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1 Incineration of Aviary Manure: the Case Studies of Poultry Litter 2 and Laying Hens Manure

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22

23 Abstract

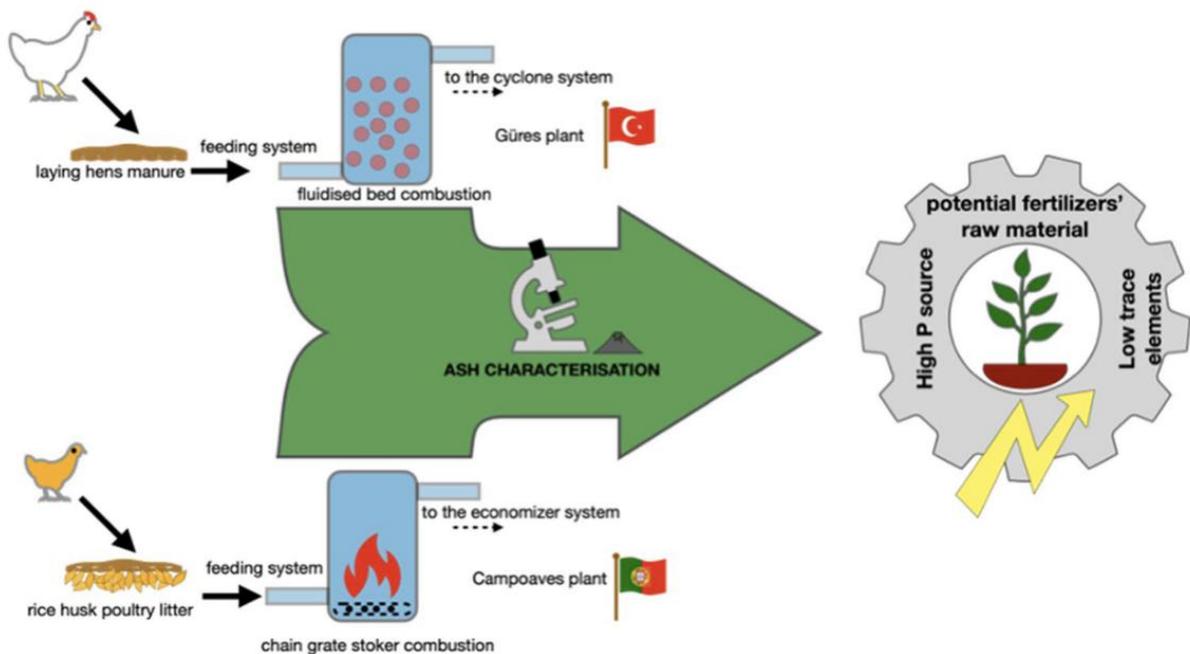
24

25 The industrial incineration of aviary manure is still far from the concept of using its ash residuals
26 for nutrient uptake by plants, and most of these materials are landfilled under futile fixed cost.
27 Aviary manure includes poultry litter mixed with different aviary bedding materials or laying hens
28 manure, which may be burned using other incineration technologies and conditions. This study
29 aims to determine the comparative characterisation of P-rich ash residues sampled at Güres
30 Energy (Turkey) fluidised bed combustion of laying hens manure and at Campoaves (Portugal)

31 chain grate stoker combustion of rice husk poultry litter. The effect of different fuels and
32 different combustion systems on P speciation in ash was investigated: the characterisation of
33 global samples (bottom ash (BA), economiser fly ash (FAECO), cyclone fly ash (FACYC)) and
34 respective size-fractions were done chemically (proximate and elemental analysis by X-ray
35 fluorescence – XRF – and Inductively Coupled Plasma Mass Spectroscopy – ICP-MS),
36 morphologically (detailed imaging and X-ray microanalysis by Scanning Electron
37 Microscopy–Energy-Dispersive X-ray spectrometry – SEM–EDS) and mineralogically (X-ray
38 diffraction – XRD). Phosphorus was detected in Güres ashes mainly as hydroxyapatite crystals
39 alongside CaCO_3 relics and CaO . At the same time, Campoaves ash fractions contained P also as
40 Na-K-Mg phosphate and significant amounts of rice husk relics, including unburnt char and silica
41 phases. Both Güres and Campoaves ashes are complex, but the combustion of aviary manure
42 under these setting conditions appears to be promising for P recovery owing to their high P
43 content and limited trace elements respecting the limitations of EU legislation for fertilisers
44 applications.

45 Graphical abstract

46



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53 **Statement of novelty**

54 This paper compares two sub-categories of incinerated aviary manure (rice husk poultry litter ash
55 and laying hens manure ash) under two different combustion systems (fluidised bed gasifier and
56 chain grate stoker) in terms of chemical, mineralogical and morphological characterisation. The
57 novelty lies in studying the effect of fuel and combustion systems on the P speciation and possible
58 use in the fertiliser industry. The results showed the trace element contents in acid leachate
59 comply with EU fertilisers regulations: this paves the way for future study about plant availability
60 tests and eventual direct application in agriculture as fertilisers.

61

62

63 **Keywords**

64 Phosphorus; Incineration; Ash; Characterisation; Aviary manure; Sustainability

65

66 **Introduction**

67

68 Phosphorus is a vital micronutrient, mostly occurring as phosphate (PO_4^{3-}), for food and crop
69 production that is mainly obtained from phosphate rocks mining, from which P-bearing minerals
70 (e.g. apatite) are concentrated and then processed to obtain fertilisers [1].

71 The demand for P-based fertilisers is expected to double by 2050 due to population growth [2].
72 Still, the concentration of phosphate rock deposits in a few countries and markets instability and
73 uncertainty could lead to eventual spikes in the market price affecting the fertilisers industry,
74 which covers up to 80 % of the market related to P [3, 4]. This situation led the European
75 Commission to include phosphate rocks on the list of the 20 most critical raw materials to
76 stimulate proper management of the resource from farmers, agricultural industries and
77 policymakers, and P-recycling [5].

78 On the other hand, it has to be considered that only less than 20 % of the P used in the food and
79 feed production sectors are anthropogenically consumed [6]. Meaning that we must focus on the
80 significant losses (primarily associated with meat production and crop farming [7]). Among the
81 principal waste streams, animal manure represents the most important secondary source of P in
82 order of importance under the European Commission [8,9].

83 In particular, aviary manure (e.g. poultry litter and laying hens manure) is a promising secondary
84 source of P [10] since one-third of the P is digested during the bird life cycle, and the remaining P
85 is excreted in manure [11]. Additionally, the amount of manure being produced will increase since
86 poultry meat production alone already covers approximately 35% of global meat production,
87 owing to an increase of more than 12 fold over the last 50 years [12]. In the past, farmers already
88 used aviary manure as a substitute for chemical fertilisers in croplands and soil amendments [12–
89 14]. Still, it has been exclusively applied to the local farms due to its high density/volume ratio
90 leading to the high cost of transportation to incinerators [15].

91 The manure composition is variable and is based on the type of housing system, diet and manure
92 handling (e.g., bedding material, storage, reuse frequency). However, apart from P, it also contains
93 other plant macronutrients such as N and K, which together seem readily plant available.
94 However, the latter may cause plant stress (also known as plant burning) due to their excessive
95 concentration in the soil [16, 17]. Alongside it, there are issues related to the presence of
96 pathogenic microorganisms, ammonia emissions and the eventual eutrophication of surface and
97 ground waterways via nutrient runoff [6, 13, 18–21] that could jeopardise the environment:
98 specific limits about nutrient contents in are set in waste streams to preserve a proper ecological
99 condition (e.g., Sewage Sludge Directive 86/278/ECC, Water Framework Directive 2000/60/EC,
100 Nitrates Directive 91/676/EEC) [6].

101 The incineration of poultry manure effectively reduces the waste volume to alleviate the disposal
102 problem, avoids the leaching of nutrients, eliminate pathogens and toxic organic substances, and
103 evaporate nitrogen. The P-rich ash residue may be usable as a possible substitute of phosphate
104 rock for the production of fertilisers with a low concentration of rare earth elements [2, 21].

105 The incineration of poultry litter on farms has been incentivised across the EU since 2014 to
106 produce green energy with the economic advantage of a shorter pay-back period [19][22].
107 However, there were some drawbacks due to using a high moisture fuel with low energy value,
108 variable chemical composition with increased contents of S, N and Cl – being considered in the
109 category of agricultural biomass [23] – which can lead to metal corrosion. Finally, high ash content
110 may lead to deposit formation such as slagging and fouling due to the low-temperature melting
111 materials formed under the presence of elements such as Si, K [19, 21]. In addition, aviary manure
112 ash has been impeached by legal limits regarding elements such as Cu and Zn [2]. Thus, as a
113 consequence, despite its qualities as an organic fertiliser and P-Ca source in poultry feeds [24], it is
114 treated as a residue and not as a by-product and is usually landfilled [25].

115 Considering the lack of information regarding solutions for aviary manure ash, it seems pertinent
116 to promote aviary manure ash for different possible applications. The characterisation of different
117 types of aviary manure ash in terms of elemental and mineral composition for the description of P
118 speciation has been thus undertaken. Leaching tests were used then to estimate the P
119 extractability of the final potential for nutrient reuse [26].

120 However, it would be essential to explain the broad P chemical speciation after undergoing
121 different thermal reactions to form dissolved salts and mineralised materials (e.g.,
122 hydroxyapatite). Following this perspective, developing strategies for recovering and valorising P
123 (as critical raw material to be kept in the value chain) represents a pillar in managing agricultural
124 waste within a circular economy [20].

125 Therefore, this research aims to identify the ash specificities depending on the aviary manure,
126 incineration technologies and sampling locations. For this purpose, detailed characterisation by a
127 combination of multiple techniques was carried on aviary ash from two different sub-categories of
128 aviary production after the combustion: ash from the chain grate stoker incineration of rice husk
129 poultry litter and, and ash from fluidised bed combustion of laying hens manure.

130

131

132 **Materials and Methods**

133

134 *Sampling location*

135

136 The fuel and ash samples were collected at the incinerators of Campoaves (Figueira da Foz,
137 Portugal; hereinafter referred to as “CA”) and Güres Energy (Manisa, Turkey; referred to as “GU”).
138 These two incinerators show fundamental concept differences between them regarding the fuels
139 and the combustion technologies. The two produced ash types consequently pose contrasted
140 challenges for P-recovery and the utilisation of residues after P-recovering:

141 (i) at Campoaves (CA), the manure is a rice husk poultry litter

142 (referred to as “RHPL”) composed of poultry excreta mixed with the rice husks used as aviary
143 bedding from the surrounding rice fields. The fuel, however, is composed of woodchips and RHPL.
144 These components may be in the form of thick crusts (5-10 cm) of rice husk (RH) cemented by
145 poultry excreta formed in the aviary bedding top layers and as loose RH with some faeces from the
146 deepest layers of the aviary bedding. Before incineration, the RHPL is pre-dried, and its

147 combustion is then made together with large (approx. 5 cm) woodchips in a chain grain stoker for
148 several minutes and a temperature set to reach 1000 °C to comply with the directive 2000/76/EC
149 [27] aimed for the removal of pathogens (Fig. 1A).

150 (ii) At Güres (GU), where eggs are produced, the manure is coming from laying hens kept in
151 cages (no bedding) and composed of a mixture of excreta, broken eggshells and feathers (laying
152 hens manure, referred to as "LHM"). At Güres Energy, the manure is dried, and the moisture is
153 reduced to 20 wt. %. Before combustion, the LHM mixed with biomass is firstly gasified and then
154 burnt, for ca. 2 s at 850-950 °C, inside a fluidised bed reactor. In the combustion chamber, quartz
155 (SiO₂) sand is initially used as a solid heat carrier for furnace heat distribution, and then calcite
156 (CaCO₃) sand is used for sulfur capture (Fig. 1B).

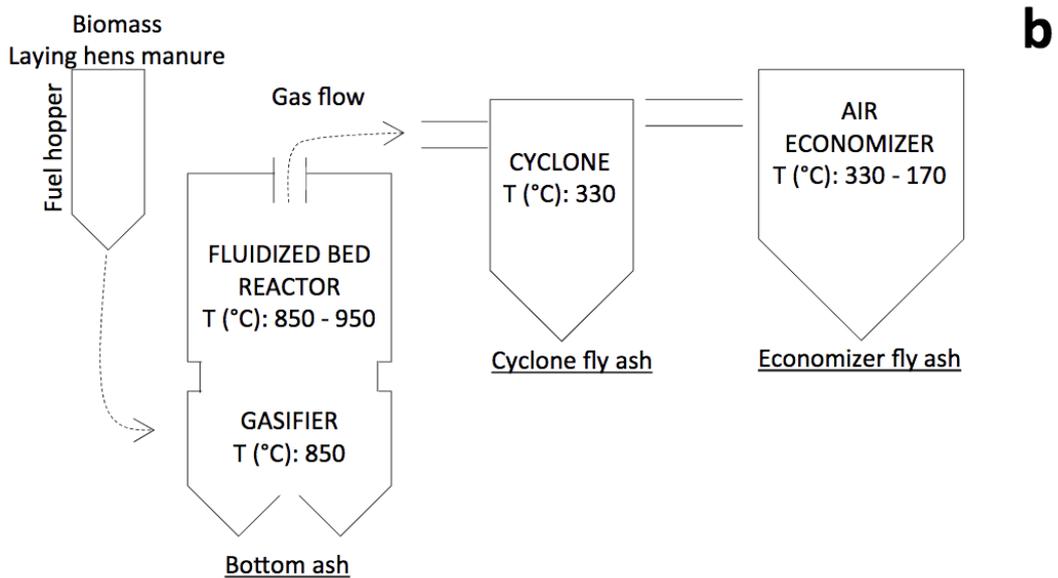
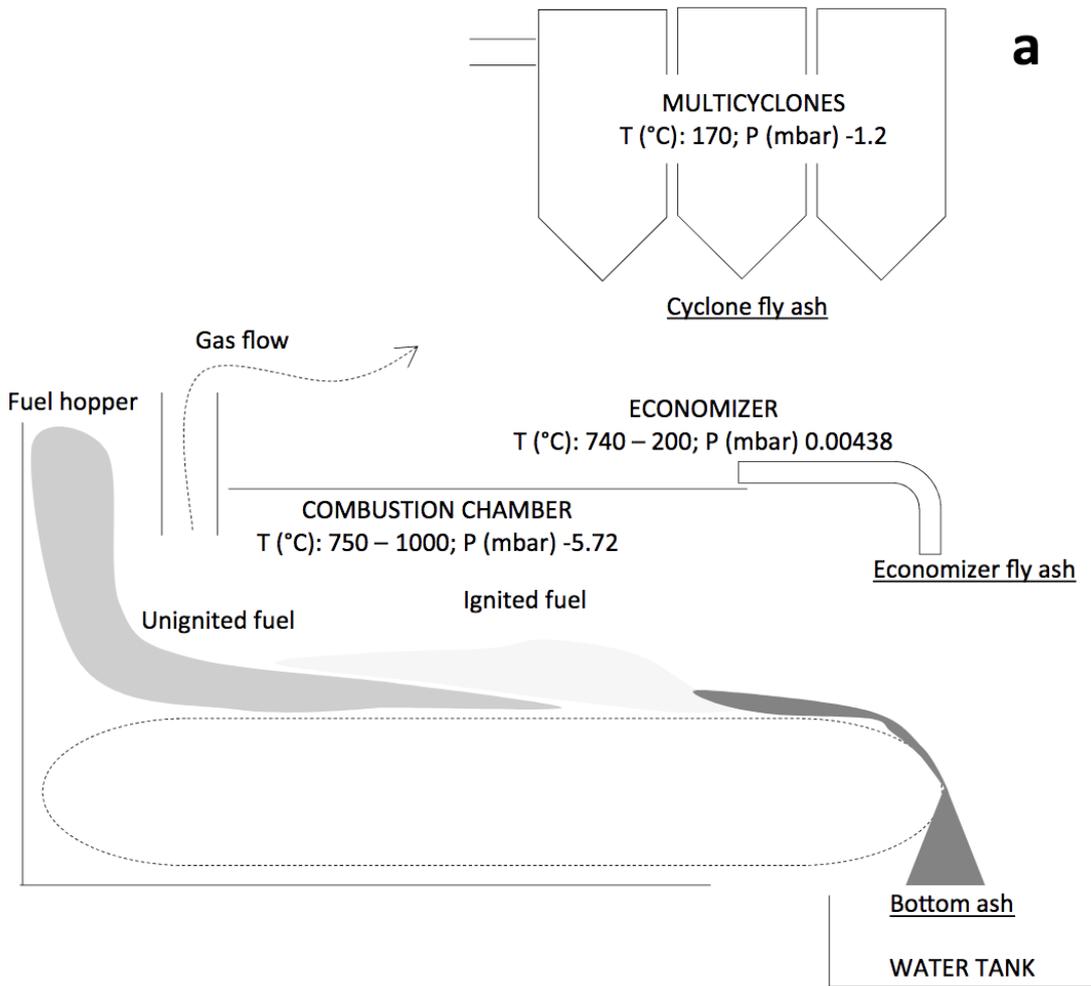
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158 *Samples*

159

160 At Campoaves, the raw RHPL was randomly sampled directly from different parts and depths of
161 the pile using a plastic shovel and then mixed to ensure the sampling representability. Specific
162 portions of droppings crusts and loose poultry litter were also collected to obtain rich and poor
163 droppings fractions. All samples were immediately stored in thick plastic bags and analysed on
164 that same day.

165 Simultaneously, global ash samples from three different spots were also collected: bottom ash
166 (BA) directly from the exit of the water tank; economiser fly ash (FAECO) from the economiser ash
167 hopper adjoining the combustion chamber; cyclone fly ash (FACYC) from the multi-cyclone
168 hopper. The samples were stored in thick plastic bags and were oven-dried at 50 °C the same day
169 until reaching a constant weight. Manually, they were split through the coning method after
170 getting 100 g samples using a riffing splitter. Finally, one of the 100 g sub-samples was divided
171 into 12.5 g sub-samples via a rotary sample divisor combined with a vibratory feeder (Retsch PT
172 100 + DR 100, Hann, Germany) [28]. Workers at Güres Group sampled fresh and undried LHM
173 after being conveyed from the laying hens building. BA, FACYC and FAECO samples were collected
174 from the respective hoppers and dried and sorted as mentioned for Campoaves samples.



175

176 Figure 1. Schematic process diagram of the combustion systems: A) Chain grate stoker at
 177 "Campoaves" (Figueira da Foz, Portugal); B) Gasifier and fluidised bed reactor at "Güres Energy"
 178 (Izmir, Turkey).

179

180 *Size-determination via sieving*

181

182 The RHPL sampled from Campoaves (crusts not included) was manually sieved using 5 and 10
183 mesh sieves (4 mm and 2 mm, respectively). Different size fractions were obtained from the global
184 ash samples of Güres. For this purpose, dry sieving was carried using a sieve agitator (Retsch
185 AS200, Hann, Germany) in 2 rounds of 10 min agitation at 70% vibration amplitude (as an
186 adaptation according to DS/EN 15149-2 [29]), and a column of sieves of 150 µm, 75 µm, 45 µm
187 and 25 µm for FACYC and FAECO sample, while for BA sample a different column of sieves was
188 used: 4 mm, 2 mm, 1 mm, 0.5 mm, 250 µm, 125 µm and 63 µm. Size-fractions were not obtained
189 from Campoaves ashes due to particles agglomeration generating false coarse particles and
190 reducing the amount and type of fine particles.

191

192 *Proximate and elemental analysis and loss on ignition (LOI)*

193

194 The proximate analyses were made for both Campoaves and Güres (here also for the different size
195 fractions) samples to determine moisture, volatile matter, ash, and the fixed carbon calculation.
196 For each test, 1 g ± 0.1 of samples was weighed on a laboratory balance (Sartorius Analytic,
197 Göttingen, Germany), and all global ash samples and the size-fraction samples >75 µm were
198 grounded with a mortar to pass the 200 mesh (75 µm) sieve. The moisture content was measured
199 in compliance with ISO 11722 [30]. The samples were oven-heated at 105 °C until reaching a
200 constant weight in a Carbolite Furnace with nitrogen flow and then cooled in a desiccator to reach
201 room temperature (25 °C) and weighed. The ash and volatile matter content were measured
202 according to ISO 1171 [31] and ISO 562 [32]. For the ash determination, the samples were heated
203 inside crucibles at 815 °C until reaching a constant weight in a muffle furnace (47900-Thermolyne).
204 After that, the ash was cooled in a desiccator to reach room temperature (25 °C) and weighed. The
205 samples were heated inside crucibles at 900 °C for 7 minutes in a muffle furnace to determine the
206 volatile matter (47900-Thermolyne). After that, the ash was cooled in a desiccator and weighed.
207 Major oxides, Loss on Ignition (LOI) and total C and S were determined at Bureau Veritas
208 Commodities Canada Ltd. (Vancouver, Canada). Major oxides were determined by X-Ray
209 Fluorescence (XRF) after samples fusion with lithium tetraborate/metaborate and casting into
210 glass discs, and LOI was determined at 1000 °C.

211

212 *Total Phosphorus determination, minor and trace elements*

213

214 Spectrophotometry measurements for the quantification of total P were made both for
215 Campoaves and Güres samples using QE65000 spectrophotometer (Ocean Optics) both at the
216 laboratories of the University of Brescia (Italy) and University Politecnica of Bucharest (Romania),
217 respectively. The measures were made using polystyrene cuvette (1 cm optical path) and
218 evaluating the P wavelength (650 nm) in the visible domain (400 nm – 750 nm). The method
219 followed the Romanian standardised method: STAS 9621-74 “COKE and SEMICOKE. Determination
220 of phosphorus content”, point 3, colourimetric method, variant II [33].

221 For all minor elements (0.1 %<wt. %<1 %), including Cu, Zn, Sr, Ba and some trace elements
222 (wt.%<0.1%) including Mo, Pb, Ni, As, Cd, Sb, Au and Hg, the ash samples were digested with aqua
223 regia (1:1:1 HNO₃:HCl:H₂O) followed by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)
224 analysis at Bureau Veritas Commodities Canada Ltd. (Vancouver, Canada). To determine elements
225 down to part per million level concentration in rocks, the analysis was made in the same
226 laboratory after the ashes were fused with lithium tetraborate/metaborate followed by ICP-MS
227 [34].

228

229 *Detailed imaging experiments by Scanning Electron Microscopy combined with X-ray microanalysis*
230 *(SEM-EDX) and optical microscopy*

231

232 The SEM-EDX analysis was carried from raw samples, i.e. without previous preparation, and
233 realised as petrographic analysis in polished blocks adapted according to ISO-7404-2 [35]. The
234 experiments were done at Centro de Materiais da Universidade do Porto (CEMUP) using an FEI
235 Quanta 400 FEG ESEM/EDAX Genesis X4M operated in low vacuum mode at 15 kV. The raw
236 samples were adhered to the mounting block with double-sided adhesive carbon tape. The
237 experiments were focused on the surface morphology via secondary electron detector mode (SE)
238 alternating with backscattered electron detection mode (BSE) for different phases identification.
239 For samples mounted on resin polished blocks, only the BSE mode was used to obtain detailed
240 imaging of the particles internal structure. In both cases, EDX semiquantitative analyses were
241 made in representative areas of the ash morphotypes. The optical microscopy analysis was carried
242 out following sample preparation and measurements according to international standards (ISO-

243 7404-2), methodology and specific classifications of the International Committee of Coal and
244 Organic Petrology. The experiments were done at University Politehnica of Bucharest (UPB-
245 CPMTE) using an Olympus BX51M optical microscope, with the possibility of transmitting the
246 image to a display with a CCD-1300QB model camera, in reflected and polarised light, glycerin
247 immersion and 500 X magnifications.

248

249 *Mineralogy by X-Ray Diffraction (XRD) analysis*

250

251 The XRD analysis was carried at the University of Brescia (Italy). Powder of global samples was
252 micronised and then analysed using an X'Pert PRO diffractometer (PANalytical, Malvern, UK)
253 equipped with a Cu K α anode (40 kV, 40 mA). The phases were determined using Philips X'Pert
254 software (associated with the open crystallography database (COD)).

255

256 **Results and Discussions**

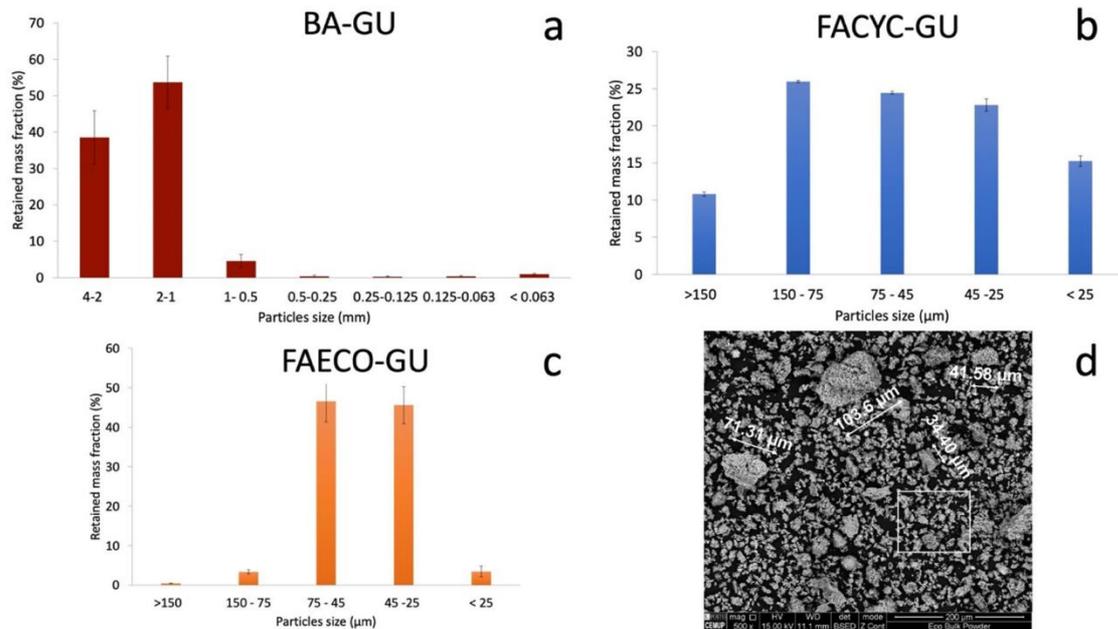
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258 *Sieving trials*

259

260 After one sieving trial with the 5 mesh sieve and another with the 10 mesh sieve with Campoaves
261 RHPL global sample, it was found that the 5 mesh sieve retains 23% of the material, while the 10
262 mesh sieve retains 46%.

263 The results of the granulometric distribution analysis carried by mechanical dry sieving for Güres
264 ash samples are shown in Figure 2. The BA-GU sample is mainly (90 %) composed of the 1-2 mm
265 and 2-4 mm size-fractions, which was confirmed during SEM experiments, while for FACYC-GU and
266 FAECO-GU samples, the size distribution has a Gaussian shape. However, as the SEM experiment
267 shows, sieving clog by small-size particles caused the overestimation of the 45-75 μm (e.g. Fig. 2D)
268 and 25-45 size-fractions of FACYC and FAECO.



269
270
271

272 Figure 2. Size distribution analysis via mechanical dry sieving: A, B, and C) distribution of mass
273 fraction (%) for Güres samples (number trials per each sample=5); D) SEM micrograph for FAECO-
274 GU showing a background of micrometric and submicrometric particles there were also retained
275 in the 325 mesh (45 µm) sieve due to sieve blinding (200×; BSE mode).

276

277 *Proximate Analysis*

278

279 The proximate analysis results of the fuel and the ash (BA, FAECO, FACYC) are presented in Table
280 1. Size-fractions are evaluated for the fuel in the case of Campoaves samples, meanwhile, for the
281 ash they are evaluated in the case of Güres samples. These data are also plotted on a ternary
282 diagram characterised by the comparison of three parameters for the proximate analysis (ash
283 content, volatile matter, fixed carbon; Fig. 3) originally for biomass-based materials [23].

Sample		Moisture	Ash	Volatile Matter	Fixed Carbon
		(%)	(d.b. wt. %)		
Güres					
Fuel	Global	27.63	26.14	43.19	3.04
BA	Global	0.11	80.63	9.59	9.78
	4-2 mm	0.14	79.77	9.29	10.94
	2-1 mm	0.16	81.76	10.12	8.12
	1-0.5 mm	0.20	77.87	12.04	10.09
	<0.5 mm	0.14	76.46	14.08	9.46
FACYC	Global	0.05	90.69	7.26	2.05
	> 150 µm	0.34	88.87	10.02	1.11
	150-75 µm	0.14	91.37	7.44	1.19
	75-45 µm	0.02	90.96	7.89	1.15
	45-25 µm	0.03	89.84	6.23	3.92
	< 25 µm	0.02	89.85	6.25	3.90
FAECO	Global	0.15	91.18	6.72	2.10
	> 75 µm	0.32	89.93	8.06	2.01
	75-45 µm	0.18	91.07	6.28	2.65
	45-25 µm	0.23	90.92	6.00	3.08
	< 25 µm	0.27	90.59	6.57	2.83
Campoaves					
Fuel	Global	37.42	11.20	49.64	11.93
	> 4 mm	30.84	9.65	51.67	11.45
	< 4 mm	26.86	9.24	51.27	12.25
	> 2 mm	27.74	10.57	50.28	11.92
	< 2 mm	47.78	17.29	35.74	19.74
BA	Global	9.50	45.14	19.35	8.29
FAECO	Global	3.54	57.25	11.61	3.92
FACYC	Global	3.18	61.91	9.71	1.57

All the values referred to Ash, Volatile Matter and Fixed Carbon are normalized with respect to one another reflecting data shown in the ternary plots in Fig. 3. (d.b. = dry basis)

284

285

286 Table 1 Results of proximate analysis and fixed carbon calculation from Güres and Campoaves ash
287 samples.

288

289 Considering the fuel (RHPL and LHM) results, only the volatile matter values are similar for
290 Campoaves and Güres global samples. Campoaves fuel contains higher moisture amounts and
291 fixed carbon value (approximately four times), while Güres fuel contains two and a half more ash.

292 These results explain why the fluidised bed combustion may be the technology chosen to burn
293 LHM, while RHPL can be burned in a chain grate stoker.

294 Significant differences characterise moisture, ash, volatile matter and fixed carbon among the size
295 fractions of Campoaves RHPL. For a trial using the 5 mesh sieve, the fraction >4 mm, corresponds
296 to 23 % of RHPL and contains approximately 25 % more moisture than the fine fraction. However,
297 for a trial using the 10 mesh sieve, the fraction passing this sieve (<2 mm) corresponds to 54 % of
298 the RHPL, and the coarser fraction (>2 mm) contains approximately double of the moisture, two
299 times more ash and fixed carbon, and 1.5 times less volatile matter.

300 Such results are interesting to save energy with fuel drying, improve the incineration efficiency
301 and obtain two or more ash categories, as sieving sand-size particles is an efficient and
302 inexpensive separation method.

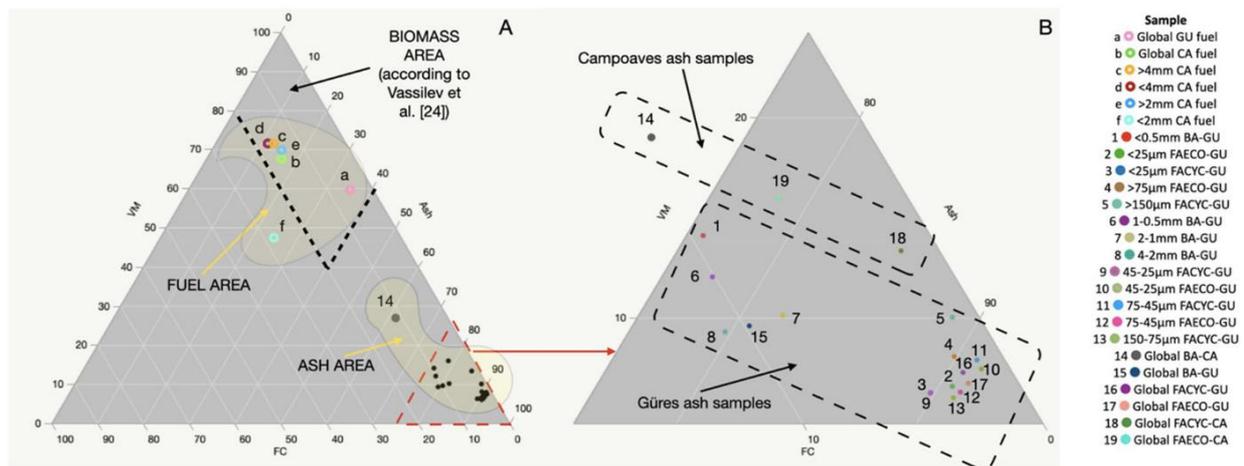
303 The amount of moisture in Güres global ash samples and respective size-fractions is residual
304 (<0.34 %), while it is almost 10% in the case of Campoaves BA. Regarding the ash content, Güres
305 FAECO and FACYC samples and respective size fractions contain approximately 90 % ash. In
306 comparison, the ash percentage in Güres BA and respective size-fractions range between 76 % and
307 82 %, compensated by a higher rate of volatile matter and fixed carbon, most probably related to
308 CaCO₃ sand relics decomposition during the analytical methods progress [36].

309 About Güres ashes, Campoaves ash global samples have much higher moisture percentages
310 (about 10 % in the BA-CA sample), lower ash content (between 45 and 62 %), and a volatile matter
311 content ranging between 10 and 19 %. However, the fixed carbon is similar to that of Güres global
312 samples. All these differences are related to the manure composition and technologies: rice husk
313 and wood chips contributing to higher volatile matter values in Campoaves ashes, the use of
314 CaCO₃ sand bed contributing to higher ash content at Güres. However, the high amount of
315 moisture and volatile matter found in the BA-CA sample are indicators of low-burning efficiency.

316 Vassilev et al. [24] reported that a classification based on a ternary diagram allows comparing
317 biomass and biomass ash based on their proximate analysis (ash, volatile matter and fixed
318 carbon). The RHPL and the LHM samples are plotted well inside the limits found by Vassilev et al.
319 [24] for biomass (on a dry basis - d.b.: ash <40 %, volatile matter >40 %, and fixed carbon <20 %).
320 However, Campoaves <2 mm, owing to its high volatile matter content and fixed carbon value (Fig.
321 3A), results out of the limit area.

322 In the case of the ash samples of the present study (Fig. 3), the dominant parameter here is the
323 ash content which ranges between 45 % and 91 % with low volatile matter (<20 %) and fixed
324 carbon (<11 %).

325 The BA-CA sample is the only ash sample plotted away from the other samples owing to its lower
326 ash content and higher volatile matter (Fig. 3 A). Zooming out the ternary diagram (Fig. 3 B), three
327 plotting areas can be noticed: the area of BA-GU sample and its size-fraction samples plotted
328 around 10 % FC and 70-80 % ash; the Güres fly ashes (FACYC-GU and FAECO-GU global and size-
329 fraction samples) with >89 % ash; and Campoaves fly ash samples (FAECO-CA, FACYC-CA), and
330 outside the zooming also BA-CA, with low fixed carbon values (<13 %) but broader volatile matter
331 and ash contents. Overall, the diagrams (Fig. 3 A and B) characterise very well the difference
332 between the fuel and respective ashes, the bottom ash and fly ash, and ashes from different fuels
333 and technologies.



334
335 Figure 3. A) Positions of ash samples in a classification system based on data from proximate
336 analysis; Dashed black lines are the limits of biomass in Vassilev et al. [24]. B) zoom of dashed red
337 area in "A". Abbreviations: VM, volatile matter; FC, fixed carbon. The parameters are all expressed
338 with d.b. wt.%. A ternary diagram was made with JMP software.

339 340 *Elemental Analysis*

341
342 The results of the major oxides determination for Güres and Campoaves ash samples are
343 presented in Table 2. These are similar to other concentrations reported for ash derived from the
344 incineration of animal by-products [26, 28, 37, 38]. However, the P₂O₅ concentrations of the ash
345 samples studied are within the range of mined phosphate rock grades, especially the medium-low

346 grade phosphate rocks [39, 40]]. For instance, they are lower than grades from the best
347 sedimentary ores from Morocco or Jordan, reaching 30 to 38 %. Grades in these latter deposits
348 increased during the last decade thanks to technological improvements (Steiner et al., 2015).

349 The major oxides analysis highlights fundamental differences between Campoaves and Güres, but
350 also between the BAs and respective FAs:

351 (1) the concentration of SiO_2 is much higher in Campoaves ashes due to the SiO_2 layer in the
352 rice husk used as poultry bedding, while the hens are kept inside cages at Güres;

353 (2) the concentration of CaO is approximately five times higher in Güres ashes since CaCO_3
354 sand is used to capture S in the fluidised bed chamber, and also due to eggshells;

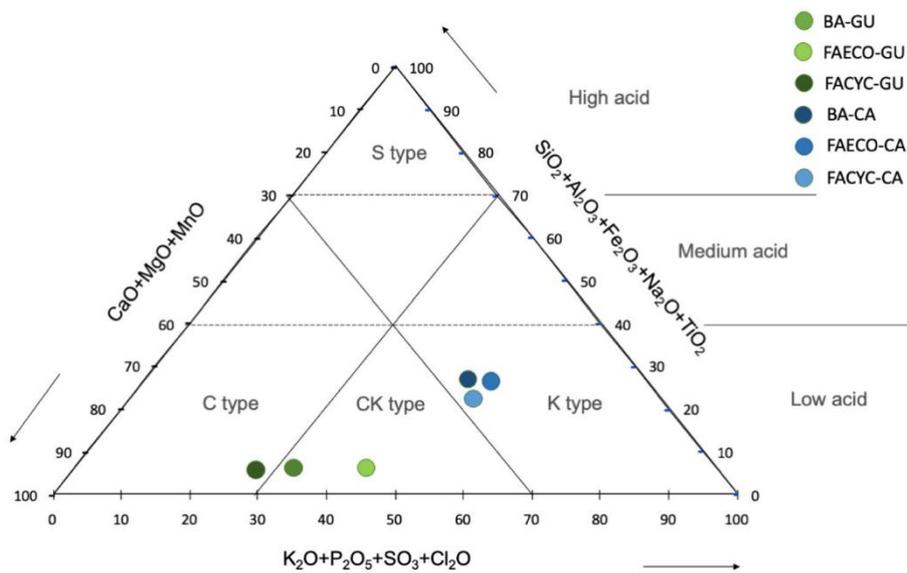
355 (3) the K and P oxides follow the concentration trends: $\text{BA} < \text{FAECO} < \text{FACYC}$ at Campoaves, and
356 $\text{BA} < \text{FACYC} < \text{FAECO}$ at Güres. This evolution is related to the position of each sampling location
357 (Fig. 1) since coarse particles tend to be collected firstly by the dust capture equipment. As the
358 flue gas cools, condensation reactions occur on finer particle surfaces. Campoaves rice husk relics
359 are the dominant particles of the ashes. In contrast, at Güres, coarse particles are mainly CaCO_3
360 sand particles more or less decomposed with (Ca-P-K-S)-rims developed on them, and in both
361 cases, the fine particles are composed of neo-formed morphotypes (or rims fragments) K- and P-
362 rich.

363 For both Campoaves and Güres samples, the BA samples' LOI and total C values are very high and
364 approximately double that in the FAECO and FACYC samples. The relatively low amount of P_2O_5 in
365 the BA may be related to the combustion efficiency in the case of Campoaves. In contrast, in the
366 case of Güres, it is related to combustion technology, i.e., the utilisation of a fluidised bed
367 composed of CaCO_3 .

368 Vassilev et al. [41] proposed a second classification for the materials derived from biomass to give
369 additional information on potential applications of the ash. For example, from the combustion
370 process perspective, it provides indications on how to deal with technological problems such as
371 corrosion, accumulation of materials inside the ducts (cloggings, foulings). This scheme was
372 developed for the present samples due to their biomass-based nature and incineration, which
373 yield similar features to ashes obtained after coal burning.

374 Figure 4 shows the Vassilev 's classification under three categories (C, S, K types). Campoaves
375 samples are close to the "K-type" typical of materials containing phosphates, sulphates, chlorides
376 and amorphous material. They have alkaline pH and water-soluble components (Cl, K, Na, Ca) that
377 indicate they could be suitable soil improvers in acidic soils. On the other hand, the constituents

378 have low-T melting that can affect biomass processing. Güres samples, instead, are located in an
 379 area shared between C-type and CK-type, characteristic of Ca-bearing minerals. They have an
 380 alkaline pH with possible low melting T compounds during combustion, so they should be taken
 381 into account for the constant deposition of material on the internal surface of ducts [42].
 382 Both Güres and Campoaves samples are far from the S type area, typical of more acidic materials
 383 which consist of detrital minerals (e.g., silicates) characterised by higher stability during
 384 weathering and chemical elements less mobile in water.
 385



386
 387
 388 Figure 4. Ash analysis under the classification method reported by Vassilev et al. for biomass
 389 materials [41]. All the parameters are expressed in wt.%. Ternary diagram was made via XLSTAT
 390 plug-in for Microsoft Excel.
 391

	Campoaves*			Güres		
	BA	FAECO	FACYC	BA	FACYC	FAECO
SiO ₂	11.2	14.5	12.7	2.1	2.4	1.6
Al ₂ O ₃	0.7	0.8	1	0.3	0.3	0.3
Fe ₂ O ₃	0.7	0.7	0.9	0.4	0.5	0.7
CaO	9.9	10.3	12.3	48.3	47.7	36.2
MgO	5.4	5.8	8.2	3.1	5.6	6.3
Na ₂ O	2.5	2.9	3.3	1.3	2.1	2.5
K ₂ O	14.4	> 15	> 15	6.5	6.8	12.2
MnO	0.3	0.3	0.4	0.1	0.2	0.2
TiO ₂	0.04	0.05	0.06	0.03	0.04	0.03
P ₂ O ₅	12.8	13.3	17.6	9.3	17.5	17
SO ₃	2	8.7	6.9	4.7	4	8
Cr ₂ O ₃	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	<0.01	0.03	0.03	<0.01	<0.01	<0.01
Sr	<0.002	0.009	0.017	0.051	0.047	0.053
LOI	40.7	22.1	17.2	22.8	12.1	14
C _t	21.6	15.1	10	5	2.2	1.9
S _t	1	3.1	2.6	1.9	1.6	2.8

Major elements determined with X-ray fluorescence analysis on fused lithium tetraborate/metaborate discs

*Campoaves 2nd sampling (14Jun2019); LOI—loss on ignition; Ct—total carbon; St—total sulphur. All the value are expressed in wt%

392

393

394

395 Table 2. Elemental composition of laying hens manure ash from Güres (BA, FAECO, FACYC) and
 396 rice husk poultry litter ash from Campoaves (BA, FAECO, FACYC). Major elements determined with
 397 X-ray fluorescence analysis on fused lithium tetraborate/metaborate discs.

398

399 *Total Phosphorus determination, minor and trace elements*

400

401 Table 3 lists the results of Total P and trace elements determination. The P-trend is the same
 402 found for P₂O₅, i.e., P is more concentrated in the fly ashes, but the increase downward the flue
 403 gas stream is not evident in the case of Güres fly ashes. However, the values are comparable with
 404 the P content in medium-low grade phosphate rocks [33,34].

405 Most of the elements determined by ICP-MS are present at low concentrations. For example, the
 406 sum of total Rare Earth Elements plus yttrium (REE+Y) ranges between 21 ppm for the FAECO-GU
 407 sample and 7 ppm for FACYC-CA. The higher REE+Y and Th and U concentration on the Campoaves

408 samples may be related to the rice husk used for the bedding [43–46] since the fertilisers used on
409 rice fields are enriched in REE, U and Th from the phosphate rocks.

410 Some elements such as Cu, Zn, Ba, Rb, Sr are present in higher concentrations with contents up to
411 2516 ppm in the case of Zn. Meanwhile, many elements (the exceptions are W and REE+Y) are
412 present in higher concentrations in the fly ashes. Some chemical elements have their
413 concentration increasing in the stream downwards due to their volatilisation and condensation
414 when the gas cools (e.g., Se) and their occurrence as fine particles.

415

		Campoaves			Güres		
		BA	FAECO	FACYC	BA	FACYC	FAECO
*Colorimetry (wt.%)	*TP	4.4	5.2	7.8	3.8	8	7.9
Lithium tetraborate/ metaborate fusion, ICP-MS (ppm)	Ba	133	155	190	39	77	80
	Be	<1	<1	<1	<1	<1	<1
	Co	2.6	3.2	4.4	4.3	5.1	7.9
	Cs	0.3	1.0	0.9	<0.1	<0.1	0.8
	Ga	0.9	1.1	1.1	<0.5	<0.5	<0.5
	Hf	0.3	0.5	0.4	0.1	0.3	0.2
	Nb	1.1	0.6	1.0	0.2	0.3	0.3
	Rb	69	149	129	40	34	93
	Sn	<1	2	2	<1	<1	<1
	Sr	123	138	200	753	652	773
	Ta	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Th	0.8	1.0	1.1	0.3	0.2	0.4
	U	29	32	35	0.6	0.7	1.1
	V	36	30	42	<8	<8	<8
	W	4.7	2.2	3.7	<0.5	<0.5	6
	Zr	15	19	18	5	12	5
	La	2.6	2.8	3.4	1.5	1.8	1.4
	Ce	3.8	4.5	5.0	1.8	2.0	1.9
	Pr	0.4	0.5	0.6	0.2	0.2	0.2
	Nd	1.8	2.1	2.2	0.9	0.9	1.0
	Sm	0.3	0.4	0.4	0.1	0.2	0.2
	Eu	0.1	0.1	0.1	0	0	0
	Gd	0.3	0.4	0.5	0.2	0.2	0.2
	Tb	0.1	0.1	0.1	0	0	0
	Dy	0.4	0.4	0.5	0.2	0.2	0.2
	Y	5.3	5.8	6.8	1.4	1.2	1.2
Ho	0.1	0.1	0.1	0	0	0	
Er	0.4	0.4	0.5	0.1	0.1	0.1	
Tm	0.1	0.1	0.1	<0.01	0	0	
Yb	0.7	0.8	0.9	0.1	0.1	0.1	
Lu	0.2	0.2	0.2	0	0	0	
	ΣREE + Y	16.5	18.5	21.4	6.6	7	6.5
Aqua Regia diges- tion (1:1:1 HNO ₃ :HCl:H ₂ O), ICP-MS (ppm)	Mo	18	19	25	6	9	13
	Cu	393	430	488	137	208	297
	Pb	0.7	3.9	3.9	0.4	1.4	4.2
	Zn	838	2516	2221	994	1120	2356
	Ni	32	37	54	19	20	42
	As	0.6	1.7	<0.5	3.1	1.4	6.1
	Cd	0.1	2.8	1.8	<0.1	0.7	2.0
	Sb	0.1	0.3	0.4	0.4	0.3	0.7
	Bi	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Ag	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Au (ppb)	<0.5	<0.5	0.6	1.8	0.5	1.2
	Hg	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
	Tl	<0.1	<0.1	<0.1	<0.1	<0.1	0.3
	Se	1.8	3.5	12.7	0.6	1.9	6.5

*TP stands for total phosphorus and the colorimetric method was done by UV-VIS spectrophotometer

416

417

418 Table 3. Total phosphorus determination and minor and trace composition of laying hens manure

419 ash from Güres (BA, FAECO, FACYC) and rice husk poultry litter ash from Campoaves (BA, FAECO,

420 FACYC).

421

422

423 *Ash Mineralogy and Morphology*

424

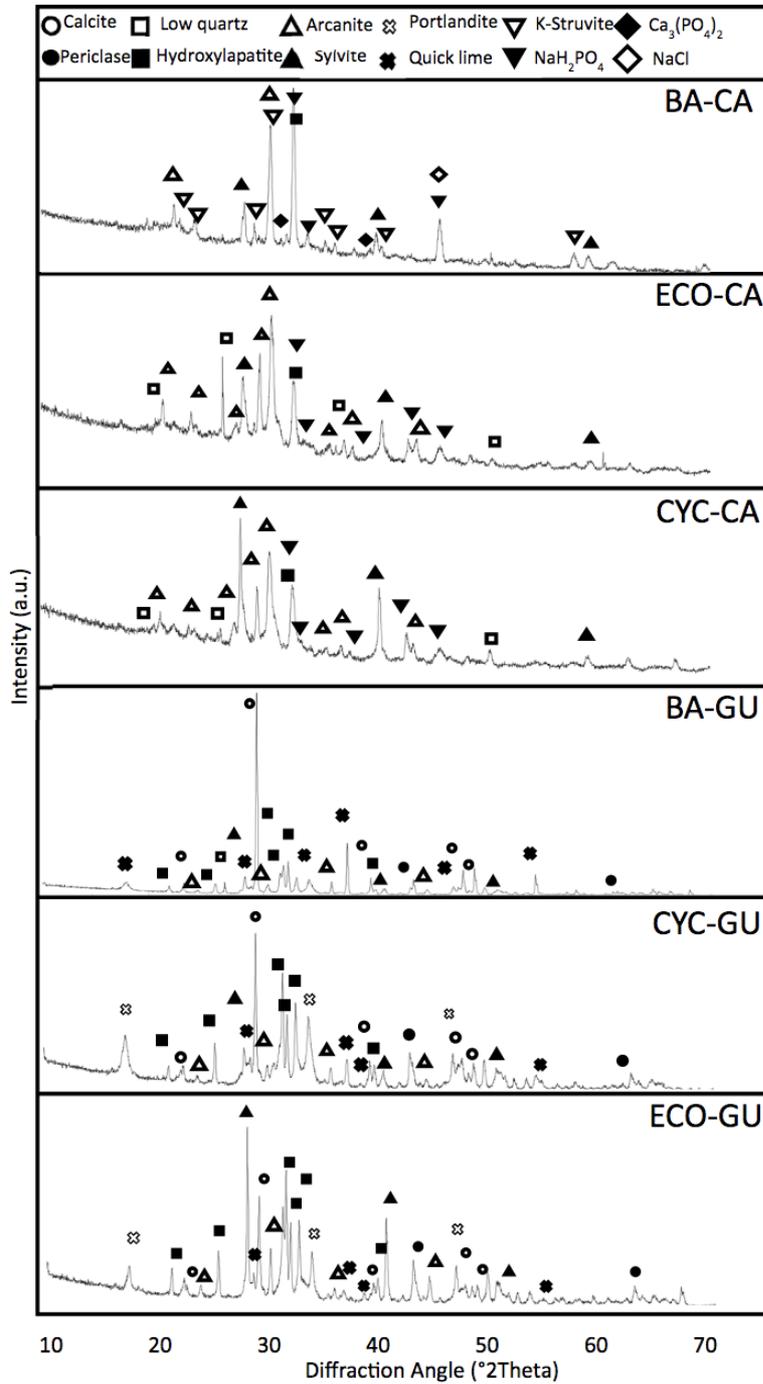
425 The results of the XRD analysis of the ash samples that include the determination of the
426 amorphous and crystalline phases are shown in Fig. 5. In Güres samples, the main crystalline
427 phases are those containing Ca, such as hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$), calcite (CaCO_3), calcium
428 hydroxide (CaOH) and lime (CaO). These Ca-crystalline phases, specifically of CaCO_3 sand, and
429 minor amounts of associated dolomite (MgCO_3), result in the fluidising bed during combustion for
430 the neutralisation of S. The Ca content is high because Ca it is an essential diet for the laying hens
431 and concentrates in the excrements. Consequently, phosphorus combined entirely with Ca and
432 formed hydroxyapatite. Meanwhile, other minor phases were also determined at Güres: a
433 complex form of Si-containing Na, Mg and K is also present, which is probably related to a small
434 fraction of quartz sand used during the early stages of the boiler heating that combine with
435 volatilised Na, Mg and K; Mg is oxidised mostly as periclase in the combustion chamber and is
436 carried by the flue gas; portlandite ($\text{Ca}(\text{OH})_2$), formed due to the decomposition of calcite (CaCO_3)
437 into calcium oxide (CaO) and the subsequent interaction of CaO with the moisture (H_2O); finally,
438 when comparing the different ashes from Güres one may see that sylvite (KCl) amount is higher in
439 the fly ash, this is a consequence of Cl, and K reaction as the flue gas cools leading to sylvite
440 condensation on the surface of the fly ash particles.

441

442 The mineralogical composition of Campoaves ashes is also quite different from Güres BA owing to
443 the reduced amount of Ca leading phosphates to form different compounds. Campoaves ashes are
444 mainly composed of amorphous materials, and the crystalline phases are primarily composed of
445 arcanite (K_2SO_4), hydroxyapatite and other forms of P-bearing minerals and sylvite (KCl). However,
446 these phases are not equally distributed among all Campoaves ashes. In the bottom ash, other
447 forms of P-bearing minerals (tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) and K-struvite ($\text{KMgPO}_4(6\text{H}_2\text{O})$))
448 equal hydroxyapatite, indicating a low-combustion efficiency since some of these phosphates may
449 have formed at atmospheric temperature.

450 The Na-phosphate (NaH_2PO_4) and sodium hydrogen phosphate hydrate [$\text{Na}_3\text{HP}_2\text{O}_7(\text{H}_2\text{O})$], also
451 found in Fiameni et al. [37], is a residual phase in BA but is significant in FAECO and FACYC
452 samples. Low-temperature (α -)quartz (probably a polymorph) and amorphous SiO_2 are expected
453 phases at Campoaves ashes since the aviary bedding is composed of rice husk that contains Si.

454 Meanwhile, K-sulfate is more dominant than sylvite at Campoaves due to a higher K to Cl ratio for
 455 a given amount of sulfate and because S is not captured inside the combustion chamber like in
 456 Güres. Finally, Mg-based phases (e.g., periclase) are absent in Campoaves, indicating that most Mg
 457 reacts with phosphates in the combustion chamber.
 458



459
 460
 461
 462 Figure 5. XRD spectra with the mineralogical identifications of Güres and Campoaves samples

463

464

465 *Detailed imaging experiments by Scanning Electron Microscopy combined with X-ray microanalysis*
466 *(SEM-EDS)*

467

468 Detailed imaging and X-ray microanalysis via SEM-EDS experiments allowed us to corroborate the
469 particle size distribution, chemical analyses and the phases determined by XRD.

470 SEM-EDS images for Campoaves are reported in figures 6-7-8-9, while for Gures are reported in
471 figures 10-11-12-13-14-15.

472

473 The RH is composed of a low-temperature Si-layer intimately attached to thick-wall cells, and the
474 poultry excreta attaches to the outer surface of the husk or fills in the void left by the rice grain
475 (Fig. 6 A-C). This way, Campoaves BA is mainly composed of partially baked RH (Si and unburned C)
476 mixed with partially baked poultry excreta (Fig. 6 D-F), which are the components of the
477 amorphous P and SiO₂ phases and unburned carbon.

478 The melting of the RH silica with P and other elements from the poultry excreta generates
479 millimetric P-rich morphotypes composed of neo-formed crystalline and amorphous phases of P-
480 Ca blebs embedded in a silicate matrix with K, Mg and Ca (and residual Fe and Al) (Fig. 6 G-L).
481 Therefore, chemical compounds such as KMgPO₄(6H₂O) and CaO, MgO, sulfates, and chlorides can
482 be found at the particle surfaces.

483

484 The size analysis of on Campoaves FAECO sample shows that this material is mainly composed by
485 three size fractions (Fig. 7 A, C and G): >500 μm; between 75 and 250 μm; and <75 μm, mainly
486 composed of fragments of particles identified in the other size-fractions.

487 The >500 μm size-fraction consists of two main morphotypes: partially baked RH relics with
488 approx. 1.5 mm length, Si-crenulated outline, semi-detached unburned carbon and a thin Si-
489 internal layer (Fig. 7 B); large (approx. 500 μm) P-rich rounded morphotypes (phosphospheres)
490 composed of P-Ca blebs embedded by a (K, Mg, Ca)-silicate matrix (Fig. 7 G and H).

491 The 75-250 μm size fraction (Fig. 7 C and G) is composed of baked fragments of the RH Si-
492 materials, Ca-idioblasts relics from the wood chips (Fig. 7 C and D), partially baked poultry excreta
493 without Si (Fig. 7 C and E), and (Si-Ca-K-Mg)-phosphospheres, some with quartz inclusions (Fig. 7 C
494 and F).

495

496 Although Si is not found in some partially baked particles of poultry excreta (Fig. 7 G and I), all
497 analysed P-rich spherical morphotypes contain Si (Fig. 7 G, H, J-L). Some Si from the RH silica must
498 react with the poultry excreta while Ca binds with Si and P forming Ca-P blebs cement by a Ca-
499 silicate. Like K, some P de-volatilise and react with S forming P-sulphate, which on cooling
500 condensates at the surface of the particles. However, the main compounds of these condensation
501 reactions are 1-2 μm rims composed of K-sulphate and KCl (Fig. 7 J-L). Therefore, it might be
502 possible that most devolatilized P is released into the atmosphere.

503 At Güres, however, the CaCO_3 sand decomposition releases calcium and CO_2 , recombining to
504 capture S, P and K and forming thick rims around the sand grains. The presence of calcite explains
505 why the end-products are different from those from Campoaves.

506

507 The fraction $<75 \mu\text{m}$ from the Campoaves FACYC sample is characterised by fragments of partially
508 to entirely baked poultry excreta, Si- P- and Ca-rich spheres and fragments of biochar, Si from RH,
509 and Ca-oxide grains (Fig. 8 A). The particle above $75 \mu\text{m}$ RH biochar and Si-relics, phosphospheres
510 (Fig. 8 A and B), Ca-idioblast relics from wood chips (Fig. 8 E), partially baked poultry excreta (Fig. 8
511 F and G), and bone fragments (Fig. 8 H and I).

512

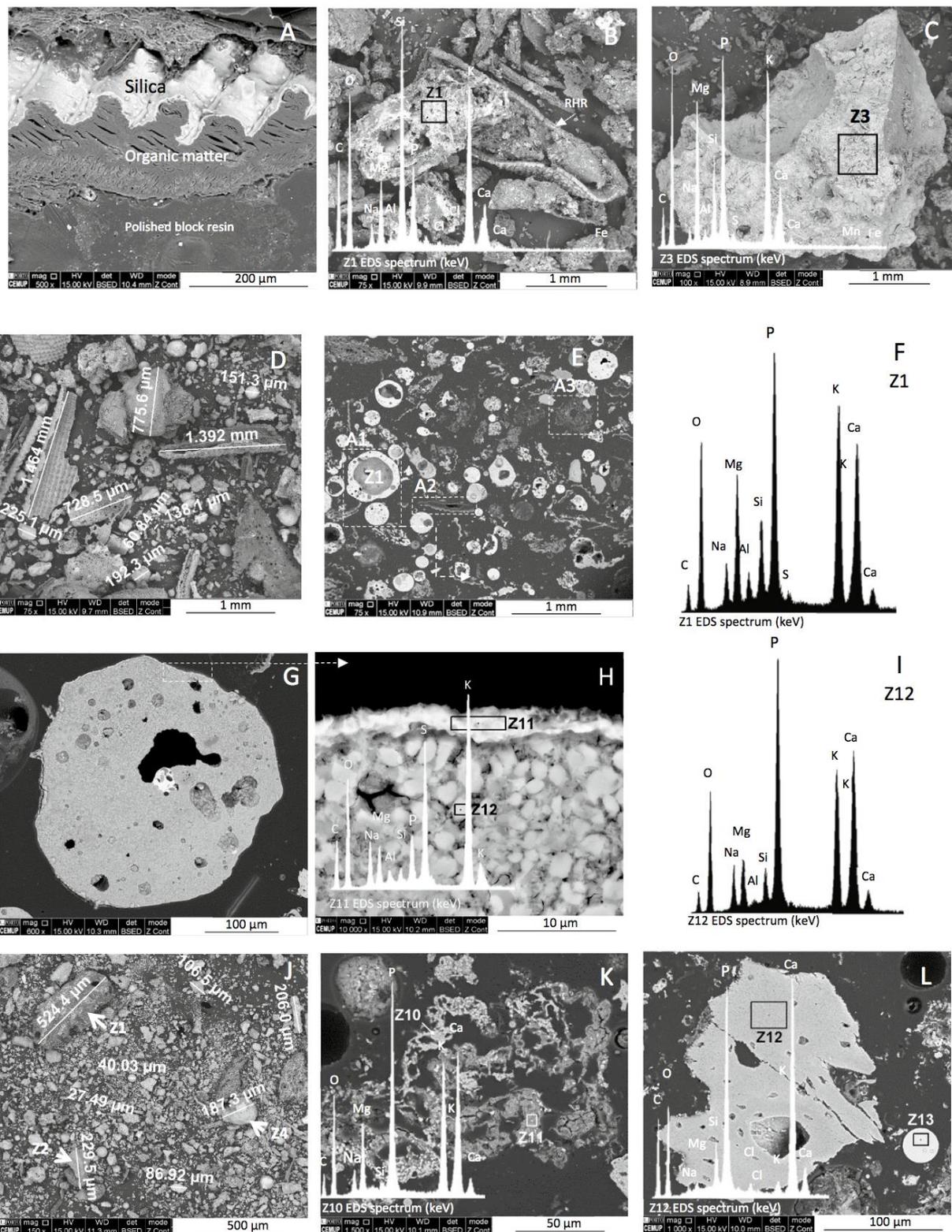
513

514

515 *Campoaves phosphospheres*

516

517 Phosphospheres are one of the main P-source in Campoaves fly ash, but there is no evidence of
518 phosphospheres in BA, only RH relics and partially baked excreta (Fig. 9 A). The SEM-EDS
519 experiments carried on FAECO show abundant phosphospheres with diameters ranging from
520 approx. 100 to 500 μm , composed of P-K-Ca blebs embedded by an Mg-Si-Al matrix (Fig. 9), is
521 related to the high amount of Si available from the rice husk and is a distinctive characteristic of
522 these ashes.

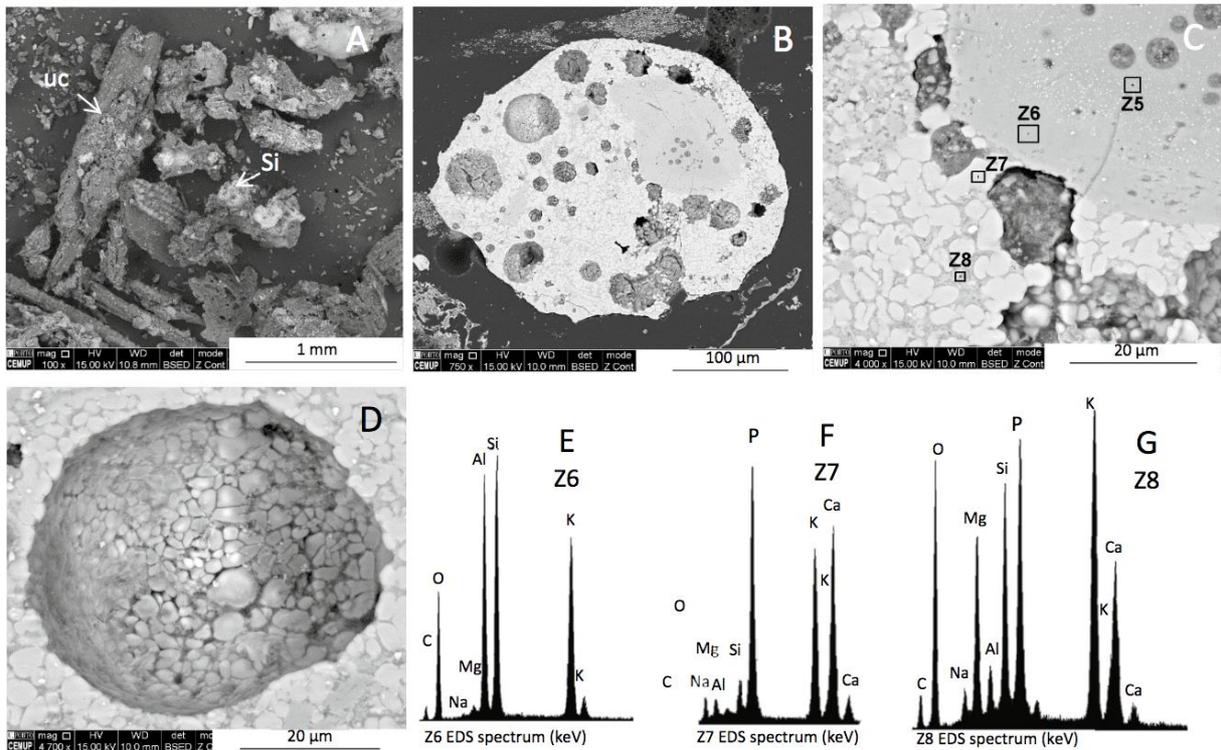


523

524 Figure 6 Micrographs and EDS spectra of rice husk (RH) in the fuel of “Campoaves” (Figueira da
 525 Foz, Portugal) and respective bottom ash (BA) (SEM-EDS BSE mode): A) cross-section of one RH
 526 measuring approx. 3×3 mm (×65; polished block); B) magnification of dashed square in “A” detailed
 527 image of the organic matter and silica layers in RH (×500); C) EDS spectrum in the dashed square in
 528 “B”, with major Si and O peaks and residual K; D) Bottom ash, a silicate-rich particle with sulfates

529 and KCl at the surface (Z1 EDS spectrum), and below this a partially baked RH relic (RHR; ×75;
 530 global sample); E) Bottom ash, partially baked poultry excreta (×95; polished block); F)
 531 magnification of dashed square in “E” detailed image of partially baked P-rich fraction in poultry
 532 litter excreta (×500); G) Bottom ash, irregular-shaped (P-K-Mg)-rich morphotype (×100; global
 533 sample); H) cross-section showing the internal structure of an irregular-shaped P-rich morphotype
 534 (×2500; polished block); I-L) EDS spectra in “H” to show the chemical composition of the silicate
 535 matrix (Z2 and 3), the embedded P-blebs (Z4), and a residual Fe sulfate grain (Z5).

536

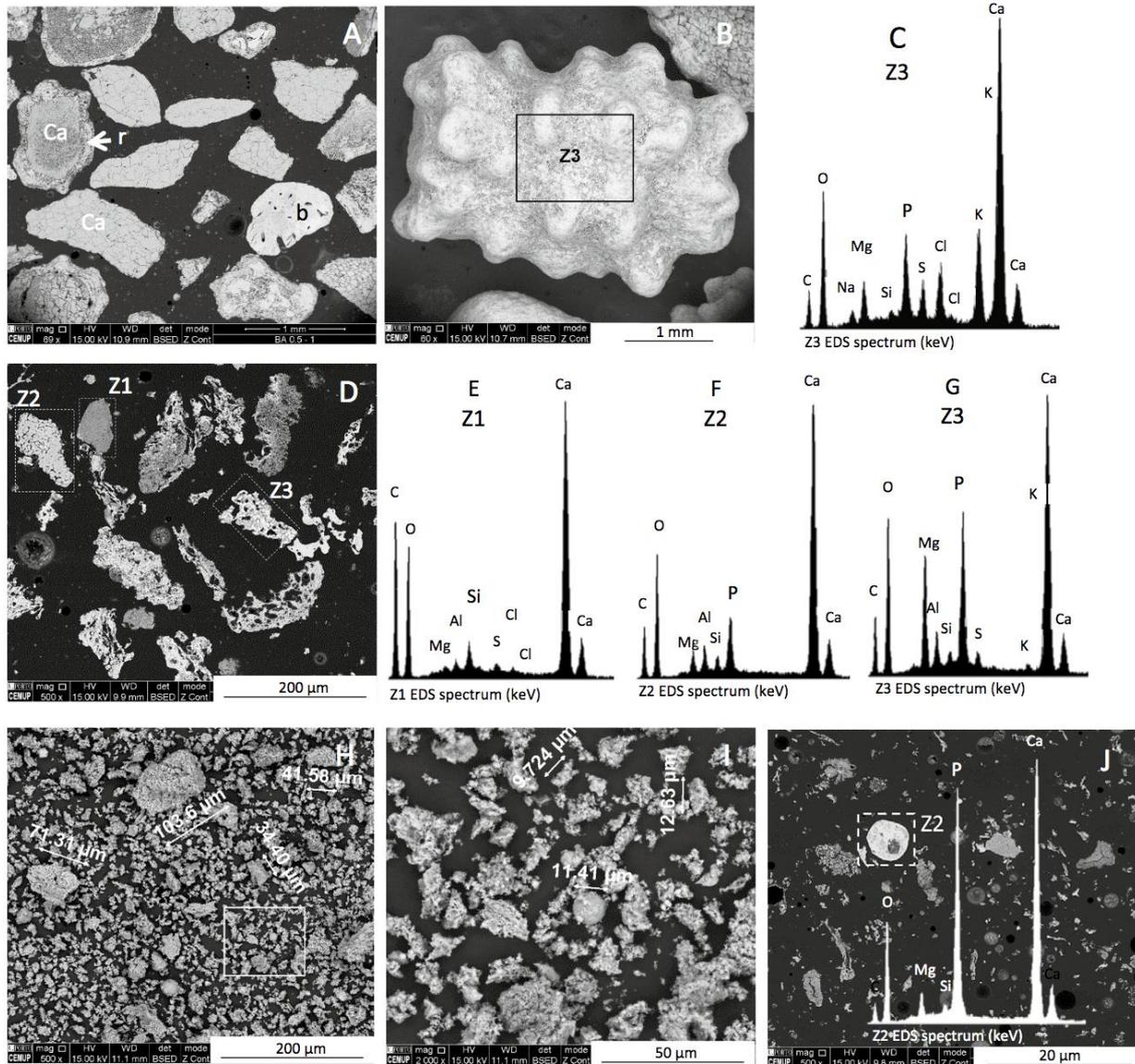


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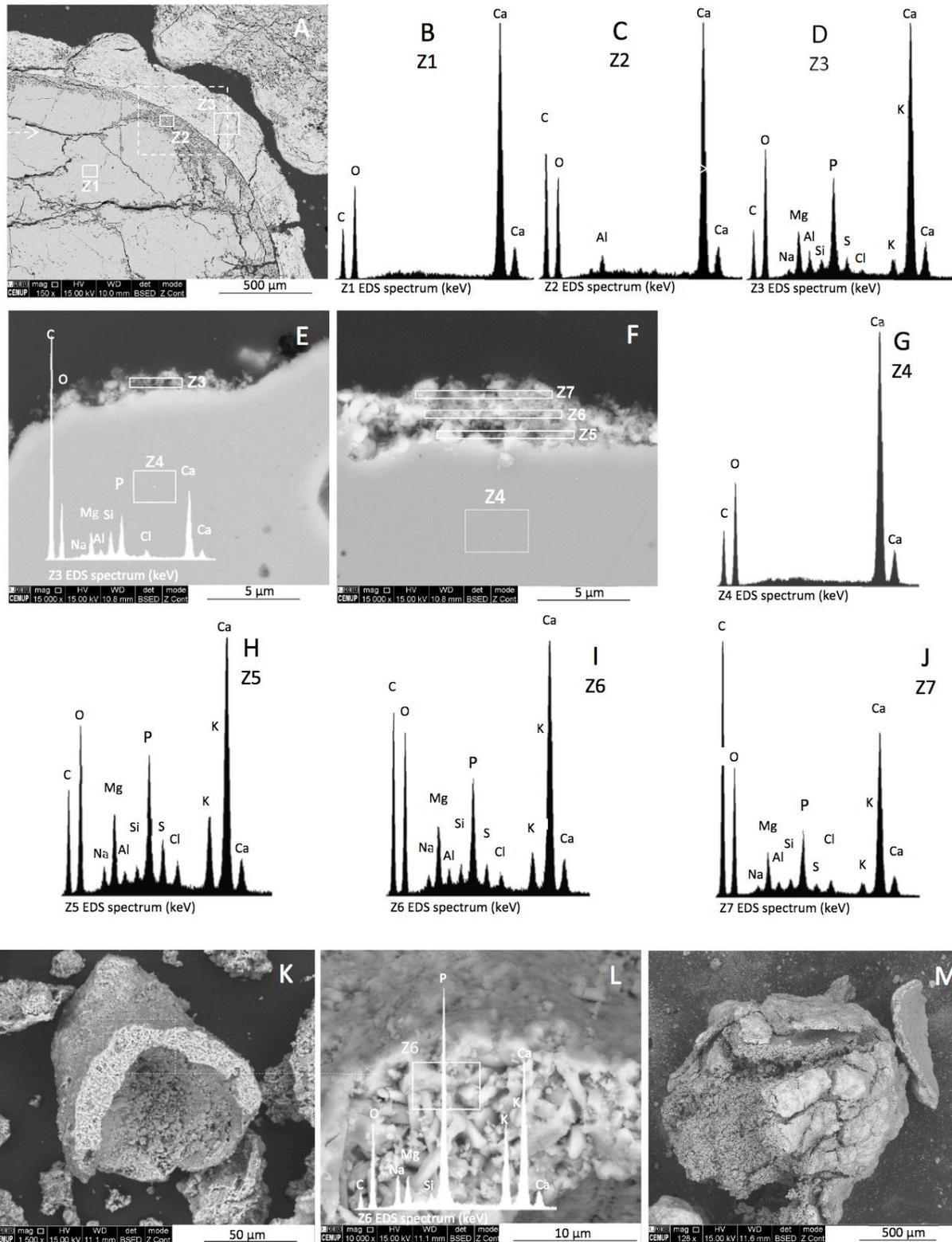
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539 Figure 7 Micrographs and EDS spectra of “Campoaves” (Figueira da Foz, Portugal) Economizer fly
 540 ash (FAECO) (SEM-EDS BSE mode): A) overview and particles measurement (×75); B) unburned
 541 carbon and silica layers in RH relic (×200); C) overview of the 75-250 μm with marked EDS areas; D)
 542 Z7 EDS spectrum in “C” of a Ca-idioblast relic from wood chips; E) Z8 EDS spectrum in “C” of an
 543 irregular Si-poor P-(Ca-Mg-K)-rich morphotype; F) Z9 EDS spectrum in “C” of a rounded Si-rich P-
 544 (Ca-Mg-K)-rich morphotype; G) polished block overview showing the main morphotypes: A1 dense
 545 and hollow phosphospheres (EDS spectra Z1 marked), A2 RH relics, A3 partially baked poultry
 546 excreta (×75); H) Z1 EDS spectrum in “G”; I) partially baked poultry excreta and EDS spectrum with
 547 major Mg, P and K peaks, and without Si and Ca (×1000); J) cross-section of a phosphosphere and

548 Z11 EDS spectra in “K” (×600; polished block); K) magnification of “J”, the surface is composed of K-
 549 sulfate (Z1), while the interior is composed of P-K-Ca-blebs embedded by a silicate matrix
 550 (×10000); L) EDS spectra in “K” showing the chemical composition of P-blebs (Z12).



551
 552 Figure 8 Micrographs and EDS spectra of “Campoaves” (Figueira da Foz, Portugal) Cyclone fly ash
 553 (FACYC) (SEM-EDS BSE mode): A) overview, particles measurement and EDS measured areas
 554 (×150); B) Z1 EDS spectrum in “A” of an unburned carbon particle; C) Z2 EDS spectrum in “A” of a
 555 Si-relic from RH; D) Z4 EDS spectrum in “A” of a phosphosphere; E) Ca-idioblast relic from wood
 556 chips and respective EDS spectra; F) partially baked poultry excreta. A mixture of P-K-Ca (Z10 EDS
 557 spectrum) and Si in darker portion (Z11) (×1000); G) Z11 EDS spectrum in “F”; H) bone fragment
 558 and small Si-rich K-Ca-P-Mg sphere (×1000); I and J) EDS spectra Z12 and Z13 in “H”.



559
 560 Figure 9 P-inorganic amorphous and phosphospheres in Campoaves bottom ash, Economizer
 561 (FAECO) and Cyclone (FACYC) fly ash samples (polished blocks; SEM-EDS BSE mode): A) overview of
 562 bottom ash: rice husk relics with silica (Si) and unburned carbon (uc) (global sample; $\times 100$); B)
 563 overview of FACYC with rice husk relics (RH) and phosphospheres (pho) ($\times 75$); C overview of FAECO
 564 with rice husk relics (RH) and phosphospheres (pho) ($\times 75$); D) overview of FACYC ($\times 75$); E)

565 phosphosphere with pomegranate structure and silicate inclusion ($\times 750$); F) magnification of
566 pomegranate structure in "E" with marked EDS spectra areas ($\times 4000$); G) magnification of hole in
567 "E" with P-blebs ($\times 4700$); H) EDS spectra Z6 in "F"; I) EDS spectra Z7 in "F"; J) EDS spectra Z8 in "F".

568

569

570 The main characteristic of Güres BA is its content in particles similar to those of the CaCO_3 sand
571 (Fig. 10 A). Many of these are covered by a thick layer composed of sulphates and chlorides (Fig.
572 10 B-D). Some sand may still be almost pristine, while other is already under decomposition (Fig.
573 10 E-F). However, some particles have a core made of bone or miscellaneous material (Fig. 10 E-F).

574

575 Güres FACYC sample granulometry ranges from $<25 \mu\text{m}$ to $>200 \mu\text{m}$ particles, corroborating the
576 sieving analysis. The morphotypes composition is quite heterogeneous, including fragments of
577 CaCO_3 sand (pristine or decomposed), rims of S, K and P retention, bone fragments, RH relics,
578 partially baked excreta, and phosphospheres (Fig. 11).

579

580 The measurement of particles on the Güres FAECO sample confirms that this material is composed
581 of three size fractions (Fig. 12 A-B), but the most abundant is the one below $25 \mu\text{m}$. The coarse
582 particles are mainly decomposed CaCO_3 sand fragments and some phosphospheres (Fig. 12 C-H).
583 In contrast, the fine fraction is almost entirely composed of rough Ca-P particles and decomposed
584 CaCO_3 sand fragments covered by sulfates and chlorides (Fig. 12 I-K).

585

586 *Decomposition of CaCO_3 sand and P-rich rims formation*

587

588 The CaCO_3 sand is used in fluidising bed combustion to capture S, forming calcium sulfate. One can
589 see in Fig. 13 A-I that CaCO_3 sand decomposes and cracks from its surface to the interior while Ca
590 moves to the surface and reacts with S, K, and P, among other elements, forming a rim. With time
591 the particle becomes an "old" grain from cryptic CaCO_3 , the edge detaches (Fig. 13 J and K).

592 The rim formed around the CaCO_3 sand may start with a micrometric layer of Na, S, Ca, and K
593 sulfates (Fig. 14 A-C), which then alternate and include amorphous and crystalline Ca-phosphate
594 (Fig. 14 D-H).

595

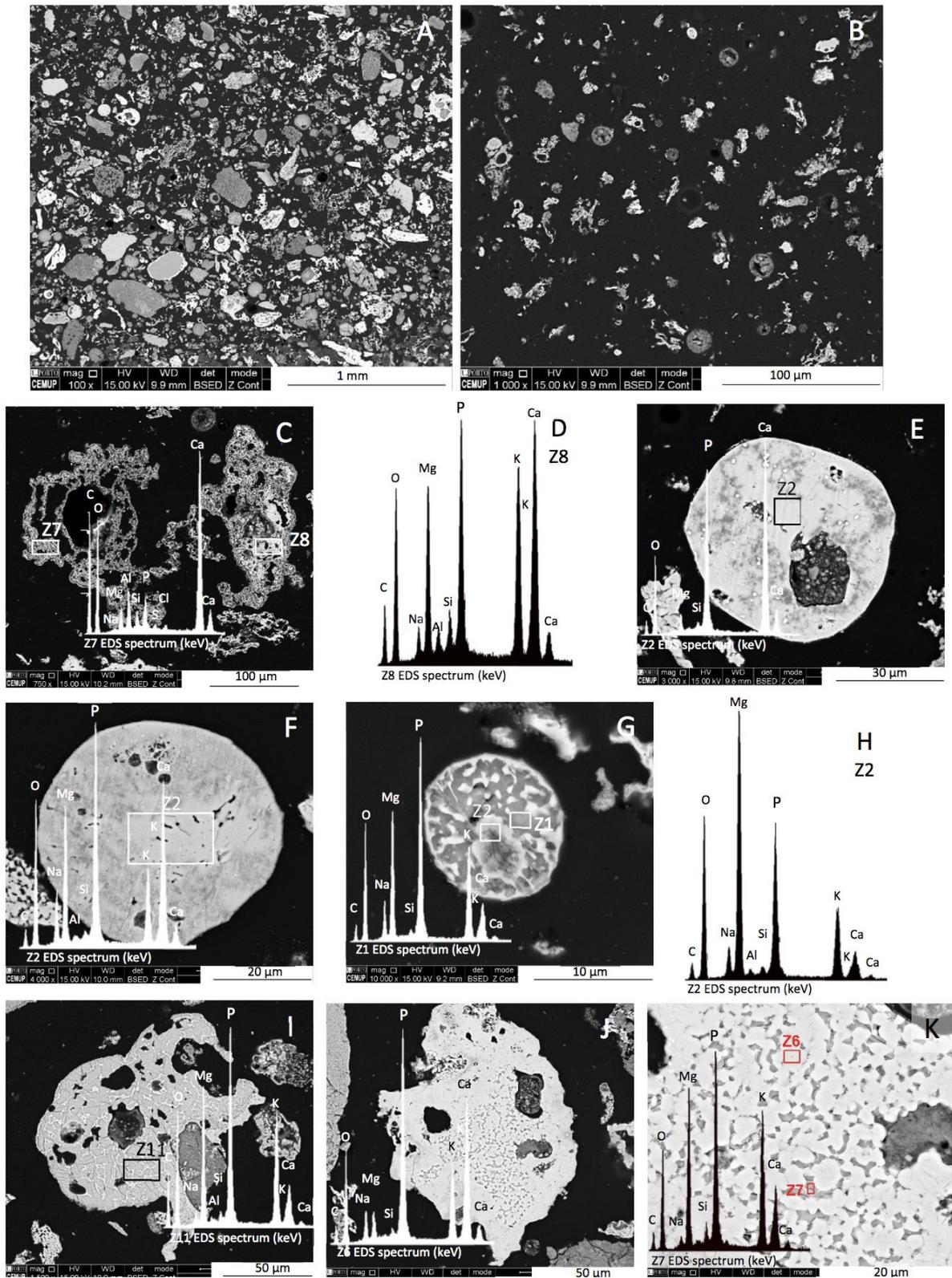
596

597 *Güres phosphospheres*

598

599 The main origin of P in Güres ashes is related to P-rich rims formed around CaCO₃ sand and
600 amorphous particles probably formed from partially baked laying hens manure. Glassy P-rich
601 spheres (phosphospheres) seem scarce (Fig. 15 A and B), and the ones observed have a
602 composition similar to the one of partially baked laying hens manure, i.e. with dominant Mg, P and
603 Ca and residual Si and Al (Fig. 15 C-K).

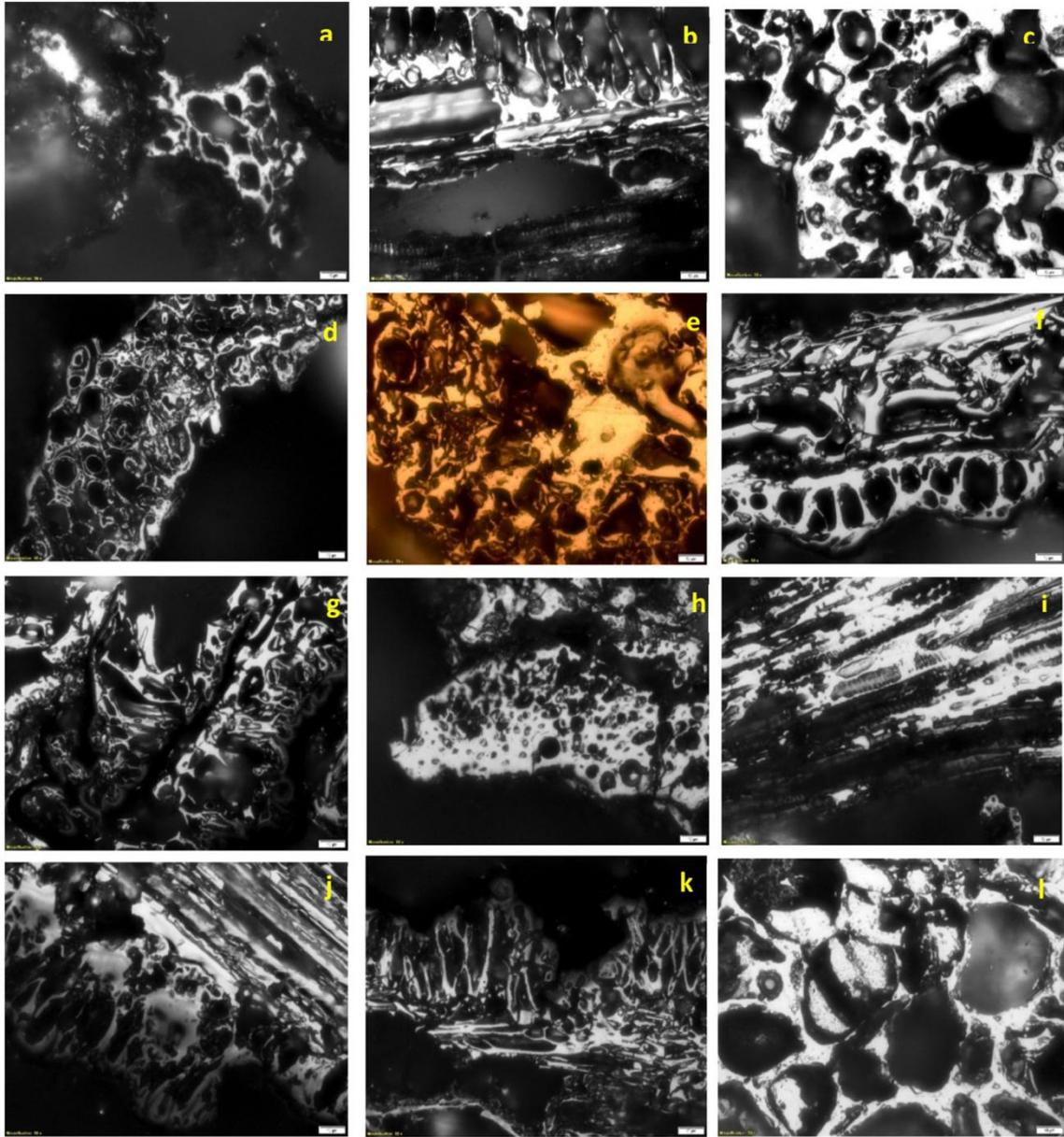
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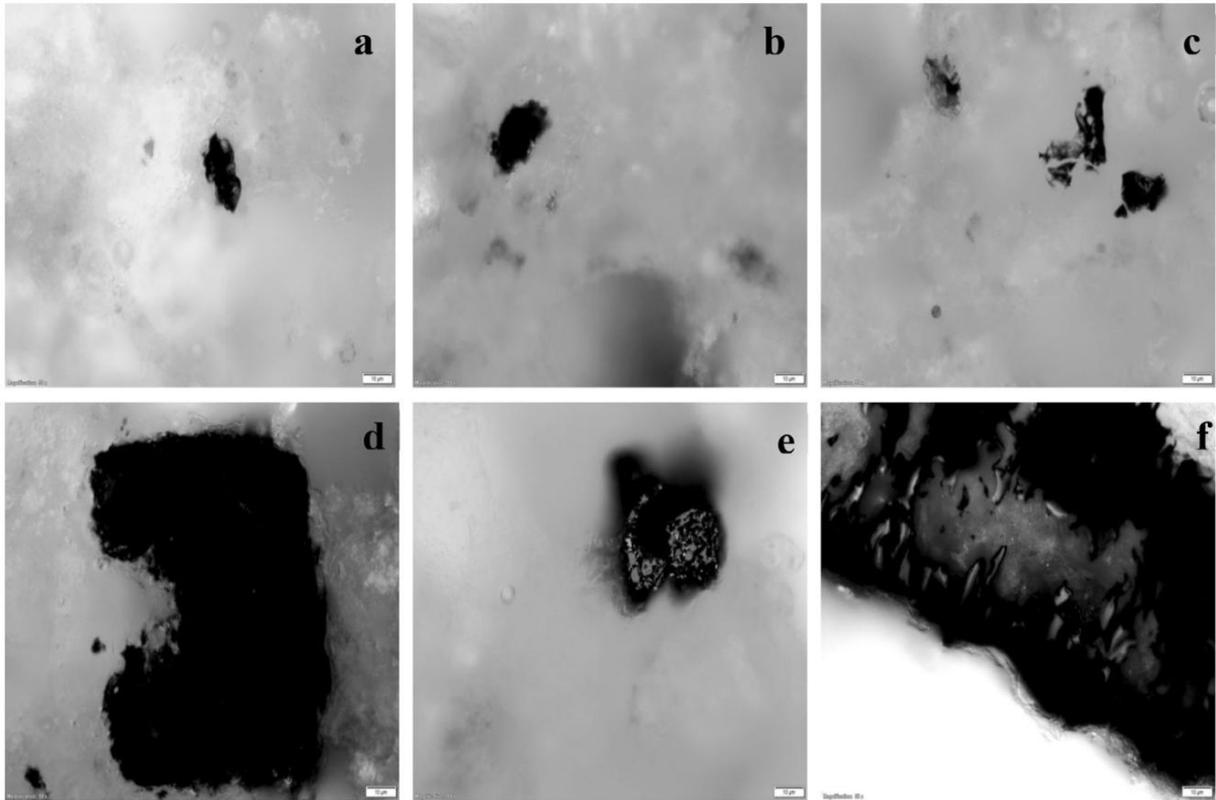
607 Figure 10 Micrographs and EDS spectra of "Güres" (Turkey) bottom ash (SEM-EDS BSE mode): A)
608 polished block overview: CaCO₃ sand (Ca) with and without rim (r), and bone fragment (b) (×69); B)
609 particle covered by a rim (global sample; ×60); C) Z3 EDS spectrum in "B"; D) fragmented CaCO₃
610 particle showing a thick rim (global sample; ×44); E) CaCO₃ particle without rim (polished block;

611 $\times 100$); F) old CaCO_3 particle fragmented and showing with heavy signs of reaction (polished block;
 612 $\times 128$); G) bone fragment with rim (polished block; $\times 100$); H) particle with miscellaneous nucleus
 613 and rim (polished block; $\times 100$).



614
 615
 616 Figure 11 Micrographs and EDS spectra of “Gures” (Turkey) Cyclone fly ash (SEM-EDS BSE mode):
 617 A) polished block sample overview with marked common coarse morphotypes: CaCO_3 sand (Ca), P-
 618 rich subrounded particle (pho), and bone fragment (b) ($\times 500$); B) polished block sample overview
 619 with marked common middle-size morphotypes: CaCO_3 sand (Z1), Ca-fragment with P (Z2), and
 620 irregularly-shaped and networked particle of Ca-P-Mg (Z3) ($\times 500$); C-E) EDS spectra Z1, Z2 and Z3
 621 in “B”; F) global sample overview of coarse particles ($>150 \mu\text{m}$) includes rice husk relics (RH), bone

622 fragments (b) and P-rich particles (pho) covered by KCl and MgO ($\times 100$); G) rice husk relic (polished
 623 block; $\times 650$); H) irregularly shaped with networked structure particle composed of Ca-Si-P and
 624 minor concentrations of Na, Mg and K (polished block; $\times 500$).



625
 626
 627 Figure 12 Micrographs and EDS spectra of “Gures” (Turkey) Economizer fly ash (SEM-EDS BSE
 628 mode): A) global sample overview ($\times 500$); B) magnification of white square in “A” ($\times 2000$); C)
 629 polished block overview and EDS marked morphotypes ($\times 500$); D) magnification of Z1 area in “C”
 630 and EDS spectrum: irregular Ca-Si<<(Al-Mg) particle ($\times 4000$); E) magnification of Z2 area in “C” and
 631 EDS spectrum: phosphosphere ($\times 3000$); F) magnification of Z3 area in “C” and EDS spectrum:
 632 irregular CaO particle with Mg-Si-K ($\times 4000$); G) Ca-Si (Z6) and CaCO_3 sand (Z7) fragments, and Z6
 633 EDS spectrum (polished block; $\times 2500$); H) Z7 EDS spectrum in “G”; I) size-fraction $< 25 \mu\text{m}$: Z1
 634 particle and respective EDS showing high-peaks of P and Ca and minors of K and Mg (global
 635 sample; $\times 5000$); J) Z2 EDS spectra in “I” of a CaCO_3 fragment covered by KCl and Ca-sulfate; K) KCl
 636 crystals (Z3 EDS spectrum) adsorbed at a particle surface (global sample; $\times 15000$).

637
 638

639 Figure 13 Rim mineralogy and evidence of particles ageing (micrographs A-C and G-I are polished
640 blocks; bottom ash from "Gures", Turkey; SEM-EDS BSE mode): A) grain of CaCO_3 with a thick rim
641 ($\times 53$); B) magnification of dashed square in "A": CaCO_3 (Z1), cryptic CaCO_3 (Z2), rim (Z3) ($\times 150$); C)
642 magnification of dashed square in "A": ($\times 500$); D-F) EDS spectra Z1, Z2 and Z3 in "B"; G)
643 magnification of dashed square in "C": cryptic CaCO_3 ($\times 2500$); H) CaCO_3 grain partially fragmented
644 with a cryptic surface surrounded by a rim ($\times 67$); I) magnification of dashed square in "K": rim with
645 Ca and Ca-P bands ($\times 750$); J) "old" grain with cryptic CaCO_3 with detaching rim ($\times 128$); K)
646 magnification of dashed square in "C": cryptic CaCO_3 ($\times 900$).

647

648

649 Figure 14 Rim formation (polished blocks of bottom ash from "Gures", Turkey; SEM-EDS BSE
650 mode): A) CaCO_3 sand (Ca) with an early stage rim formation (r) ($\times 100$); B) magnification of white
651 square in "A" and EDS (Z8) of the CaCO_3 ($\times 2000$); C) Z7 EDS spectrum in "B": rim composition; D)
652 early-stage formation Ca-P rim (Z3 EDS spectrum) at CaCO_3 surface ($\times 15000$); E-F) variation of rim
653 composition as it gets thicker ($\times 15000$); G) fragment of a detached rim ($\times 1500$); H) magnification of
654 dashed square in "G": hydroxyapatite crystals and respective EDS (Z6) spectrum ($\times 10000$).

655

656

657 Figure 15 P-inorganic amorphous and phosphospheres in Gures Economizer (FAECO) and Cyclone
658 (FACYC) fly ash samples (polished blocks; SEM-EDS BSE mode): A) overview of FACYC ($\times 100$); B)
659 overview of FAECO ($\times 1000$); C) Ca- (Z7) and P-rich (Z8) inorganic amorphous from laying hens
660 excreta and Z7 EDS spectrum (FACYC; $\times 750$); D) EDS spectra Z8 in "C"; E) structureless
661 phosphospheres will hole (FAECO; $\times 3000$); F) dense and structureless magnesia-phosphosphere
662 (FACYC; $\times 4000$); G) Mg-K-phosphosphere with pomegranate structure and Mg-rich matrix, and Z1
663 EDS spectrum (FAECO; $\times 10000$); H) EDS spectra Z2 in "G"; I) phosphosphere with pomegranate
664 structure and Mg-K-rich matrix, and Z11 EDS spectrum (FACYC; $\times 1500$); J) phosphosphere with
665 pomegranate structure and Mg-K-rich matrix, and Z6 EDS spectrum (FACYC; $\times 1500$); K)
666 magnification of pomegranate structure in "J", and Z7 EDS spectrum ($\times 5000$).

667

668 *Organic matter morphotypes identification by optical microscopy*

669

670 The petrographic study of the ash samples aims the evaluation the structural and textural
671 composition. The research of microtexture and microstructure highlight some aspects of
672 theoretical and practical interest regarding the aviary waste combustion process, as evolution and
673 efficiency, as well as on characteristics of resulting ash, respectively: development of the process
674 and phenomena that take place; details on combustion parameters, combustion plant
675 optimisation and thermodynamic parameters; origin of biomass; type and size of the porosity [47].
676 In this study, optical microscopy was used to identify the residual carbon resulting from
677 incomplete rice husk combustion generates interesting morphological aspects complementary to
678 those identified by electron microscopy (SEM analysis revealed by Figures 6A and B, 7A, and B, 9B
679 and 11F, G).

680 The analysis of residual carbon originating from biomass - rice husks (used as aviary bed at
681 Campoaves) is observed mostly in BA than FA in the studied samples. Some textural aspects of
682 partially burned carbon, sporadically identified, corresponds to low carbon contents below 10%.
683 Residual carbon (biochar) appears in the photomicrographs of Figure 16 (A-F), in which the char
684 derived from rice straw can be easily identified by its elongated and porous appearance.

685

686 Figure 16 Photomicrographs of rice husk biochar (Campoaves samples), Reflected Light, oil
687 immersion, 500x.

688

689 The optical appearance of carbon particles is exclusively isotropic and intensely porous.
690 The existence of biochar porosity may facilitate the condensation in these pores of certain
691 substances removed during devolatilisation. In the case of using ash as a soil supplement, they
692 may be released sequentially in contact with rainwater and depending on the soil pH.

693 In Güres ash samples, biomass is sporadic and difficult to evaluate from a morphological point of
694 view. The optical aspect of carbon particles is exclusively isotropic, dense, and free of
695 porosity. However, some char particles can be identified with specific biomass textures but with
696 an uncertain aspect regarding the origin, in Figure 17. Although at Güres, a vegetable bed was not
697 used for poultry farms, the source of these microscopically identified char fragments is explained
698 by the presence of plant remains leftover from bird feed.

699

700 Figure 17. Photomicrographs of residual carbon of biomass origin from fluidised combustion of
701 aviary waste (Güres samples), Reflected Light, oil immersion, 500x.

702

703 The analysis of the ash samples by both SEM and optical microscopy highlights similar
704 morphological aspects, easy to identify. The micrographs taken under the optical microscope are
705 like those identified by SEM (magnification 300X) in which fragments of biomass char (residual
706 carbon) appear with porous structures. In addition to the optical, morphological analysis by which
707 the presence of carbon is identified, EDS analysis confirms this aspect. The inner layer of rice husks
708 was spectrally identified (see SEM-EDS results).

709

710

711 *Trace elements evaluation: EU regulatory framework for fertilisers application*

712

713 Based on the chemical characterisation, rice husk poultry litter ash and laying hens manure (with
714 CaCO₃ sand) ash are potential direct fertilisers according to the EU regulation 209/1009 of the
715 European Parliament of 5 June 2019 [48]. The latter defines a fertiliser as follows: “shall be an EU
716 fertilising product the function of which is to provide nutrients”. Therefore, thanks to
717 macronutrients such as P and K, Campoaves and Güres ash samples are among the materials
718 candidate to show good bioavailability in pot and field tests. In addition, these incinerated ashes
719 are free of pathogenic substances [49].

720 Trace elements such as Cu, Zn, Rb, Ba, Sr were quantified using digestion and lithium
721 tetraborate/metaborate fusion (Table 3), including REE+Y and seventh-period elements such as
722 uranium. Campoaves and Güres samples have similar concentrations of Ni, Co, W, Se and Pb. The
723 REE+Y, U and Th concentrations are relatively higher in Campoaves samples. They may be due to
724 the rice husk as poultry litter taken from paddy fields that typically contains trace elements such
725 as rare earth elements [45]. However, in both cases, the concentrations of REE+Y, U and Th are
726 low. Results are, therefore, promising for the use of ashes as fertilisers since the trace element
727 concentrations are lower than that reported in the literature for phosphate rocks (see Table 5).

728 At this point, it could be interesting to evaluate if the quantity of the trace elements and minor
729 elements, specifically Zn and Cu, comply or not with EU regulation. This legislative act reports that
730 for particular recovered wastes, such as struvite, biochar and ash-based products (like in the
731 present case), within the meaning of Directive 2008/98/EC [50], market demand for the use of
732 these ashes as a fertilising product is possible as long as specific requirements are fulfilled. Article
733 4 of this document reports that the product should meet the criteria set out in Annex I for the

734 function category as a significant obstacle rather than Annex II providing for the component
735 category and Annex III related to the labelling requirements.

736 There are specific limits for contaminants (Hg, Cr(VI), Ni, Pb, As, Cd, Cu, Zn) based on the function
737 categories differentiated by application purpose: fertilisers for nutrient uptake for the plants,
738 liming material, soil-improving, growing medium for inhibition of urease and
739 nitrification/denitrification inhibitor, plant bio-stimulation. Based on the amount of the
740 macronutrients present on Campoaves and Güres samples, all the samples have nutrients in oxide
741 form such as P₂O₅ (3 %), K₂O (3 %), MgO (3 %), CaO (1.5 %), SO₃ (1.5 %) and NaO (1 %), higher than
742 3, 3, 3, 1.5, 1.5 and 1 %, respectively, required for inorganic macronutrient fertilizers. Under the
743 EU regulation, this material shall provide plants or mushrooms with at least two primary nutrients
744 among P, K, N and at least two secondary nutrients among Ca, Mg, S, Na.

745 Regarding this function category, all the samples comply with the limits set for Cd (values under
746 the limit of 6 ppm in case of P₂O₅>5 %), Cr(VI) (in the present work, Total measured Cr is less than
747 1 ppm), Hg (lower than 1ppm), Ni (under the limit of 100 ppm), Pb (<120 ppm), As (<40 ppm), Cu
748 (<600 ppm).

749 Zinc, however, is an exception since FAECO-CA (2516 ppm), FACYC-CA (2221 ppm), and FAECO-GU
750 (2356 ppm) samples do not respect the limits (1500 ppm) for this category. The reason relies on
751 the oxidation in lighter particles corroborating the data shown in the elemental analysis in Table 1
752 where the concentration of minor elements increased in the post-combustion section.
753 Nevertheless, beneficiation of the ashes via excluding some ashes or its dilution overcome the
754 problem if a direct application as fertilisers is considered.

755

756 Table 4. Comparison of selected trace elements concentration (ppm) from ICP-MS data of Table 3
757 with data reported for phosphate rock [51].

758

759

760

761

762 **Conclusions**

763

764 The comparative characterisation study between two sub-categories of incinerated aviary by-
765 products has been done for the first time yield the following results

766 - P in the ash is speciated in different minerals: the Güres ash is dominated by hydroxyapatite
767 mineral form, and the Campoaves ash contains, in addition to hydroxyapatite, other P-bearing
768 minerals, such as K-struvite, $\text{Ca}_3(\text{PO}_4)_2$ and NaH_2PO_4 , as the main phases.

769 Ca-rich Güres ash and Si-rich Campoaves ash are characterized by two different mineral
770 assemblages resulting from two distinct combustion systems. In the Güres plant, the use of calcite
771 as a bed particle for the fluidised combustion explains the formation of Ca phases. The typology of
772 the flock (poultry excreta, spilled feed and feathers are retained by rice husk, rich in SiO_2 , forming
773 poultry litter) also differs in the two sites.

774 - These two ashes display features corresponding to the K type for Campoaves and the C/CK type
775 for Güres from Vassilev's classification.

776 The other difference concerns the trace elements contents, linked to the geo-location of the fuel
777 material: the higher REE, Th concentrations of Campoaves samples are due to their presence in
778 open area agricultural fields.

779 - Finally, both samples showed that under the EU regulatory framework, they could readily comply
780 with the limitations set for the functional category of inorganic macronutrient fertilisers
781 application, which facilitates the way to push for marketing these ash residuals as nutrient
782 providers for plants.

783

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788 **Declarations**

789

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791

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795

796 *Conflicts of interests*

797

798 All authors certify that they have no affiliations with or involvement in any organisation or
799 entity with any financial or non-financial interest in the subject matter or materials
800 discussed in this manuscript.

801

802 **Data availability**

803

804 All data generated or analysed during this study are included in this published article (and
805 its supplementary information files).

806

807

808 **References**

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