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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 SO<sub>2</sub> 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 SO<sub>2</sub> 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, SO<sub>2</sub> 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: SO<sub>2</sub> 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 SO<sub>2</sub> impact, as can be seen from the Catalan Government Air**  
95 **Quality monitoring program: the average SO<sub>2</sub> concentration in 4**  
96 **stations around the Cercs plant (St. Corneli, St. Jordi, Vallcebre and**  
97 **La Nou de Berguedà) was 40,5 µg/m<sup>3</sup>, compared to 6,3 µg/m<sup>3</sup> (n=33)**  
98 **in the rest of the monitoring stations around Catalonia (Data for**  
99 **2002-03; Anon. 2004).**

100

101           **Because of this SO<sub>2</sub> rich climate in the area, a study was**  
102 **necessary to document the effects of the power plant SO<sub>2</sub> 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 H<sub>2</sub>S 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 200m<sup>2</sup> 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<sup>-1</sup>, mean DBH (diameter breast height) was 18 cm, mean tree height  
164 was 10.4 m, mean canopy area was 9.8 m<sup>2</sup> 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 SO<sub>2</sub> emissions were sampled **on** the 21<sup>st</sup> 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 H<sub>2</sub>O<sub>2</sub> 3% solution kept at pH 4-5 with 0.01 M HClO<sub>4</sub>

195 to oxidize SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup>. 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 BaCl<sub>2</sub>·2H<sub>2</sub>O 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, BaCl<sub>2</sub>·2H<sub>2</sub>O was added in the laboratory. A Student t**  
203 **test of paired samples comparing the δ<sup>34</sup>S 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<sup>®</sup> filter of 0.45 μm pore  
218 size. Major anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were analysed by ionic  
219 chromatography and NH<sub>4</sub><sup>+</sup> by continuous flow injection analysis at  
220 CREAM. Na<sup>+</sup> and K<sup>+</sup> were analysed by flame emission and Ca<sup>2+</sup> and Mg<sup>2+</sup>

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 BaSO<sub>4</sub> during field sampling **or at the laboratory (Table XX)**, were  
242 filtered with Millipore<sup>®</sup> filter of 3 µm pore size. Since the BaSO<sub>4</sub> 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 BaSO<sub>4</sub>**  
246 **precipitate** were analyzed as blanks.

247

248 The sulphate-rich solutions obtained from the SO<sub>2</sub> emissions  
249 sampling were treated in order to precipitate the sulphate as BaSO<sub>4</sub> for δ<sup>34</sup>S  
250 determinations. According to the method of Coleman and Moore (1978), 2  
251 mL of H<sub>2</sub>O<sub>2</sub> were added to 100 mL of sample solution, then they were  
252 acidified with 2 mL of HCl 6M and reacted with excess of BaCl<sub>2</sub>·2H<sub>2</sub>O 6%  
253 at 90°C. Once BaSO<sub>4</sub> was precipitated, the solutions were filtered with  
254 Millipore® filter of 3 μm pore size and the collected BaSO<sub>4</sub> 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 SO<sub>2</sub>, 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 δ<sup>34</sup>S 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 NO<sub>3</sub>-N and  
299 NH<sub>4</sub>-N fluxes at Vallcebre to the deposition of the NO<sub>x</sub> from power plant  
300 emissions and to the NH<sub>3</sub> 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 <sup>35</sup>S 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 SO<sub>2</sub> 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 (SO<sub>4</sub> = 0.28 plus NO<sub>3</sub> = 0.10) was  
331 nearly compensated by the sum of Ca (0.23) and NH<sub>4</sub> (0.12). Therefore,  
332 the high input fluxes of SO<sub>4</sub> and NO<sub>3</sub> 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 SO<sub>2</sub> emissions*

346

347 The  $\delta^{34}\text{S}_{\text{SO}_2}$  value of the gas emitted was  $-2.75 \pm 0.05$  ‰.  
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 SO<sub>2</sub> 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/SO<sub>4</sub> ratio. By contrast, throughfall has a  
393 positive correlation with Cl/SO<sub>4</sub> 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  $\text{SO}_2$  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 SO<sub>2</sub> 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 SO<sub>2</sub>,  
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 SO<sub>2</sub> 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 -  $\omega$  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  $\text{SO}_2$ -  $\text{SO}_4^{2-}$  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  $6 \text{ km h}^{-1}$  and  $\text{SO}_2$ -  
480  $\text{SO}_4^{2-}$  oxidation rate is between 1 and 6%  $\text{h}^{-1}$ , depending on the exposure  
481 time (Querol et al., 2000), thus we have considered that  $\text{SO}_2$  is transformed  
482 into  $\text{SO}_4^{2-}$  at a rate of  $P = 0.04$ .

483 -  $B$  is the non-oxidized  $\text{SO}_2$  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  $B = \frac{\sqrt{200\text{m}^2}}{6000\text{m}} = 0.0023$ .

487 -  $C$  is the fraction of deposited  $\text{SO}_2$  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  $\text{SO}_2$   
494 oxidation in the stack and during atmospheric transport. Taking the  
495 measured isotopic compositions  $\delta^{34}\text{SSO}_2$  (CPP) (g) =  $-2.8\text{‰}$ ,  $\delta^{34}\text{SSO}_4$  (CPP) (particle)  
496 =  $-2.0\text{‰}$  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  $\omega$  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  $\text{SO}_4^{2-}$  availability is directly affected by the  $\text{SO}_2$  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  $\omega$  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  $\text{SO}_2$  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  $[\text{SO}_4^{2-}]$  (CPP)  
578 and  $\omega$  (SE-E wind fraction), whose values were well determined. E  
579 (scavenging ratio) and P ( $\text{SO}_2$ - $\text{SO}_4^{2-}$  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  $\text{SO}_2$  emissions is  
582 mainly subjected to the characterization of atmospheric conditions. Finally,  
583 the mixing model was hardly dependant on B (non-oxidized  $\text{SO}_2$  fraction  
584 that can reach the studied area and be dry deposited onto the canopy) and C  
585 (fraction of deposited  $\text{SO}_2$  onto canopy that is oxidized inside stomata)  
586 parameter variations.

587

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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<sup>-1</sup> year<sup>-1</sup>, except for alkalinity (meq  
 830 m<sup>-2</sup> year<sup>-1</sup>) and rainfall (mm year<sup>-1</sup>). 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*.

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837

	Rainfall	Alk.	H+	Na+	K+	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	SO <sub>4</sub> <sup>2-</sup> -S	Cl <sup>-</sup>
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 <sup>1</sup>	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 <sup>1</sup>	337*	75.0	-0.11	1.7	25.2	7.6	1.9	1.2	0.3	3.8	7.5
Net Throughfall											
Prades <sup>2</sup>	551*	29.6	-0.05	1.8	13.7	9.5	1.8	0.4	1.4	5.0	2.6
Net Throughfall											
Filabres <sup>3</sup>	-	49.8	-	4.8	11.5	19.5	3.2	-0.5	0.2	3.5	15.7

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

839 \* Net rainfall= Rainfall-throughfall (mm)

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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 <sub>2</sub> emissions	-2.75	-2.8 to -2.7
SO <sub>4</sub> <sup>2-</sup> 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

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850

851 Table 4. Isotopic difference of SO<sub>2</sub> to SO<sub>4</sub><sup>2-</sup> 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

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855

856 Table 5. [SO<sub>2</sub>] emission values (mg/Nm<sup>3</sup>) (both gas and particle phases)  
 857 measured in the stack, the corresponding SO<sub>4</sub><sup>2-</sup> concentrations (μeq/L) and  
 858 the SO<sub>4</sub><sup>2-</sup> concentrations calculated by equation 2.  
 859

	[SO <sub>2</sub> ]	[SO <sub>4</sub> <sup>2-</sup> ] <sub>stack</sub>	[SO <sub>4</sub> <sup>2-</sup> ] <sub>(CPP)</sub>
	mg/Nm <sup>3</sup>	μeq/L	μeq/L
Gas	2645.3	82.6	1177.5
Particle	-	13.7	10.8*

860 \*The [SO<sub>4</sub><sup>2-</sup>]<sub>(CPP)</sub> associated to the particle phase has been calculated by means of:  
 861 [SO<sub>4</sub><sup>2-</sup>]<sub>(CPP)</sub> = [SO<sub>4</sub><sup>2-</sup>]<sub>stack</sub> · ω · E · B, because the oxidation of SO<sub>2</sub> 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	$[\text{SO}_4^{2-}]$	$\delta^{34}\text{S}_{\text{SO}_4}$
	$\mu\text{eq/L}$	$\text{‰}$
Regional Background (RB)	40.0	+7.2
Cercs Power Plant (CPP)	1188.3	-1.1

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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/SO<sub>4</sub>**  
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  $+7.2\text{‰}$ ,  $[\text{SO}_4] = 40.0 \mu\text{eq/L}$ ) and the Cercs power plant (CPP) SO<sub>2</sub>  
883 emissions ( $\delta^{34}\text{S}_{\text{SO}_4} = -1.1\text{‰}$ ,  $[\text{SO}_4] = 1188.3 \mu\text{eq/L}$ ).  $[\text{SO}_4]_{\text{(CPP)}}$  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 SO<sub>4</sub> 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 SO<sub>4</sub> contribution from the CPP  
892 according to the mixing model.

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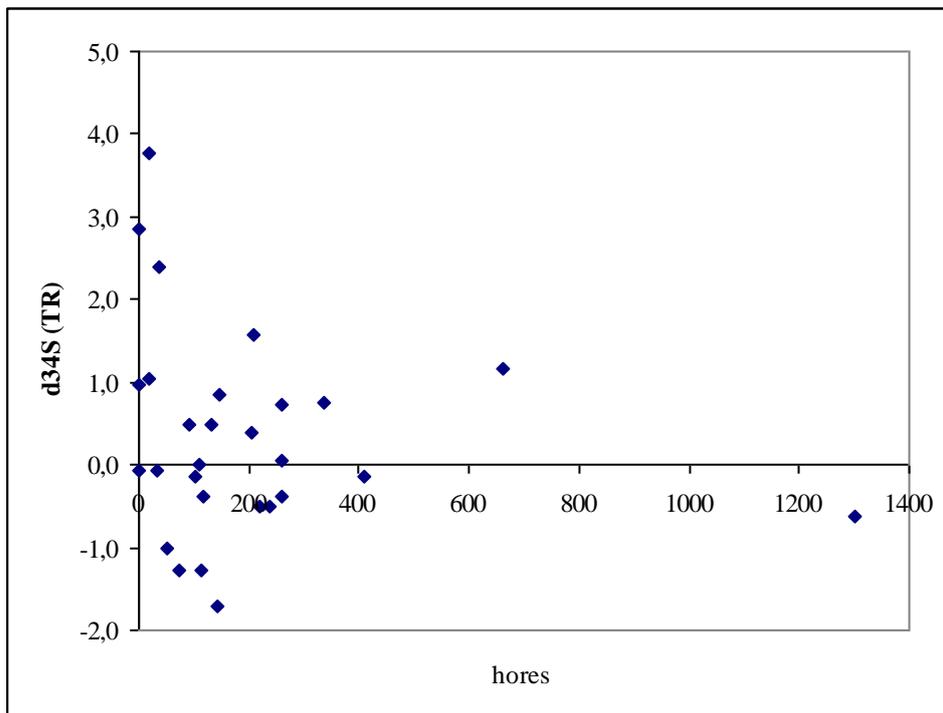
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899

900 **Fig. 2**

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913 **Fig. 3**

