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29 **Use of ammonium sulphate as a sulphur fertilizer: implications for**  
30 **ammonia volatilization**

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36

37 **Abstract**

38 Ammonium sulphate is widely used as a sulphur (S) fertilizer, constituting about 50%  
39 of global S use. Within nitrogen (N) management it is well known that ammonium-  
40 based fertilizers are subject to ammonia (NH<sub>3</sub>) volatilization in soils with pH >7, but  
41 this has been overlooked in decision making on S fertilization. We reviewed 41  
42 publications reporting measurements of NH<sub>3</sub> loss from ammonium sulphate in 16  
43 countries covering a wide range of soil types and climates. In field experiments loss  
44 was mostly <5% of applied N in soils with pH (in water) <7.0. In soils with pH >7.0  
45 there was a wide range of losses (0-66%), with many in the 20-40% range and some  
46 indication of increased loss (ca. 5-15%) in soils with pH 6.5-7.0. We estimate that  
47 replacing ammonium sulphate with a different form of S for arable crops could  
48 decrease NH<sub>3</sub> emissions from this source by 90%, even taking account of likely  
49 emissions from alternative fertilizers to replace the N, but chosen for low NH<sub>3</sub>  
50 emission. In temperate climates emission from soils of pH >7.0 would decrease from  
51 35.7 to 3.6 t NH<sub>3</sub> per kt ammonium sulphate replaced. Other sources of S are readily  
52 available including single superphosphate, potassium sulphate, magnesium  
53 sulphate, calcium sulphate dihydrate (gypsum) and polyhalite (Polysulphate). In view  
54 of the large areas of high pH soils globally, this change of selection of S fertilizer  
55 would make a significant contribution to decreasing NH<sub>3</sub> emissions worldwide,  
56 contributing to necessary cuts to meet agreed ceilings under the Gothenburg  
57 Convention.

58

59 **KEYWORDS**

60 Ammonium sulphate, sulphur, fertilizer, ammonia, volatilization, Gothenburg  
61 Convention

62

63 **1. Introduction**

64 It has been recognised for over 50 years that surface application of ammonium-  
65 based fertilizers or urea can lead to rapid and significant evolution of ammonia (NH<sub>3</sub>)  
66 gas to the atmosphere (Gasser, 1964, and references therein). It is also well  
67 established that loss is greater in soils with pH >7 and/or containing calcium  
68 carbonate (Fenn and Kissel, 1973; Fenn and Hossner, 1985). For example, in

69 laboratory experiments Fenn and Kissel (1975) found that up to 50% of the nitrogen  
70 (N) applied as ammonium sulphate could be volatilized as NH<sub>3</sub> depending on calcium  
71 carbonate content of the soil. Losses are often greater with urea because rapid  
72 conversion of urea-N to ammonium-N by the urease enzyme in soil increases pH in  
73 the vicinity of fertilizer particles (Rachhpal-Singh & Nye, 1986; Kirk & Nye, 1991).  
74 These well-established principles were summarised by Harrison & Webb (2001) in  
75 the context of comparing gaseous N losses from urea with those from ammonium  
76 nitrate and other forms of N fertilizer.

77 In addition to being a cause of decreased N use efficiency by crops, NH<sub>3</sub> emission  
78 has adverse environmental and public health impacts, including the following:

- 79 1. Redeposition of NH<sub>3</sub> on to soil or water causes nutrient enrichment which is  
80 particularly damaging to the ecology of semi-natural sites (Guthrie *et al*, 2018;  
81 Stevens *et al*, 2004).
- 82 2. Microbial nitrification of redeposited NH<sub>3</sub> causes acidification of soil and water  
83 because the process produces protons and, thus, acidification of the environment  
84 (Goulding *et al*, 1998; Johnston *et al*, 1986).
- 85 3. Ammonia gas in the atmosphere can react with other substances to form  
86 particulate materials including ammonium sulphate, ammonium nitrate and  
87 ammonium chloride. Human exposure to these particulates (PM10 and PM2.5)  
88 can lead to increased rates of respiratory and cardiovascular illness (Wu *et al*,  
89 2016; Moldanová, *et al*, 2011).

90

91 All European countries (including the EU as a whole), plus several others including  
92 USA, Canada and Russia, are signatories to the UN Gothenburg Convention on  
93 Long-range Transboundary Air Pollution: see UNECE (2015) for guidance on  
94 preventing and abating ammonia emissions from agricultural sources in accordance  
95 with the convention. These countries are therefore committed to decreasing  
96 emissions of NH<sub>3</sub> and other pollutant gases. Agriculture is a major source of NH<sub>3</sub>,  
97 estimated at >90% of total emissions in the European Union in 2018 (EEA, 2020a)  
98 and 87% of UK emissions in 2018 (Defra, 2020). The majority of agricultural  
99 emissions are associated with manure, with 18% from fertilizers in the UK (Defra,  
100 2020). Consequently, there is strong pressure to decrease agricultural emissions  
101 across much of the world.

102 In recent years studies on NH<sub>3</sub> emissions from agriculture have focussed mainly on  
103 animal manure and urea because these are the major sources (Bouwman *et al*,  
104 2002; Del Moro *et al*, 2017). Globally ammonium sulphate is a relatively minor  
105 contributor to nitrogen (N) fertilizer use, global production being estimated as 5.67 Mt  
106 N in 2017 compared to 77.87 Mt N as urea and 16.11 Mt N as ammonium nitrate  
107 (IFA, 2017; internal data used with permission). However, in recent years ammonium  
108 sulphate has become a major source of sulphur (S) for fertilizer use because it is  
109 readily available, being a by-product of various industrial processes, and has been  
110 relatively cheap compared to most other forms. Global use of S fertilizer in 2015 was  
111 reported as 13.3 Mt S (equivalent to 33.3 Mt SO<sub>3</sub>, the unit in which S fertilizer

112 quantities are usually quoted in the context of production and agronomic use) of  
113 which about 50% was as ammonium sulphate, used either as the pure material, in  
114 blends with other straight nitrogen fertilizers or as part of compound NPKS fertilizers  
115 (IFA, 2017).

116 With ammonium sulphate being used more widely as a source of S for crops, it is  
117 inevitable that some  $\text{NH}_3$  will be volatilised, thus working against the aim of the  
118 Gothenburg Convention. Volatilisation will be greatest from calcareous soils and  
119 others with a pH of 7 or greater. There are significant areas of such soils globally in  
120 places where there is high-yielding agriculture, and where S fertiliser is either already  
121 widely used or its use is likely to increase. These include regions of China, India,  
122 Pakistan, USA, France, and UK. The aims of this paper are: (1) to review data on  
123  $\text{NH}_3$  emissions from ammonium sulphate; (2) estimate the decrease in  $\text{NH}_3$  emission  
124 achievable through a change to alternative sources of S. Such information is  
125 required as a basis for decisions regarding management practices including  
126 alternative sources of S, especially for top-dressing on high pH and calcareous soils.

127

## 128 **2. Materials and Methods**

129 We summarise the estimations of  $\text{NH}_3$  emission factors (EFs) for ammonium  
130 sulphate proposed in documents from several major regulatory authorities  
131 internationally and from previously published literature reviews. We then summarise  
132 results from experiments in which ammonia volatilization from ammonium sulphate  
133 has been measured in both laboratory and field experiments (Supplementary Tables  
134 1 and 2). This was based on a literature search using *Web of Science* during  
135 February to March 2019 using the search term “ammonium sulphate” or “ammonium  
136 sulfate” modified by “fertilizer” or “fertiliser” and “ammonia”. In most parts of the world  
137 ammonium sulphate is no longer widely used as an N fertilizer but, in experimental  
138 studies, it is sometimes included for comparison with losses from urea or animal  
139 manures. We excluded publications where information on the soil type or  
140 environmental conditions were lacking or where the data on ammonium sulphate  
141 were non-quantitative (e.g. ammonia volatilization simply stated as being less than  
142 that from urea). This review led to publications from 17 countries covering a wide  
143 range of climatic conditions, with 11 reporting results from laboratory experiments  
144 and 30 field measurements. Where publications report EFs for urea, we include  
145 these data for comparison. For the purposes of national reporting under the  
146 Gothenburg Convention, EFs are normally quoted as g  $\text{NH}_3$  evolved per kg N  
147 applied; this unit is used in Table 1 (taken from EEA, 2019) and in our estimations in  
148 Table 3 of the potential for decreasing  $\text{NH}_3$  emissions by changing S applications  
149 from ammonium sulphate to a different fertilizer form. However, in scientific studies  
150 of  $\text{NH}_3$  volatilization it is more usual to quote losses as the quantity of  $\text{NH}_3$ -N emitted  
151 as a percentage of N applied so, in our review of published data (Supplementary  
152 Tables 1 and 2) we use these units.

153

## 154 **3. Results**

155 3.1 *Emission factors from official and regulatory bodies*

156 The United Nations Economic Commission for Europe (UNECE) Framework Code  
157 for Good Agricultural Practice for Reducing Ammonia Emissions (UNECE, 2015)  
158 does not state a specific EF for ammonium sulphate but includes the following  
159 statement: “On calcareous soils (pH > 7.5) do not use ammonium sulphate fertilizers  
160 if rapid incorporation, injection into the soil, immediate irrigation or the use of  
161 polymer-coated fertilizer is not possible, but seek alternative sources of N and  
162 sulphur”. Similarly, the UK Code of Good Agricultural Practice for Reducing  
163 Ammonia Emissions (Defra, 2018), based in part on the model of Misselbrook *et al*  
164 (2004), does not cite an EF for ammonium sulphate but states that, to minimise  
165 volatilization, surface application should be avoided on calcareous soil of pH >7.5  
166 unless it can be rapidly incorporated into soil.

167

168 Table 1 about here

169 The European Environment Agency (EEA) publishes technical guidance for  
170 preparing national emissions inventories for a range of atmospheric pollutants  
171 including NH<sub>3</sub> (EEA, 2019). The guidance includes the EFs shown in Table 1 for Tier  
172 2 level calculations for use in Europe and the wider UNECE geographical area.  
173 Values are expressed in units of g NH<sub>3</sub> emitted per kg N applied (as published by  
174 EEA) in the upper part of the Table and converted to NH<sub>3</sub>-N emitted as % of N  
175 applied in the lower part. The proposed values show three main trends. First, in  
176 agreement with other studies, soil pH has a large influence on NH<sub>3</sub> volatilization from  
177 ammonium sulphate. For example, under temperate climatic conditions, the EF for  
178 soil with pH ≤ 7.0 is 7.6% of N applied compared with 14% at pH >7.0 (changing  
179 from 92 to 170 g NH<sub>3</sub> per kg N applied). Second, there is a modest influence of  
180 temperature with slightly increased EF values in warmer climates. Third, in soils of  
181 neutral pH or lower, volatilization from ammonium sulphate is markedly less than  
182 from urea; e.g. in temperate climates, 7.6% of N applied compared to 13.1%. But in  
183 soils with pH >7.0, which are normally calcareous, the difference virtually disappears.

184

185 The US Environmental Protection Agency recommended EFs for ammonium  
186 sulphate and urea of 8% and 15% of N applied, respectively (i.e. 97 and 187 g NH<sub>3</sub>  
187 per kg N applied, respectively; EPA, 1994). In this they followed the values  
188 recommended by Asman (1992). It was noted that soil pH and clay content (taken  
189 as a proxy for cation exchange capacity) were factors influencing NH<sub>3</sub> loss, but it  
190 was decided to give only a single EF value for each N fertilizer type.

191

192 3.2 *Earlier reviews*

193 Bouwman *et al* (2002) reviewed published literature at that time on NH<sub>3</sub> volatilization  
194 from fertilizers and manures as a basis for estimating the contribution of agriculture  
195 to global emissions. Although their data are not ideal for our current purpose, some  
196 general points emerge. First, based on about 150 publications, they concluded that  
197 laboratory measurements of NH<sub>3</sub> volatilization gave values that were 47-64% higher

198 than field measurements. This is almost certainly because the commonly used  
199 laboratory techniques involve air being forced through an incubation vessel,  
200 removing NH<sub>3</sub> from the soil atmosphere and stimulating further emission by altering  
201 equilibria in soil solution. Second, they concluded that the overall mean emissions  
202 factors were 18.7% of N applied for ammonium sulphate and 21% for urea, based on  
203 86 data points. The corresponding median values were 11.2% and 14%,  
204 respectively. Third, their review showed an effect of soil pH, with EF increasing from  
205 15% of N applied for soils with pH ≤ 5.5 to around 20% for soil with pH > 7.5.  
206 However, it should be emphasised that these latter values are means for all forms of  
207 N fertilizer, not specifically ammonium sulphate.

208 On the basis of a meta-analysis of >800 publications concerning N fertilizer  
209 management, Pan *et al* (2016) concluded that NH<sub>3</sub> volatilization averaged 74% less  
210 from non-urea based fertilizers compared to urea, though this is not in agreement  
211 with the findings of Bouwman *et al* (2002). However, Pan *et al* (2016) did not  
212 explicitly identify losses from ammonium sulphate.

213

### 214 3.3 Laboratory experiments

215 Results from 11 publications we reviewed giving results from laboratory experiments  
216 are summarised in Supplementary Table 1. The earliest papers cited are Martin &  
217 Chapman (1951) and Gasser (1964). These authors refer to papers dating back to  
218 1939, though they mainly refer to losses from urea. As with the earlier reviews, a  
219 clear conclusion is that soil pH and CaCO<sub>3</sub> content both have a major influence on  
220 NH<sub>3</sub> volatilization from applied ammonium sulphate, with high pH favouring greatly  
221 increased loss. This was shown in two ways: by comparing NH<sub>3</sub> loss from soils that  
222 naturally differed in pH (e.g. Martin and Chapman, 1951; Whitehead and Raistrick,  
223 1990) or by adjusting the pH of a single soil in the laboratory (He *et al*, 1999). In a  
224 well-known paper, Whitehead and Raistrick (1990) applied N-containing fertilisers to  
225 the surface of a set of UK soils in columns and measured NH<sub>3</sub> volatilization over 8  
226 days. In a soil of pH 6.1 containing 0.6% CaCO<sub>3</sub> emission from ammonium sulphate  
227 was small (4% of applied N; Supplementary Table 1) but increased to 31% in a soil  
228 of pH 7.1 and containing 1.8% CaCO<sub>3</sub>. A similar trend with increasing soil pH was  
229 seen in soils from the USA (Martin & Chapman, 1951; Liu *et al*, 2007) and Kenya  
230 (Siguna *et al*, 2002). He *et al* (1999) took a soil from Florida of pH 7.9 and adjusted  
231 pH by adding HCl or NaOH. When soil pH was below 5.5 there was no measurable  
232 volatilization of NH<sub>3</sub> from ammonium sulphate but when adjusted to pH 6.5 or above,  
233 emission was around 30% of applied N (Supplementary Table 1). On the basis of his  
234 own and earlier studies, Gasser (1964) noted that there was a close relationship  
235 between NH<sub>3</sub> loss and soil cation exchange capacity (CEC) but later authors state  
236 that pH has a much stronger effect.

237 A sharp increase in the likelihood of substantial NH<sub>3</sub> loss as soil pH exceeds 7.0 is  
238 clearly shown in Fig.1: with only one exception, losses from soil with pH <7.0 were  
239 <10%, and mostly <5% of the N applied as ammonium sulphate. In soils of pH >7.0  
240 losses were very variable but with many at 20% or higher. In the one example of a  
241 large loss from a soil with pH <7.0 (a 32% loss from a soil at pH 6.5; He *et al*, 1999),

242 the authors noted that nitrification was unusually slow in this soil which had been  
243 adjusted to this pH from its natural value of 7.9; N remained in the ammonium form  
244 for longer than in the soils adjusted to pH 7.5 or 8.5 which gave a slightly smaller  
245 loss (Supplementary Table 1). This longer persistence of ammonium-N in a soil with  
246 artificially adjusted pH almost certainly permitted a greater conversion of N to NH<sub>3</sub>  
247 and its subsequent gaseous loss and is unlikely to be relevant to practical field  
248 situations.

249 Fig. 1 about here

250 Ammonia volatilization from ammonium sulphate generally increases at higher  
251 temperature as shown by a comparison of EF at 22 and 32° C in soil from Trinidad  
252 (Prasad *et al*, 1976). Soil moisture is also an influencing factor, with wetter conditions  
253 tending to decrease loss (Supplementary Table 1: Liu *et al*, 2007; Prasad, 1976). As  
254 expected, where surface application was compared with ammonium sulphate mixed  
255 with the soil (Gasser, 1964), mixing decreased volatilization somewhat.

256 In several cases, though not all, volatilization from ammonium sulphate was less  
257 than that from urea under the same conditions (Liu *et al* 2007; Prasad *et al*, 1976;  
258 Shahandeh *et al*, 1992; Whitehead & Raistrick, 1990; Supplementary Table 1). This  
259 is because of the well-known effect of urea hydrolysis causing an increase in soil  
260 solution pH in the vicinity of fertilizer granules (Rachhpal-Singh & Nye, 1986;  
261 Rochette *et al*, 2009). A result of this is that volatilization from urea can occur in soils  
262 that have a more acidic pH. One example is in the data of Whitehead & Raistrick  
263 (1990); where soil pH was 6.1 or 5.5 NH<sub>3</sub> volatilization from ammonium sulphate was  
264 negligible but from urea was 38% and 22% of applied N respectively.

265

### 266 3.4 Field experiments

267 Data from 30 publications showing results from field experiments are summarised in  
268 Supplementary Table 2. In most studies the main focus was NH<sub>3</sub> volatilization from  
269 urea, with ammonium sulphate being included as a comparison and expected to give  
270 a smaller loss. Where there are data from a urea treatment under equivalent  
271 conditions, these are included. The studies are from 11 countries with climates  
272 ranging from cool temperate (including USA, UK, Denmark) to tropical with climates  
273 having either lower rainfall (e.g. Syria, Sudan) or higher (Brazil).

274 A wide range of measurement methods were used. In the majority of cases it was  
275 some form of semi-open chamber such that air in a chamber inserted into soil could  
276 exchange with the atmosphere via a filter impregnated with acid in order to trap NH<sub>3</sub>  
277 which was then quantitatively determined. In a few cases there was an arrangement  
278 for scrubbed air to flow through the chambers prior to absorption of NH<sub>3</sub> and in some  
279 earlier studies completely closed chambers were used (Musa, 1968; Volk, 1959). In  
280 some micrometeorology was used (Hayashi *et al*, 2011; Huo *et al*, 2015; Turner *et al*,  
281 2012) and in 5 cases NH<sub>3</sub> volatilization was calculated from <sup>15</sup>N recovery in  
282 situations where it was deduced that other N loss processes were small (Fenilli *et al*,  
283 2008; Isa *et al*, 2006; Malhi *et al*, 1996; Pilbeam *et al*, 1997; Pilbeam and Hutchison,  
284 1998). Wind tunnels, that are widely used for measuring NH<sub>3</sub> loss from manures and



285 urea, were only used in one of the studies reported in Supplementary Table 2  
286 (Sommer & Jensen, 1994). In addition to the influence of soil type, cropping system  
287 and climate, and variability due to the range of measurement methods, field results  
288 are obviously affected by method of application, agronomic factors and local weather  
289 conditions at the time of the experiment.

290 Interestingly, 10 publications were from Brazil where it appears that ammonium  
291 sulphate is more widely used as an N source than in many other regions. At all  
292 Brazilian sites soil pH was acidic, ranging from 4.4 to 5.8 and in almost all cases NH<sub>3</sub>  
293 volatilization was small: < 12% of N applied and mostly 0-5%. By contrast,  
294 volatilization from urea was often considerably greater, ranging from negligible to  
295 >40%, presumably because soil pH was increased locally by urea hydrolysis.

296 Fig. 2 about here

297 As with the data from laboratory studies, Fig. 2 shows that soil pH has a dominant  
298 influence on NH<sub>3</sub> volatilization from ammonium sulphate under field conditions.  
299 Losses of >20% of applied N were all associated with soil pH >7.3 (Fig. 2). The  
300 largest losses of 27-66% were at sites in Syria with soil pH 8.1 and 23% CaCO<sub>3</sub>  
301 (Pilbeam *et al*, 1997; Pilbeam & Hutchinson, 1998), Sudan (soil pH 8.7 with 4%  
302 CaCO<sub>3</sub>; Musa, 1968) and USA (soil pH 7.6 – 8.2, with 25% CaCO<sub>3</sub>; Hargrove *et al*,  
303 1977). However intermediate losses (up to approx. 20% of N applied) were recorded  
304 at sites with soil pH values between 6.7 and 7.3 (Fig. 2). In one set of experiments in  
305 Australia, with soil pH around 7.7, whether soils were described as having “low” or  
306 “high” calcium carbonate content made the difference between losses of <10% or  
307 20-35% (Schwenke *et al*, 2014; Supplementary Table 2). At a site in Tanzania (Isa *et al*,  
308 2006) soil salinity was associated with higher pH and increased NH<sub>3</sub> volatilisation.  
309 Hargrove *et al* (1977) noted that the measured losses (33-41% of N applied) from  
310 soils of pH 7.6 to 8.2 under pasture in the USA were influenced by temperature at  
311 the time of application. Martha *et al* (2004) found a similar trend in Brazil.

312

## 313 4 Discussion

### 314 4.1 Effect of soil factors on ammonia loss from ammonium sulphate

315 Results from laboratory and field studies clearly show that soil pH, together with  
316 calcium carbonate content, is the overriding factor determining ammonia emission  
317 from applied ammonium sulphate. In field experiments, where soil pH was below 7,  
318 N lost as NH<sub>3</sub> was well below 5% of N applied in the majority of cases (Fig. 2).  
319 Where soil pH was between 6.5 and 7.0 losses of 5-15% were observed and 5-10%  
320 in a few cases at lower pH. For soils with pH 7.0 or greater, losses of 15-35% of N  
321 applied were commonly observed with 50% or more in some cases (Fig. 2).  
322 However, there were also a few cases where losses were below 10%, even where  
323 pH was between 7.0 and 8.0; the reason is not known but is likely to be associated  
324 with the precise details of application method in relation to crop growth and weather  
325 conditions. For example, rainfall soon after application, rapid nitrification of  
326 ammonium or rapid crop uptake of N would all decrease the possibility of NH<sub>3</sub>  
327 volatilization.

328 A clear conclusion for S fertilization practice is that it is inadvisable to apply  
329 ammonium sulphate to soils with pH above 7.0 because NH<sub>3</sub> volatilization is  
330 extremely likely to be significant; even in soils with pH between 6 and 7 there is  
331 some risk of loss. By contrast, in soil of lower pH the risk is small. These general  
332 trends are in line with the EFs proposed by the EEA (Table 1). However, about half  
333 of the data points in Fig. 2 for soils with pH >7.0 indicate EFs greater than the 14-  
334 18% range proposed by EEA, in several cases considerably greater: we can offer no  
335 explanation for this. The use of average EFs defined for wide soil pH ranges and  
336 climate categories represents a broad and pragmatic generalization. The actual loss  
337 of NH<sub>3</sub> in any specific situation will be determined by specific agronomic conditions  
338 and environmental factors, including weather around the time of ammonium sulphate  
339 application. In addition, the reported losses shown in Fig. 2 will also be influenced by  
340 the different methods of measurement used. For these reasons it was concluded that  
341 detailed statistical analysis of the data was unlikely to be helpful in further identifying  
342 the relative importance of different factors influencing NH<sub>3</sub> loss.

343

#### 344 4.2 Global implications for sulphur fertilization using ammonium sulphate

345 These conclusions are extremely pertinent when considering the use of ammonium  
346 sulphate as a source of S for arable crops. Many arable soils, especially in  
347 temperate climatic zones, are limed in order to maintain a pH of around 7. In  
348 addition, significant areas of soil are naturally calcareous. This is illustrated for the  
349 UK by analyses of soils from farmers' fields conducted by professional laboratories  
350 as part of routine soil testing for fertilizer advice (PAAG, 2019). Table 2 shows mean  
351 data over 10 years, based on > 1.5M samples. Within

352 Table 2 about here

353 arable soils, 40% had pH >7.0, 21% between 6.5 and 7.0 and a further 21% between  
354 6.0 and 6.5 (Table 2). Thus, based on this large sample of arable fields, 40% were at  
355 a pH likely to lead to NH<sub>3</sub> losses of 15-35% of applied N, with a risk of 50% loss in  
356 some cases. In addition, a further 42% of fields were in the pH range 6.0-7.0, with a  
357 possibility of around 10% loss. The risk of substantial loss from grassland fields is  
358 less as only 8% of samples analysed were at pH >7.0 (Table 2).

359 For Europe as a whole, many major arable cropping areas have soil of high pH. Fig.  
360 3 (taken from Jones *et al*, 2020) shows soil pH (in water) for croplands, based on the  
361 LUCAS database and illustrated for regions within the European Union at the level of  
362 NUTS 2 (Nomenclature of Territorial Units for Statistics; see Jones *et al* (2020) for  
363 full description). Of the 238 regions where there was sufficient data for cropland soil  
364 properties to be illustrated in this way, over 30% had soil pH >7. In addition to much  
365 of southern and eastern England, substantial areas of northern and central France  
366 are in this category. These regions, including the Paris Basin, are important for  
367 cereal and oilseed production where S fertilisers are widely used and the area  
368 receiving S is likely to increase (Webb *et al*, 2016). In northern Europe, Fig. 3 also  
369 shows that significant areas used for arable cropping in Germany, Hungary and the  
370 Netherlands have soils with pH >7 and thus with a high risk of NH<sub>3</sub> emission if S is

371 supplied as ammonium sulphate. Further south, large areas in Spain, southern  
372 France, Italy, Croatia, Greece and Romania are also in this category. Across Europe  
373 a similar additional area of cropland is in the pH 6-7 category; within this there are  
374 significant areas with soil pH >6.5 and thus at some risk of NH<sub>3</sub> volatilization; see  
375 Ballabio *et al* (2019) for a soil pH map derived from the LUCAS data using Gaussian  
376 process regression modelling.

377 Fig. 3 about here

378 Globally many major agricultural regions include substantial areas of soil with pH  
379 >7.0 and/or large calcium carbonate concentrations. The Indo-Gangetic Plain in  
380 India, Pakistan, Nepal and Bangladesh is an extremely important agricultural region,  
381 with much intensive arable cropping, and significant areas with high soil pH and  
382 calcium carbonate content and, in some cases, sodic conditions (e.g. Pal *et al*,  
383 2009). In China, although there is a widespread problem of soil acidification, a recent  
384 mapping study (Chen *et al*, 2019) also showed many soils with pH >7.0 including a  
385 significant number at around pH 8.0. These were mainly located in northern and  
386 western China including the North China Plain that is important for wheat and maize  
387 production, but also includes the karst region in southwest China, covering 540,000  
388 km<sup>2</sup> (Wang *et al*, 2019). In both India and China there is widespread S deficiency in  
389 crops and increasing quantities of S fertilizers are being used. In both countries,  
390 especially in the Indo-Gangetic Plain and the North China Plain, high rates of N  
391 fertilizer are used with the aim of achieving large crop yields, so the requirement for  
392 S will almost certainly increase further. Many soils in Turkey have high pH and high  
393 Ca content; for example, Gezgin & Bayraklı (1995) measured NH<sub>3</sub> losses from  
394 ammonium sulphate of 14-20% from a soil with pH 8.44 and which contained 20%  
395 CaCO<sub>3</sub> (Supplementary Table 2).

396

#### 397 *4.3 Estimating potential for decreasing ammonia emission by replacing ammonium* 398 *sulphate with alternative fertilizers as a source of sulphur*

399 Table 3 shows an estimation of the potential for decreased NH<sub>3</sub> emissions if  
400 ammonium sulphate were replaced by an alternative source of S, not prone to NH<sub>3</sub>  
401 volatilization. The calculations are made for a unit of 1 kt of ammonium sulphate, so  
402 the resulting values can be applied generically to any region. For the purposes of this  
403 estimation, we assume that all ammonium sulphate is applied to the soil surface (i.e.  
404 top-dressed), as is commonly the case. In this estimation we use the EF values from  
405 EEA (2019; Table 1) even though, as discussed above, there was a suggestion from  
406 our review of data (Fig. 2) that EFs could often be greater. We therefore suggest that  
407 the values we derive for decreased NH<sub>3</sub> emission are conservative. The estimation is  
408 made for soils having a pH of pH > 7.0 and those with pH <7.0 in both temperate and  
409 warm climates. We make calculations using EFs expressed as g NH<sub>3</sub> kg<sup>-1</sup>N applied  
410 because this is the unit most commonly used in national inventories. Table 3  
411 indicates that applying 1 kt of ammonium sulphate to soil with pH >7.0 leads to  
412 emissions of 35.7 and 44.5 t NH<sub>3</sub> in temperate and warm climatic regions  
413 respectively; in principle, these emissions could be completely eliminated if  
414 ammonium sulphate was replaced as the source of S. However, the N supplied by

415 ammonium sulphate would need to be replaced, almost certainly leading to some  
416 emission of NH<sub>3</sub> and offsetting this reduction. Obviously, there would be no benefit  
417 from using urea as the source of N as its NH<sub>3</sub> EF is generally greater than that of  
418 ammonium sulphate. For the purposes of this calculation we assume the N is  
419 replaced by calcium ammonium nitrate (CAN), an N fertilizer with a low EF for NH<sub>3</sub>.  
420 Emissions from CAN, to replace the N previously supplied from ammonium sulphate,  
421 are estimated as 3.6 and 4.4 t NH<sub>3</sub> per kt N for soils of pH >7.0 in temperate and  
422 warm climates, respectively, about 10% of the emissions from ammonium sulphate.  
423 Hence the overall benefits from this change are still substantial for soils of pH >7.0:  
424 decreases of 32.1 t NH<sub>3</sub> (temperate climate) and 40.1 t NH<sub>3</sub> (warm climate) per kt  
425 ammonium sulphate replaced. The corresponding reductions for lower pH soils are  
426 17.7 and 22.1 t NH<sub>3</sub> per kt ammonium sulphate replaced. On all soils these  
427 represent decreases in NH<sub>3</sub> emission of over 90% compared to using ammonium  
428 sulphate (Table 3).

429 [Table 3 about here](#)

430 [Table 4 about here](#)

431 For any country or region, the absolute reduction in NH<sub>3</sub> emissions possible through  
432 a change away from using ammonium sulphate as the source of S will depend on (a)  
433 the total usage of ammonium sulphate for the region and (b) the proportion that is  
434 applied to soils of pH >7.0; in most cases specific data on the latter value are not  
435 available, so indirect deductions are necessary. Table 4 shows the annual usage of  
436 ammonium sulphate in a range of countries; the largest usages globally (>1000 kt  
437 per year) being in Brazil, USA, Indonesia, Mexico and Vietnam. Within Europe,  
438 Germany, Spain and UK are the largest users; in these countries it is likely that the  
439 majority is used as a source of S. All three countries, and many others in the EU,  
440 need to decrease NH<sub>3</sub> emissions immediately by up to 10% to meet the lowered  
441 ceilings introduced under the Gothenburg Conventions for 2020 and by up to 20% to  
442 meet the planned ceilings for 2030 (Table 5). Although the largest decreases are  
443 likely to be achieved by improved management of manure, or of urea fertilizer where  
444 this is the dominant form of N fertilizer, any additional savings will be beneficial and  
445 the alteration in S fertilizer use discussed here is relatively easy to achieve.

446 [Table 5 about here](#)

447 As an example of the benefit from making this change, total annual consumption of  
448 fertiliser S in the UK in 2017/18 was 90 kt S (AIC, 2019). It is estimated that at least  
449 90% of this was provided as ammonium sulphate, and that 70% of this quantity was  
450 applied with other nitrogen fertilisers as a topdressing on arable land. Table 2  
451 indicates that 40% of UK arable land has a pH > 7.0 so that using the estimations in  
452 Table 3 we calculate that the annual ammonia emission from this source in high pH  
453 arable land would be reduced by over 3 kt NH<sub>3</sub> by changing to a different source of  
454 S, i.e. almost 20% of the 16 kt decrease required to meet the 2020 ceiling.

455 In the global context, the relevant area of agricultural land in the UK is small. In  
456 regions with large areas of high pH soils, as discussed earlier, the absolute  
457 decreases in NH<sub>3</sub> emission possible will be considerably greater and would thus

458 make significant contributions to decreasing global emissions. With goals of  
459 increased crop yields and quality in many regions, achieved in part through  
460 application of N and other fertilizers, the requirement for S fertilizers will continue to  
461 increase. We propose the values derived in Table 3 as a basis for quantitatively  
462 estimating the benefit of changing the form of S fertilizer type used for any global  
463 region.

464

#### 465 *4.4 Implications for appropriate choice of S fertilizers*

466 For many soil types and environments ammonium sulphate is a largely satisfactory  
467 source of S and has the advantage of simultaneously supplying part of the crop N  
468 requirement. But this analysis has strongly emphasised that it is highly undesirable  
469 to use it on soils with pH >7.0, or even slightly lower. Although the risk of ammonia  
470 volatilization from ammonium-based fertilizers has long been recognised in the  
471 context of N fertilizer use, it appears to have been overlooked in the context of  
472 selecting an appropriate S-supplying fertilizer suitable for different soil types. It is  
473 common practice to surface-apply S during the period of rapid crop growth, often  
474 together with at least part of the N application. Consequently practices that could  
475 decrease NH<sub>3</sub> volatilization from ammonium sulphate, such as incorporation into soil,  
476 are not feasible.

477 Several alternative sources of S, without any associated nitrogen, are available that  
478 would be preferable on high pH soils. These include potassium sulphate (often  
479 referred to as SOP, abbreviation for sulphate of potash), magnesium sulphate  
480 (kieserite), polyhalite (also known as Polysulphate, a mineral containing sulphates of  
481 potassium, calcium and magnesium), calcium sulphate dihydrate (gypsum) and  
482 single superphosphate SSP, (comprising a mixture of monocalcium phosphate and  
483 gypsum). Obviously, with each of these S fertilizer materials, the content of P, K, Mg  
484 or Ca needs to be taken into account when deciding on other nutrient applications.  
485 Elemental sulphur can also be used but is more slowly available to crops than the  
486 other forms because it first has to be oxidised to sulphate by soil bacteria and the  
487 rate of conversion is somewhat unpredictable (e.g. Malhi et al, 2005; McGrath et al,  
488 2002). Because several alternatives to ammonium sulphate are readily available and  
489 cost-effective, replacing it by one of these, at least on soils of pH 7.0 or higher (and  
490 perhaps also on soils in the pH range 6.5 – 7.0) is a relatively easy change in  
491 agronomic practice that would make a significant contribution to reducing NH<sub>3</sub>  
492 emissions in many countries as required for compliance with the Gothenburg  
493 Convention.

494

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499

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733

734 **Table legends**

735 Table 1. Emission factors (EFs) for ammonium sulphate, urea and calcium  
736 ammonium nitrate (CAN) from EEA (2019). Ammonia emitted expressed as g NH<sub>3</sub>  
737 per kg N applied (upper part of Table) and as NH<sub>3</sub>-N emitted as percentage of N  
738 applied (lower part of Table).

739 Table 2. Soil pH of UK agricultural soils. Based on > 1,500,000 samples analysed  
740 over the 10-year period 2009/10 to 2018/19, as reported by PAAG (2019).

741 Table 3. Estimation of NH<sub>3</sub> emission from application of ammonium sulphate as an S  
742 source to soils of pH >7.0 and < 7.0 and potential decrease from replacing the N  
743 supplied from ammonium sulphate by calcium ammonium nitrate (CAN). Calculated  
744 for a unit 1 kt ammonium sulphate.

745 Table 4. Consumption of ammonium sulphate by country in 2017, kt product. Data  
746 from IFA (2020).

747 Table 5. Percentage ammonia emission reductions required by EU Member States  
748 and the UK to meet 2020 and 2030 emission reduction commitments. Based on  
749 emissions in 2018. Data from EEA (2020b).

750 Supplementary Table 1. Ammonia losses from ammonium sulphate: measurements  
751 under laboratory conditions.

752 Supplementary Table 2. Ammonia losses from ammonium sulphate: measurements  
753 under field conditions.

754

755 **Figure legends**

756 Figure 1. Influence of soil pH on NH<sub>3</sub> emission from ammonium sulphate. Emission  
757 from urea included, for comparison, if included in reviewed literature article. Data  
758 from laboratory experiments.

759 Figure 2. Influence of soil pH on NH<sub>3</sub> emission from ammonium sulphate. Emission  
760 from urea included, for comparison, if included in reviewed literature article. Data  
761 from field experiments.

762 Figure 3. Topsoil pH (in water) in croplands within the European Union. Derived from  
763 LUCAS 2015 topsoil survey, JRC Technical Report, EU, 2020 (Jones *et al*, 2020).

765 Table 1. Emission factors (EFs) for ammonium sulphate, urea and calcium  
 766 ammonium nitrate (CAN) from EEA (2019). Ammonia emitted expressed as g NH<sub>3</sub>  
 767 per kg N applied (upper part of Table) and as NH<sub>3</sub>-N emitted as percentage of N  
 768 applied (lower part of Table).

769

N fertilizer form	Climate					
	Cool		Temperate		Warm	
	Soil pH					
	≤ 7.0	>7.0	≤ 7.0	>7.0	≤ 7.0	>7.0
	g NH <sub>3</sub> per kg N applied					
Ammonium sulphate	90	165	92	170	115	212
Urea	155	164	159	168	198	210
CAN	8	17	8	17	10	21
	NH <sub>3</sub> -N as % of N applied					
Ammonium sulphate	7.4	13.6	7.6	14.0	9.5	17.5
Urea	12.8	13.4	13.1	13.8	16.3	17.3
CAN	0.7	1.4	0.7	1.4	0.8	1.7

770

772 Table 2. Soil pH of UK agricultural soils. Based on > 1,500,000 samples analysed  
 773 over the 10-year period 2009/10 to 2018/19, as reported by PAAG (2019).

774

	Percentage of samples in class – 10-year average							
	pH							
	<5.00	5.00-5.49	5.50-5.99	6.00-6.49	6.50-6.99	7.00-7.49	7.50-7.99	>8.00
Arable	1	5	13	21	21	16	16	8
Grass	2	18	36	26	11	4	3	1

775

777 Table 3. Estimation of NH<sub>3</sub> emission from application of ammonium sulphate as an S  
 778 source to soils of pH >7.0 and < 7.0 and potential decrease from replacing the N  
 779 supplied from ammonium sulphate by calcium ammonium nitrate (CAN). Calculated  
 780 for a unit 1 kt ammonium sulphate.

781

Item	Unit	Climate			
		Temperate		Warm	
Soil pH <sub>aq</sub>		> 7.0	< 7.0	> 7.0	> 7.0
Per kt ammonium sulphate					
Nitrogen (N) content of 1 kt ammonium sulphate	t N	210	210	210	210
NH <sub>3</sub> emission factor for ammonium sulphate on soils of different pH (EEA 2019)	g NH <sub>3</sub> per kg N	170	92	212	115
Total potential emission of NH <sub>3</sub> from use of ammonium sulphate to supply required nutrient sulphur	t NH <sub>3</sub>	35.7	19.3	44.5	24.2
NH <sub>3</sub> emission factor for CAN on soils of different pH (EEA 2019)	g NH <sub>3</sub> per kg N	17	8	21	10
Total potential emission of NH <sub>3</sub> from CAN used as replacement for the N from ammonium sulphate	t NH <sub>3</sub>	3.6	1.7	4.4	2.1
NH <sub>3</sub> emission reduction from replacing ammonium sulphate with CAN plus a zero-N sulphur source	t NH <sub>3</sub>	32.1	17.6	40.1	22.1
Potential percent reduction in NH <sub>3</sub> emissions from replacement of ammonium sulphate by CAN	%	90.0	91.3	90.1	91.3

782

783

785 Table 4. Consumption of ammonium sulphate by country in 2017, kt product. Data  
786 from IFA (2020).

787

<b>Country</b>	<b>kt product</b>
Brazil	1,999
U.S.A.	1,919
Indonesia	1,840
Mexico	1,096
Viet Nam	1,052
Canada	823
Malaysia	745
Turkey	727
Philippines	583
India	563
Thailand	526
Germany	510
Ukraine	462
Australia	424
Spain	348
China	311
Japan	278
Russian Federation	271
Peru	250
United Kingdom	238
Egypt	231
Lithuania	215

788



790 **Table 5. Percentage ammonia emission reductions required by EU Member**  
 791 **States and the UK to meet 2020 and 2030 emission reduction commitments.**  
 792 **Based on emissions in 2018. Data from EEA (2020b)**

793

	<b>2020</b>	<b>2030</b>
Austria	X	XX
Belgium	□	X
Bulgaria	□	X
Croatia	□	X
Cyprus	X	XX
Czechia	□	XX
Denmark	XX	XX
Estonia	□	□
Finland	X	X
France	X	XX
Germany	X	XX
Greece	□	□
Hungary	X	XXX
Ireland	X	X
Italy	□	X
Latvia	X	X
Lithuania	XX	XX
Luxembourg	□	XX
Malta	□	□
Netherlands	□	X
Poland	□	XX
Portugal	□	X
Romania	□	XX
Slovakia	□	XX
Slovenia	□	X
Spain	X	XX
Sweden	X	X
United Kingdom	X	XX

794

□	Current emission levels below the emission reduction commitment
X	Emission reduction needed by less than 10 % from current levels
XX	Emission reduction needed by 10 % to 30 % from current levels
XXX	Emission reduction needed by 30 % to 50 % from current levels

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