Net Throughfall											
Montseny LC ¹	279*	52.8	-0.99	0.1	14.8	3.1	1.6	-1.6	-1.6	1.1	5.0
Net Throughfall											
Montseny RP ¹	337*	75.0	-0.11	1.7	25.2	7.6	1.9	1.2	0.3	3.8	7.5
Net Throughfall											
Prades ²	551*	29.6	-0.05	1.8	13.7	9.5	1.8	0.4	1.4	5.0	2.6
Net Throughfall											
Filabres ³	-	49.8	-	4.8	11.5	19.5	3.2	-0.5	0.2	3.5	15.7

838 ¹Rodrigo et al. (2003), ²Escarré et al. (1999), ³Domingo (1991).

839 * Net rainfall= Rainfall-throughfall (mm)

840

841

842

843

844

845 Table 3. $\delta^{34}\text{S}$ mean values and ranges of the Cercs power plant (CPP)
846 emissions, bulk deposition and throughfall (volume-weighted mean values
847 for bulk deposition and throughfall).

848

	$\delta^{34}\text{S}$ (‰)	range
SO ₂ emissions	-2.75	-2.8 to -2.7
SO ₄ ²⁻ emissions (fly ash)	-1.95	-2.0 to -1.9
Bulk deposition	+3.3	+1.1 to +6.5
Throughfall	+0.2	-1.3 to + 3.8

849

850

851 Table 4. Isotopic difference of SO₂ to SO₄²⁻ oxidation reported by various
852 authors.

853

Author	$\Delta^{34}\text{SSO}_4^{2-}\text{-SO}_2$ (‰)
Saltzman et al. (1983)	+3.0
Newman et al. (1991)	+3.0
Querol et al. (2000)	+2.6 - +2.8
Novák et al. (2000)	+2.8
Our work	+3.0

854

855

856 Table 5. [SO₂] emission values (mg/Nm³) (both gas and particle phases)
 857 measured in the stack, the corresponding SO₄²⁻ concentrations (μeq/L) and
 858 the SO₄²⁻ concentrations calculated by equation 2.
 859

	[SO ₂]	[SO ₄ ²⁻] _{stack}	[SO ₄ ²⁻] _(CPP)
	mg/Nm ³	μeq/L	μeq/L
Gas	2645.3	82.6	1177.5
Particle	-	13.7	10.8*

860 *The [SO₄²⁻]_(CPP) associated to the particle phase has been calculated by means of:
 861 [SO₄²⁻]_(CPP) = [SO₄²⁻]_{stack} · ω · E · B, because the oxidation of SO₂ particles mainly
 862 occurs inside the stack.
 863

864 Table 6. Starting values of the mixing model. $[\text{SO}_4]_{\text{(CPP)}}$ and $\delta^{34}\text{S}_{\text{SO}_4 \text{(CPP)}}$
865 are the weighted mean of gas and particle contributions.

866

End member	$[\text{SO}_4^{2-}]$	$\delta^{34}\text{S}_{\text{SO}_4}$
	$\mu\text{eq/L}$	‰
Regional Background (RB)	40.0	+7.2
Cercs Power Plant (CPP)	1188.3	-1.1

867

868

869 **Figure captions**

870

871 Fig. 1 Location of the study area and the sampling site, 6.2 km to the NW
872 of the Cercs power plant.

873

874 **Fig. 2. $\delta^{34}\text{S}$ in Vallcebre pine forest throughfall vs the intensity of the**
875 **Cercs power plant activity, computed as working hours per day.**

876

877 **Fig 3. $\delta^{34}\text{S}$ in Vallcebre bulk deposition and throughfall vs. the Cl/SO₄**
878 **ratio (in equivalents).**

879

880 Fig. 3. $\delta^{34}\text{S}_{\text{SO}_4}$ vs $[\text{SO}_4]$ diagram of bulk deposition and throughfall, with
881 the mixing model curve between the regional background ($\delta^{34}\text{S}_{\text{SO}_4} =$
882 $+7.2\%$, $[\text{SO}_4] = 40.0 \mu\text{eq/L}$) and the Cercs power plant (CPP) SO₂
883 emissions ($\delta^{34}\text{S}_{\text{SO}_4} = -1.1\%$, $[\text{SO}_4] = 1188.3 \mu\text{eq/L}$). $[\text{SO}_4]_{\text{(CPP)}}$ has been
884 calculated considering $\omega = 0.23$, $E = 1500$, $P = 0.04$, $B = 0.0023$ and $C =$
885 0.6 in equation 2. Percentages indicate the SO₄ contribution from the CPP
886 according to this mixing model.

887

888 Fig. 4. $\delta^{34}\text{S}_{\text{SO}_4}$ vs $[\text{SO}_4]$ diagrams of bulk deposition and throughfall, with
889 the mixing model calculated as in Fig. 3 but changing some parameter
890 values in equation 2: (a) $\omega = 0.5$, (b) $P = 0.01$, (c) $P = 0.06$ and (d) $E =$
891 1000 , $P = 0.06$. Percentages indicate the SO₄ contribution from the CPP
892 according to the mixing model.

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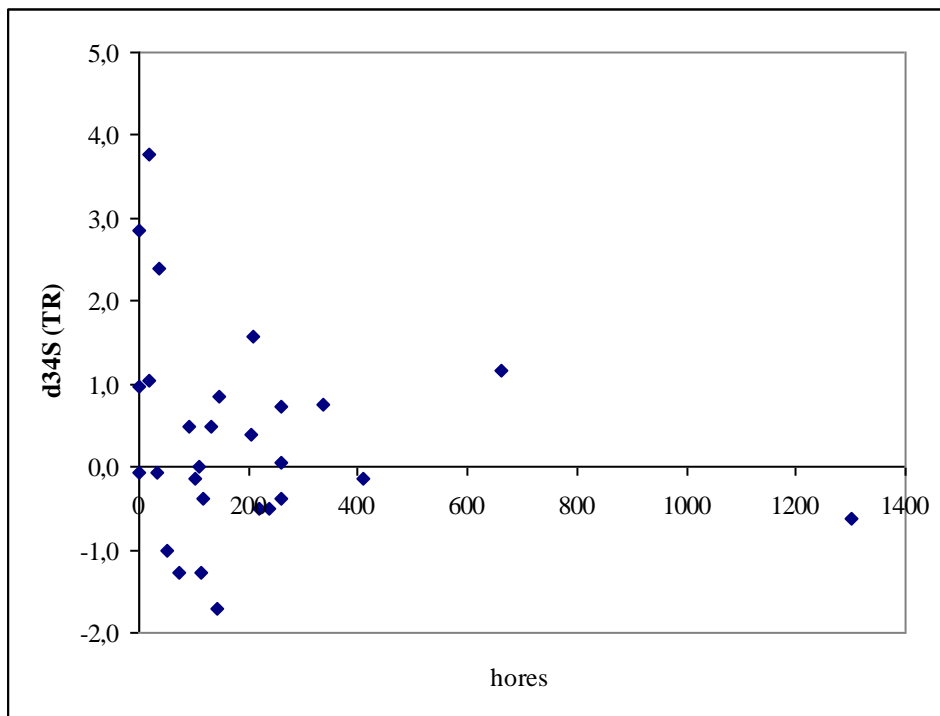
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900 **Fig. 2**

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913 **Fig. 3**

