Article

Properties of Animal-Origin Ash—A Valuable Material for Circular Economy

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Abstract: In the presented paper, two types of animal-origin biomass, cow dung and chicken litter, are characterized in terms of combustion-related problems and ash properties. It was found that these parameters strongly depend on the farming style. Whether it is cow dung or chicken litter, free-range raw materials are characterized by higher ash contents than industrial farming ones. Free-range samples contain chlorine at lower levels, while industrial farming samples are chlorine rich. Free-range samples are characterized by the predominant content of silica in the ash: 75.60% in cow dung and 57.11% in chicken litter, while industrial farming samples contain more calcium. Samples were classified by 11 "slagging indices" based on the ash and fuel composition to evaluate their tendencies for slagging, fouling, ash deposition and bed agglomeration. Furthermore, an assessment was made against the current EU law regulations, whether the ashes can be component materials for fertilizers. The phosphorus concentration in the investigated ashes corresponds to 4.09–23.73 wt% P_2O_5 and is significantly higher in industrial chicken litter samples. The concentrations of Hg, Cu, As, Ni, Cd and Pb in all samples are below the limits of the UE regulations. However, concentrations of Cr in all samples and Zn in industrial chicken litter exceed these standards.

1. Introduction

Animal-origin biomass is mainly a solid animal waste (manure) that is produced during animal breeding. Various types of animal biomass were under investigation when it comes to its energy potential and usability: cattle manure [1,2], poultry litter [3,4], turkey litter [5], goat dung [6], piggery waste [7,8], horse dung [9], deer manure [10] or even elephant dung [11].

Despite this diversity, the greatest potential of animal-origin biomass comes from poultry and cattle breeding. The daily production of droppings per bird depends on the chicken type and ranges from 150–160 g of droppings for an adult chicken to 65–110 g for pullets [12]. Poultry breeding results in massive litter production, which consists not only of manure, but waste bedding, food and feathers. The total amount of poultry litter generated per bird over the entire production cycle depends on the bedding change interval and is reported to be from 1.5 to 5.7 kg [13]. Similar to the poultry litter, the annual production of cow manure depends mainly on the bedding system. An adult cow produces 12.4–26.0 t of waste per year for deep bedding and 11.6–22.0 t/year for a bedding-less system [14].

The safe removal and utilization of animal litter is a key issue since it is considered to be a problematic type of waste. Both poultry litter and cow manure are rich in plant nutrients, such as nitrogen (N), phosphorus (P) and potassium (K) hence they have been utilized for soil conditioning as a fertilizer. However, in recent years, their effectiveness and safety as a fertilizer have become questionable. Animal manure is characterized by

low carbon/phosphorous and nitrogen/phosphorous ratios. Nitrogen and phosphorous have the potential for leaching [15] and may result in the contamination of groundwater and eutrophication of water bodies [16] since soil and water are directly linked [17]. When fresh manure is spread on land, nitrous oxide and ammonia, potent greenhouse gases, can be emitted into the atmosphere. Another issue is the pathogens present in animal waste that are a possible threat to human and animal health [18]. Alternative strategies of litter utilization assume anaerobic digestion or thermal treatment, such as pyrolysis, gasification, direct combustion and co-combustion.

Tańczuk et al. determined the technical energy potential of chicken manure for four energy conversion variants taking into account the energy degradation during the production of useful energy, e.g., heat, and pre-processing of the litter (e.g., drying) [19]. The biggest energy loss was found for anaerobic digestion, while combustion demonstrated the most efficient scenario. Furthermore, direct combustion is a convenient and cost-effective method since it can be applied locally on a small scale in the farm neighborhood. Animal-origin biomass, similarly to plant-origin biomass and lignite, may be used in a processed form, for example, torrefied or as pellets and briquets [20–22]. Szymajda et al. [1] determined the quality of cow manure pellets (kinetic durability, bulk density and particle density), as well as flue gas composition during their combustion.

Animal litter combustion is favorable not only due to its energy potential but the possibility of nutrient recycling. If the chemical composition of ash is within the European Union (EU) standards, it can be applied in agriculture as a component of fertilizes. The EU allowed the marketing of fertilizer products of various origins, including ash from biomass combustion, within the scope of solid inorganic macronutrient fertilizers. The recirculation of ash into the soil is claimed to be the most sustainable disposal method according to the circular economy idea [23]. Ash from the combustion of animal-origin biomass may be a valuable by-product since it contains residual phosphorus (P) and potassium (K), which are excellent plant nutrients and could be processed into fertilizer [24]. The use of ashes for soil conditioning can be a part of the soil remediation process since it is expected to enhance the growth of phytoremediation plants. Such action may be beneficial to avoid further land degradation and promote land restoration hence these issues are important in terms of Sustainable Development Goals (SDGs) [25,26]. The studies of biomass ashes in terms of fertilizer usefulness and environmental safety were conducted mainly for plant-origin biomass [27,28], and only limited studies for animal-origin biomass can be found in the literature. The majority of these studies relate to poultry litter ashes from combustion and gasification processes, while cow manure ash has been less studied.

Ash from poultry litter combustion is germ-free and easy to transport [29]. It contains phosphorus and potassium that shows good bioavailability during field and pot tests and can be directly applied into a field as a P source [30], applied in the form of hydrated ash or P can be recovered by extraction/elution [31,32]. However, poultry litter ash may contain heavy metals and metalloids, such as Fe, Mn, As, Zn, Cu, I, Se and Co, which are used in the breeding process to prevent deficits and defects, improve mass gain and elevate egg production [33]. Faridullah et al. [34] presented increased concentrations of metals (Cu, Mn, Zn, Pb and Ni) with increasing combustion temperature and higher amounts of chicken litter ash than duck litter ash. Fiameni et al. [35] proposed a strategy for phosphorous and silica recovery from rice husk poultry litter ash. The proposed method aims to maximize the P extraction using hydrochloric acid and minimize the possible contamination by leachable heavy metals, such as zinc.

The elemental composition of ash, including metals, is crucial when considering its potential fertilizing application since it is highly dependent on local law regulations. In the EU, the limits of Zn, Hg, Cu, Cr, Cd, Ni, Pb and As for organic and mineral fertilizers and soil improvement materials have been regulated by the recent EU Fertilising Products Regulation (EU) 2019/1009, which was approved on 5 June 2019. When the requirements of the Regulation are fulfilled, the ash is no longer considered as waste within the principles of Directive 2008/98/EC,

and it can be used as a component for fertilizing products. The products containing or consisting of such recovered ash are allowed to access the European market.

Apart from the use as a fertilizer, the chemical composition of biomass ash should be well recognized before the combustion process since it may cause severe problems in the furnace. Especially animal-origin biomass, whose composition differs significantly from coal and plant-origin biomass, is likely to cause critical combustion-related issues, and this fact determines its usability in the power sector [29,36]. The determination of the vital ash properties includes the characteristic ash fusion temperatures (AFT), chlorine content and the presence of alkalis. The AFTs for animal-origin biomass ashes are usually lower than for coal ashes. Vankát et al. determined the ash-softening temperature of animal manure to 1110–1170 °C and the flow point to 1140–1230 °C [37]. Animal feces ash is usually characterized by a relatively high chlorine content, which can exceed 10% [38]. Fahimi et al. investigated poultry litter ash that was calcium, phosphorous, potassium and sulfur-rich (>29 g/kg) [39]. The ash with high chlorine and alkali metal (K, Na) contents can lead to numerous undesirable issues, such as high-temperature corrosion, slagging, fouling, the formation of deposits on heating surfaces of the boiler and bed agglomeration in CFB boilers [40,41].

The presence of Cl in the ash deposits is vital, especially for high-temperature corrosion, since it leads to the development of low-melting mixtures containing metal chlorides. It favors the mobility of alkali compounds, which may form inorganic mixtures with silica and lower the fluid temperatures from around 1700 °C to around 750 °C. Therefore, chlorine-induced corrosion occurs in a combustion chamber according to the multi-step active oxidation model as it is the most widespread principle of high-temperature corrosion [42].

Many various indicators for classifying a fuel in terms of ash behavior are in use [43–47]. Such methods allow prediction of ash agglomeration, slagging, fouling or corrosion potential. They are based mainly on ash composition, ash fusion temperatures and fuel analysis. They were originally established for coal ashes. Nevertheless, their applicability for biomass ashes is under investigation. Garcia-Maraver et al. [43] classified 104 various biomass types by 10 commonly used slagging indices. For most cases, the coefficients show mixed results when applied to plant-origin biomass: the same fuel was categorized to have low, medium, high or extremely high slagging risk, depending on the index used for classification. However, among 104 various biomass fuels included in this research, only two animal-origin biomasses were investigated: chicken litter and meat-bone meal. Differently from other biomass types, for chicken litter, the categorization seems to be accurate: it was categorized as highly or extremely highly problematic by 7 out of 10 indices. This may suggest that these indices may be applicable to the animal-origin biomass due to its specific composition, different from plant-origin biomass. Lachman et al. [46] presented a compendium of slagging and fouling indices and their applicability to biomass fuels. Nevertheless, not enough attention was paid to animal-origin feedstock. These facts indicated the big knowledge gap when it comes to animal-origin biomass combustion problems. Hence, the presented paper covers a novel and unique research field. The problem of animal-origin biomass ash behavior prediction is still very poorly recognized and existing studies need to be supplemented.

The presented research aims to determine the ash properties of chicken litter and cow manure in terms of ash-related issues and potential use of ashes as an inorganic macronutrient fertilizer. Four types of cow manure and five types of chicken litter were investigated. The material was collected from different breeding styles: industrial farming and free-range to understand how the breeding system affects the feedstock and ash properties. According to the authors' best knowledge, there are no studies where the influence of the breeding system on fuel properties and ash composition is investigated. The ashes were examined by eleven so-called "slagging indices" to evaluate their potential for slagging, fouling and bed agglomeration. The possible application of such indices was determined for the investigated ashes since there is very limited data referring to animal-origin biomass ash behavior prediction. Further, the possible use of ashes for fertilizing

purposes was assessed together with the potential risk associated with their introduction into the environment. The ash composition was evaluated against the criteria in the current EU Fertilising Products Regulation (EU) 2019/1009, taking into account the limits of heavy metals: Zn, Hg, Cu, Cr, As, Cd, Ni and Pb in inorganic macronutrient fertilizers. The limits of other elements, such as Sb, Se, Sn, V, Mo and Co, were determined as well and compared with their average concentrations in European and North American soils. The presented research can improve the technologies of animal-origin biomass energy conversion.

2. Materials and Methods

The following types of animal-origin biomass were considered in this study:

- Cow manure from free-range farming CD1_FR, CD2_FR
- Cow manure from industrial farming CD3_IF, CD4_IF
- Chicken litter from free-range farming CL1_FR
- Chicken litter from industrial farming CL2_IF, CL3_IF, CL4_IF, CL5_IF

CD1_FR, CD2_FR and CL1_FR samples were collected from middle-size free-range animal farms located in Southern Poland.

CD3_IF and CL2_IF were collected from large industrial farms located in Southern Poland.

CD4_IF was investigated by the authors and research partners in previous research [36] and originated from a large industrial farm located in Eastern Poland.

CL3_IF, CL4_IF and CL5_IF samples were collected from a large poultry farm located in Ukraine by the Ukrainian research partner. They were collected within a time of one year to ensure seasonal diversity.

2.1. Feedstock and Ash Analysis

The biomass samples were chopped in a laboratory knife mill and stored at an ambient temperature. A small batch of feedstock was placed into a ceramic crucible, heated up to 550 °C and incinerated in a constant temperature zone in an electric muffle furnace. As a result, chemically stable ash with a minimal amount of unburned carbon (UBC) was obtained for further analysis.

Proximate and ultimate (elemental) analysis of biomass samples was conducted. For the ash, the oxide ash composition and ash fusion temperatures (AFT) were determined since they are the most common procedures for ash characterization in terms of combustion-related issues. To assess the potential risk associated with its introduction into the environment, the Zn, Hg, Cu, Cr, As, Co, Ni, Pb, Sb, Se, Sn, V, Mo and Cd concentrations were determined.

Feedstock analysis was conducted according to European standards for solid fuels: ash content PN-EN ISO 18122:2016-01, moisture content PN-EN ISO 18134-2:2017-03, Lower Calorific Value (LHV) and Higher Calorific Value (HHV) PN-EN ISO 18125:2017-07. A portion of fuel was incinerated at a constant volume in a calorimeter calibrated by the combustion of benzoic acid. C, H and N contents were determined by Infrared (IR) analyzer according to PN-EN ISO 16948:2015-07, Cl and S contents by the Ion Chromatography (IC) method according to PN-EN ISO 16994:2016-10.

The ash composition was determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). Metal and metalloid concentrations were determined according to PN-EN ISO 16968:2015-07 and PN-EN ISO 11885:2009. The ash fusion temperatures were determined by the microscope-photographic method according to standard CEN/TS 15370-1:2007. The procedure covers the identification and recording of initial deformation temperature (IDT), softening temperature (ST), hemisphere temperature (HT) and flow temperature (FT). The specific, characteristic shapes of the ash cylinders were recorded by a digital system. The procedure assumes a maximum temperature of 1500 °C and both oxidizing and reducing conditions. The only exceptions are samples CL3_IF–CL5_IF, which were collected and tested by the Ukrainian research partner. For these samples, the complete AFT investigation is not available, and only IDT and ST temperatures in oxidizing

conditions are reported. For the same reason, the chlorine content and SEM analysis of these samples are not available.

The scanning electron microscope (SEM) analysis of ash samples was performed to investigate their morphology. The Zeiss Supra 35 microscope with the Trident XM4 series (EDX) X-ray spectrometer was used. The electron high tension (EHT) voltage was set to 10 kV. The pictures were taken with two types of magnification for each sample: 1000× and 250/500×, depending on the sample morphology.

2.2. Ash Deposition, Slagging and Fouling Prediction

The ash behavior indices used in this study are presented below, together with the evaluation of their values. An index can display low, moderate, high or extremely high slagging hazards [43,48–50].

The base-to-acid ratio:

$$B/A = \frac{Fe_2O_3 + CaO + MgO + Na_2O + K_2O + P_2O_5}{SiO_2 + Al_2O_3 + TiO_2}$$
$$<0.5 \text{ low}$$
$$0.5\text{--}1.0 \text{ moderate}$$
$$1.0\text{--}1.75 \text{ high}$$
(1)

B/A may be used in a simplified form:

$$B/A_{Simpl.} = \frac{Fe_2O_3 + CaO + MgO}{SiO_2}$$
(2)

The Bed Agglomeration Index (BAI):

$$BAI = \frac{Fe_2O_3}{Na_2O + K_2O}$$
$$<0.15 \text{ high}$$
(3)

Babcock Index Rs (B/A ratio enhanced with sulfur content in fuel):

$$Rs = B/A \cdot S^d$$
$$<0.6 \text{ low}$$
$$0.6\text{--}2.0 \text{ moderate}$$
$$2.0\text{--}2.6 \text{ high}$$
$$>2.6 \text{ extremely high}$$
(4)

Fouling index Fu (B/A ratio enhanced with the alkali metals):

$$Fu = B/A \cdot (Na_2O + K_2O)$$
$$<0.6 \text{ low}$$
$$0.6\text{--}40 \text{ moderate}$$
$$>40 \text{ high}$$
(5)

Slag Viscosity Index Sr:

$$Sr = \frac{SiO_2 \cdot 100\%}{SiO_2 + Fe_2O_3 + CaO + MgO}$$
$$>72 \text{ low}$$
$$65\text{--}72 \text{ moderate}$$
$$<65 \text{ high}$$
(6)

Fuel alkalinity index μ_{alk}:

$$\mu_{alk} = \frac{1}{LHV \cdot A^d \cdot (Na_2O + K_2O)}$$

0.17–0.34 moderate

>0.34 high

(7)

Ash Fusibility Index (AFI):

$$AFI = \frac{4IT + HT}{5}$$

>1342 low

1232–1342 moderate

(8)

1052–1232 high

<1050 extremely high

The indices are supplemented by the silica content in the ash SiO_2 (<20 low, 20–25 moderate, >25 high), the chlorine content in the fuel Cl (<0.2 low, 0.2–0.3 moderate, 0.3–0.5 high) and AFTs in oxidation conditions: initial deformation temperature IDT (>1100 °C low, 900–1100 °C moderate, <900 °C high) and softening temperature ST (>1390 °C low, 1250–1390 °C moderate, <1250 °C high).

3. Results and Discussion

3.1. Feedstock and Ash Characteristics

Proximate analysis, elemental (ultimate) analysis and heating values of the feedstock samples are presented in Table 1. The ash content of cow manure from free-range (CD1_FR, CD2_FR) was found to be higher than that of cow manure from industrial farming (CD3_IF, CD4_IF): 21.4% and 22.06% vs. 16.99% and 13.86%. Similarly, the ash content of free-range chicken litter (CL1_FR) is significantly higher than that of industrial farming chicken litter (CL2_IF–CL5_IF): 30.10% vs. 7.10–17.09%. This is reflected in low calorific values of free-range chicken litter. Nevertheless, the HHV of all samples, regardless of the breeding system, is within the range provided in the literature for poultry waste [51]. The moisture content of industrial farming chicken litter is visibly higher than for other samples. The chlorine content in free-range cow manure (0.086–0.33%) is lower than in industrial farming (0.54–1.02%). The chlorine content in free-range chicken litter (0.11%) is greatly below the content of the industrial-farming samples (0.66–0.99%). The chlorine content of free-range animal waste investigated in this study is comparable to the chlorine content of plant-origin biomass, while for industrial breeding, it can be considered as undesirably high. The presented analysis shows a big impact of farming style on the feedstock properties.

The chemical composition of ashes and their AFTs are summarized in Table 2. The elemental composition of ash is a feature of the specific biomass type, but the contents of ash-forming elements can be various even within a certain fuel type [52]. Therefore, the analyzed ashes show different quantitative chemical compositions and the farming style influenced the composition of ashes as strong as animal species. All the samples contain silica, calcium and phosphorus, but for free-range samples, the content of silica is significantly higher than for industrial farming. The massive difference in SiO_2 content can be observed for both cow manure (59.63–75.60% for free-range and 18.3–33.60% for industrial) and chicken litter (57.11% for free-range and 3.66–13.26% for industrial). The high concentration of silica in free-range animal-manure ash can be caused by contamination with sand and soil since animals can freely access the outdoor environment and consume grass directly from the ground.

Table 1. Proximate and elemental (ultimate) analysis of feedstock samples (a.r.—as received, d.b.—dry basis).

Parameter	Basis	Unit	Cow Manure				Chicken Litter				
			CD1_FR	CD2_FR	CD3_IF	CD4_IF [36]	CL1_FR	CL2_IF	CL3_IF	CL4_IF	CL5_IF
Moisture	a.r.	wt%	11.4	8.4	11.1	15.5	12.10	11.1	26.7	21.9	38.8
Ash	d.b.	wt%	21.4	22.06	16.99	13.86	30.10	17.09	9.31	10.70	7.10
HHV	d.b.	MJ/kg	17.26	16.93	17.91	19.04	12.22	17.22	15.60	16.90	16.60
	a.r	MJ/kg	15.49	15.5	15.92	16.09	10.97	15.31	11.40	13.20	10.20
LHV	d.b.	MJ/kg	15.78	15.86	16.72	17.84	11.32	16.02	15.20	15.80	16.10
	a.r.	MJ/kg	13.98	14.32	14.59	14.69	10.08	13.97	10.60	11.86	8.38
Cl	d.b.	wt%	0.086	0.33	1.02	0.54	0.11	0.99	0.96	0.66	0.82
C	d.b.	wt%	41.94	38.93	44.07	45.26	31.19	41.85	39.10	40.3	37.7
H	d.b.	wt%	5.38	4.89	5.45	5.53	3.91	5.5	5.10	5.40	5.20
N	d.b.	wt%	2.59	1.61	2.5	2.79	2.90	4.89	4.70	4.80	4.70
S	d.b.	wt%	0.34	0.32	0.47	0.32	0.50	0.97	0.73	0.75	0.31

Table 2. Ash analysis (dry basis) and ash fusion temperatures.

Parameter	Unit	Cow Manure				Chicken Litter				
		CD1_FR	CD2_FR	CD3_IF	CD4_IF [36]	CL1_FR	CL2_IF	CL3_IF	CL4_IF	CL5_IF
SO_3	wt%	0.88	1.18	4.45	2.63	1.02	9.68	0.94	1.01	0.82
K_2O	wt%	3.19	8.64	18.6	5.56	2.61	25.20	13.04	20.01	16.54
SiO_2	wt%	59.63	75.60	33.60	18.30	57.11	3.66	10.30	7.13	13.26
Fe_2O_3	wt%	1.52	1.11	1.24	1.06	1.94	0.92	4.10	4.11	1.84
Al_2O_3	wt%	4.28	2.65	1.95	1.31	4.15	0.48	1.66	1.11	2.81
Mn_3O_4	wt%	0.18	0.12	0.16	0.51	0.13	0.63	1.75	1.92	1.86
TiO_2	wt%	0.21	0.24	0.15	0.09	0.23	0.04	0.63	0.51	0.43
CaO	wt%	11.85	2.11	13.6	30.60	13.55	18.3	34.07	28.18	26.61
MgO	wt%	2.72	1.56	5.55	8.14	2.15	7.45	6.73	6.48	5.72
P_2O_5	wt%	8.21	4.09	10.8	17.50	7.81	21.00	19.23	22.49	23.74
Na_2O	wt%	3.57	0.73	2.66	3.20	3.21	3.87	6.80	6.26	5.74
BaO	wt%	0.02	0.04	0.05	0.03	0.02	0.03	0.15	0.17	0.14
SrO	wt%	0.02	0.02	0.03	0.04	0.02	0.05	0.34	0.39	0.31
Cl	wt%	0.65	7.56	6.55	2.57	0.90	5.67	-	-	-
						Ash Fusion Temperatures in reducing/oxidizing atmosphere				
initial deformation temperature (IDT)	°C	910/1020	1270/1260	1140/1130	1160/1230	1060/1140	1330/1400	-/1357	-/1254	-/1303
softening temperature (ST)	°C	1150/1240	1310/1290	1170/1170	1210/1270	1170/1210	1380/1470	-/1500	-/1500	-/1439
hemisphere temperature (HT)	°C	1370/1340	1460/1420	1200/1200	1320/1300	1300/1330	1430/>1500	-	-	-
flow temperature (FT)	°C	1410/1370	>1500/>1500	1310/1310	1430/1440	1320/1360	1490/>1500	-	-	-

Silica together with alkalis favors the formation of low-melting eutectics [45,53]. This is reflected in high AFTs for CL2_IF–CL5_IF samples that are low in silica. Lower AFTs of other samples are likely to be a result of a high silica-to-alumina (S/A) ratio. Liu et al. showed that the AFTs decrease with the increasing S/A ratio [54], and the S/A ratios of CD1_FR–CL1_FR samples are significantly higher than for other ones.

On the other hand, CL2_IF–CL5_IF ashes are characterized by higher concentrations of alkaline compounds, such as Ca (up to 34.07%) and K (up to 25.20%), which are mainly responsible for slagging and fouling. Contrarily, CD2_FR is characterized by the lowest concentration of calcium, 2.11%, and CL1_FR is characterized by the lowest concentration

of potassium, 2.61%. The alumina content differs significantly as well and is higher for free-range samples than for industrial ones.

The analysis found that some samples contain chlorine at extremely high levels, up to 7.56% (CD2_FR), which may result in an active oxidation process and lead to severe corrosion damage in the furnace. On the other hand, the chlorine content in CD1_FR was only 0.65%.

The ash characteristics of both cow manure and chicken litter cannot be considered advantageous and demonstrate their high potential for ash deposition, slagging, fouling and high-temperature corrosion. If these problems appear, they can be minimized by using aluminosilicate fuel additives, such as halloysite, kaolin or bentonite. Their positive influence on plant-origin biomass and coal combustion has already been studied and successfully proven [55–57].

3.2. Ash Morphology

The SEM pictures of the analyzed ashes are shown in Figure 1. They are presented at the magnitude of $1000\times$ (left column) and $250/500\times$ (right column) for optimal morphology characterization. Numerous fibrous structures can be observed in the majority of the investigated ashes (Figure 1a,c,g,i). Most probably, they come from remaining straw bedding or plants consumed by the animals. The only exception is the CD3_IF sample, whose structure is much finer, without fibrous particles (Figure 1e,f). In all free-range ashes, particles of SiO_2 are present (Figure 1b,d,h). They are likely to be sand particles, as sand can be unintentionally consumed by the animals together with grass, plants, etc., in the outdoor environment. This fact can explain the high silica content in all free-range ashes.
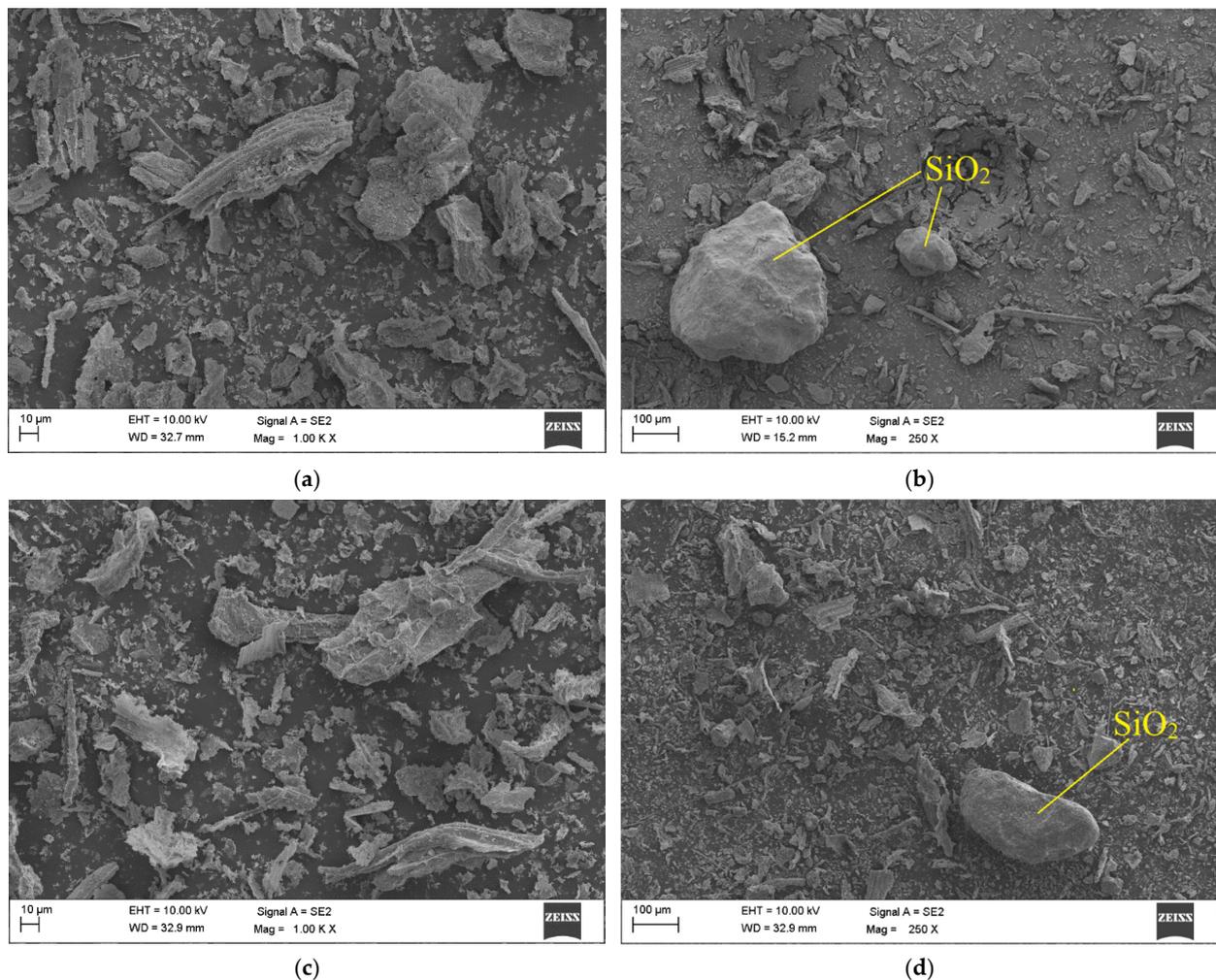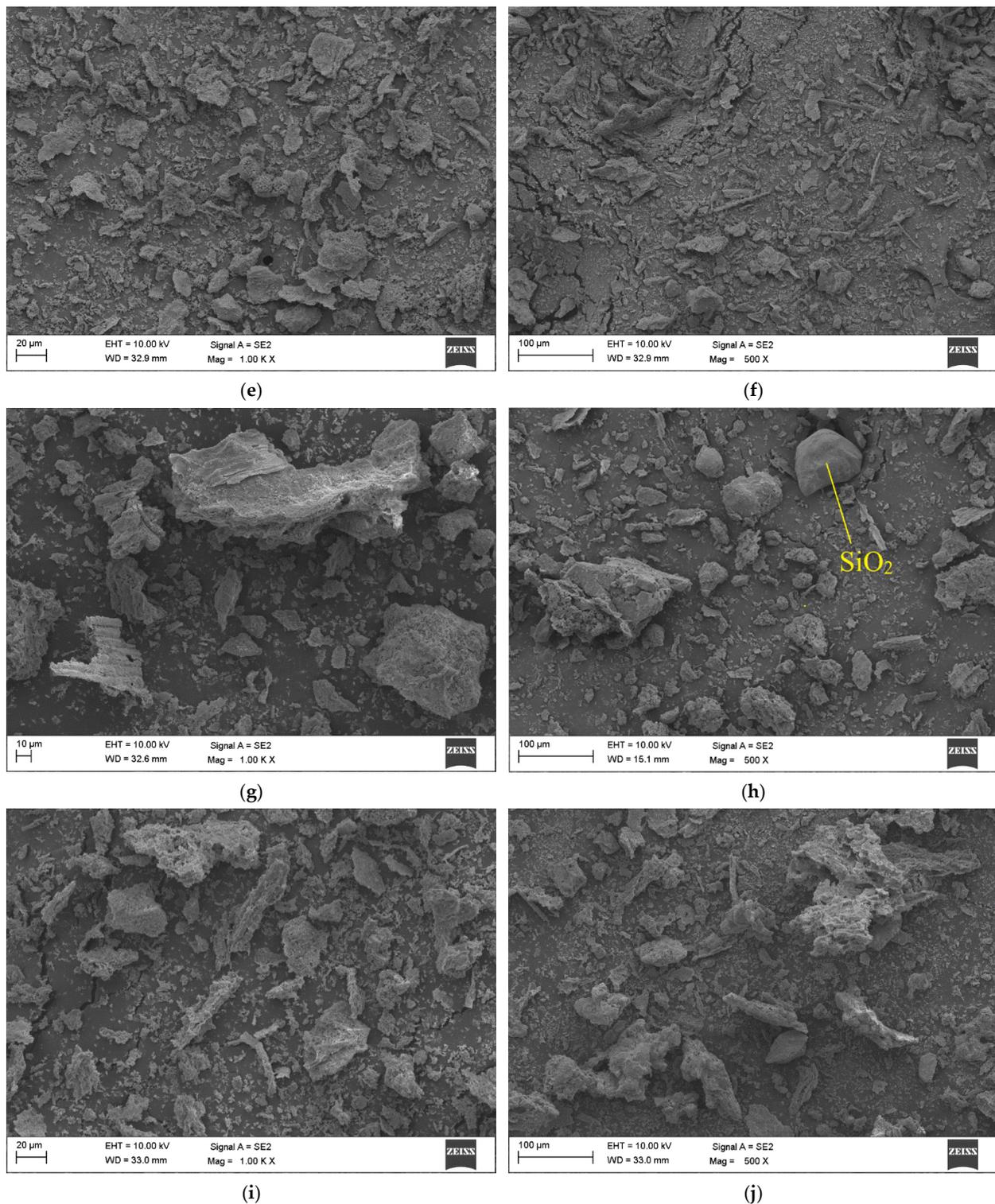

(a)

(b)

(c)

(d)

Figure 1. *Cont.*

Figure 1. SEM pictures of ash samples. (**a**) CD1_FR; (**b**) CD1_FR; (**c**) CD2_FR; (**d**) CD2_FR; (**e**) CD3_IF; (**f**) CD3_IF; (**g**) CL1_FR; (**h**) CL1_FR; (**i**) CL2_IF; (**j**) CL2_IF.

3.3. Ash Deposition Tendencies

Ash deposition is one of the most unfavorable issues connected to solid biomass fuels. According to the deposition indices, the particular fuel can be evaluated as low, moderately, highly or extremely hazardous [48–50]. The results of classification for all the samples are presented in Table 3.

Table 3. Deposition hazard evaluation according to 11 prediction indices (d.b.—dry basis).

	Index	Unit	CD1_FR	CD2_FR	CD3_IF	CD4_IF [36]	CL1_FR	CL2_IF	CL3_IF	CL4_IF	CL5_IF
1	SiO_2	%	59.63	75.6	33.6	18.3	57.11	3.66	10.3	7.13	13.26
2	Cl	% d.b.	0.086	0.33	1.02	0.54	0.11	0.99	0.96	0.66	0.82
3	B/A	-	0.48	0.23	1.47	3.35	0.50	18.36	6.67	10.00	4.86
4	BAI	-	0.22	0.12	0.06	0.12	0.33	0.03	0.21	0.16	0.08
5	Rs	-	0.16	0.07	0.69	1.07	0.25	17.81	4.87	7.50	1.51
6	Fu	-	3.27	2.18	31.23	29.37	2.94	533.69	132.32	262.79	108.28
7	Sr	-	78.75	94.05	62.23	31.50	76.40	12.07	18.66	15.53	27.96
8	μ_{alk}	kg/GJ	0.44	0.31	0.17	0.46	0.50	0.13	0.36	0.23	0.39
9	Initial deformation temperature IT	°C	1020	1260	1130	1230	1140	1400	1357	1254	1303
10	Softening temperature ST	°C	1240	1290	1170	1270	1210	1470	1500	1500	1439
11	AFI	°C	1084	1292	1144	1244	1178	1420	1086	1003	1042

Though the melting point of silica is 1700 °C, its combination with alkali, K and Na favors the formation of low-melting eutectics [45]. Thus, the index based on the SiO_2 content displays a high tendency of ash deposition for most free-range ashes that are rich in silica and low for most industrial farming ashes that are low in silica.

Chlorine is a key compound in ash fusibility since its presence leads to the forming of inorganic mixtures with Si and reducing their fluid temperatures to about 750 °C. The molten mixtures of alkali chlorides can merge, form larger droplets and thus initiate the formation of slag. Moreover, alkali vapors that contain chlorine are prone to condensation more than non-chlorinated volatile alkalis [58]. The free-range cow manure and chicken litter examined in this study contain chlorine at a relatively low level, comparable to plant-origin biomass. These two samples are classified as having low deposition risk. Contrarily, very high Cl content in other samples resulted in their classification as extremely dangerous.

For the B/A ratio, the results obtained in this study and in studies of Garcia-Maraver et al. concerning biomass fuels [43] disagree with the results presented in other studies, where a decrease in the B/A ratio is followed by an increase of HT and FT and results in the reduction of the slagging tendencies [59]. All industrial farming chicken litter samples, whose AFTs are high, are categorized as having high slagging risks. The CD1_FR sample, whose AFTs were determined to be lower than other samples, was classified to have a low slagging tendency.

When the B/A index is supplemented with the sulfur content, as stands in the Rs index, the results transform. Sulfur is expected to form sulfates during the combustion of fuels where alkalis are present; however, not when they are bound as silicates [60]. In this case, samples with lower SiO_2 contents are more prone to deposit formation.

Alkalis play a key role in the formation of deposits, especially with a low presence of chlorine [60]. For this reason, the B/A index can be complemented with the sum of Na_2O and K_2O, resulting in the Fu index. In this case, industrial-farming chicken litter samples are classified to have high deposition risk, while free-range ones and cow manure to be moderately risky.

According to the BAI index, samples show mixed results. The clear influence of the farming style on the Fe_2O_3 content in the tested samples is not observed.

The Sr index assumes that silica is one of the least responsible components of deposit formation. Hence, when applying this index to silica-rich free-range ashes, they are classified as low risk, while all industrial farming ashes are classified as highly dangerous.

The indices that are based on ATFs (IT, ST and AFI) classified industrial-farming chicken litter ashes as less risky than cow manure ashes. Especially the CL2_IF sample, whose AFTs can be considered as very high, is classified to have low deposition risk.

3.4. Metals and Metalloids Concentration

EU legislation on heavy metal concentrations regulates the agricultural applications of inorganic macronutrient fertilizers. The concentrations of selected elements in the analyzed samples, together with their regulation limits, are presented in Table 4. For phosphorus concentration, an assumption was made that all phosphorous in the ashes is in the form of P_2O_5 [9]. The recalculation was made with the following conversion factor according to EU Regulation 2019/1009:

$$\text{phosphorus (P)} = \text{phosphorus pentoxide (P}_2\text{O}_5) \times 0.436$$

Table 4. Concentration of selected elements in ash samples (dry basis) confronted with current UE limits.

	Unit	CD1_FR	CD2_FR	CD3_IF	CL1_FR	CL2_IF	CL3_IF	CL4_IF	CL5_IF	EU Regulation 2019/1009 [1]
P_2O_5	wt%	8.21	4.09	10.8	7.81	21.00	19.23	22.49	23.74	
P [2]	wt%	3.58	1.78	4.71	3.41	9.16	8.38	9.81	10.35	
Zn	mg/kg	980	493	938	846	2787	3400	2700	2700	1500 [3]
Hg	mg/kg	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	1
Cu	mg/kg	138	35	129	109	612	232	321	280	600 [3]
Cr	mg/kg	22	178	52	24	36	73	65	44	2 [4]
As	mg/kg	8.86	1.78	1.38	9.99	<1.0	<1.0	<1.0	<1.0	40
Cd	mg/kg	4.35	2.23	2.43	<0.05	2.93	0.19	0.13	0.17	3 [5]
Cd^{recalc}	mg/kg P_2O_5	52.98	54.52	22.50	<0.64	13.95	0.99	0.58	0.72	60 [6]
Ni	mg/kg	18.1	14.1	22.6	16.0	41.8	99.0	75.0	58.0	100
Pb	mg/kg	40.00	16.40	18.80	49.30	5.24	4.26	2.37	3.39	120

[1] The EU Fertilising Products Regulation 2019/1009 of heavy metals concentration in inorganic macronutrient fertilizers. [2] An assumption was made that all P in the ashes is in the form of P_2O_5. The conversion factor was used according to EU Regulation 2019/1009: phosphorus (P) = phosphorus pentoxide (P_2O_5) × 0.436. [3] These limit values shall not apply where copper (Cu) or zinc (Zn) has been intentionally added to an inorganic macronutrient fertilizer for the purpose of correcting a soil micronutrient deficiency. [4] The limit value is 2 mg/kg dry matter is for Cr (VI) while in this table the total Cr concentrations are given. [5] Where an inorganic macronutrient fertilizer has a total phosphorus content of less than 5% P_2O_5: 3 mg/kg dry matter. [6] Where an inorganic macronutrient fertilizer has a total phosphorus content of 5% P_2O_5: 60 mg/kg P_2O_5.

Phosphorus is the desired element, and therefore, it is important to evaluate its concentration in ashes from various sources and breeding systems. From Table 4 it is evident that industrial farming chicken litter ashes have greatly more phosphorus than other samples.

Mercury and copper contents in all samples are greatly below the limits of the EU regulations. They are the most volatile of the heavy metals hence even if present in the biomass, they volatilize during the combustion process, which is the reason for their very low concentrations in the ashes.

For cadmium concentration in fertilizers, the EU regulation has two different limits depending on the P_2O_5 concentration in the investigated material. When the P_2O_5 concentration is below 5 wt%, the limit is 3 mg Cd per kg dry matter. When the P_2O_5 concentration is above 5 wt%, the limit is 60 mg per kg P_2O_5. Evaluating the Cd levels in the ashes against the EU limit needs an assumption that all phosphorus in the ashes is bound in the form of P_2O_5. With the following assumption, the concentration of Cd is recalculated in Table 4 (Cd^{recalc} expressed in mg per kg P_2O_5), which indicates that the ashes have Cd concentrations below the EU limit.

Arsenic and lead concentrations are below the limits, and none of the samples is over the limit of nickel concentration as well; however, the CL3_IF sample is close to the limit.

The concentrations of zinc in industrial farming chicken litter ashes are beyond the limits of UE regulations, reaching 3400 mg/kg. For cow manure and free-range chicken litter ashes,

the limit is not exceeded. A possible explanation of the high Zn content is its addition as a food supplement. Zinc is used in industrial poultry breeding to improve reproduction, increase mass gain and boost egg production. High Zn content is, in general, an issue of animal-origin biomass. Nordin et al. [9] determined the Zn concentration in ash from the combustion of a mixture of horse manure and sewage sludge to 1400 mg/kg. Zhang et al. reported the Zn concentration in unprocessed chicken manure reaching up to 1063.32 mg/kg [61].

The elevated Cr concentration of chromium in all samples is likely to be a result of unregulated Cr limits in animal feed. Chromium concentration in chicken manure was reported to range up to 2402.95 mg/kg for a flock size of 2000–20,000 birds [61]. However, due to significant phosphorus concentrations, ashes with exceeded chromium levels can be used in a smaller amount as an additive for fertilizing products.

The limits of other metals and metalloids, such as Sb, Se, Sn, V, Mo and Co, in fertilizers are not controlled under EU regulations. In Table 5, the concentration of these elements in ash samples (dry basis) are presented together with their average concentrations in European or North American soils to assess the potential risk of their introduction into the environment.

Table 5. Concentration of selected elements in ash samples (dry basis) together with their concentrations in European/North American soils.

	Unit	CD1_FR	CD2_FR	CD3_IF	CL1_FR	CL2_IF	CL3_IF	CL4_IF	CL5_IF	Concentration in European/USA Soils
V	mg/kg	<0.05	29.7	15.1	34	13.4	88	49	36	median 60 [62]
Sb	mg/kg	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	0.02–31.1 median 0.60 [63]
Se	mg/kg	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	up to 600 [64]
Sn	mg/kg	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<2–106 median 3.0 [63]
Mo	mg/kg	5.59	10.90	11.80	6.25	46.50	43.00	31.00	40.00	<0.1–17.2 median 0.62 [63]
Co	mg/kg	6.07	2.97	4.57	7.61	3.66	31.00	10.70	7.03	0.1–7.0 [65]

The knowledge of vanadium behavior in soils is poor compared with other heavy metals, such as Cu, Pb and Zn. However, the median value of total vanadium concentration in European surface soils is 60 mg/kg, with maximum values up to 500 mg/kg. Most toxicity-based limits for unacceptable risks range from 90 to 500 mg/kg for those EU members that have established limitations for vanadium concentration in soils [62]. Thus, the content of vanadium in the tested ashes can be considered harmless.

The content of antimony, tin and molybdenum in the European surface soils was found to be in the ranges <0.02–31.1, <2–106 and <0.1–17.2 mg/kg, respectively [63]. Selenium was found in soils with concentrations up to 600 mg/kg [64]. The normal range of cobalt concentration in agricultural soils are 0.1–7.0 mg/kg [65]. Among these elements, only molybdenum is present in the investigated ashes in amounts exceeding the typical values of soil. However, molybdenum is a micronutrient necessary for the proper development of plants. Its deficit leads to the appearance of light flaws on the leaves, the death of buds and difficulty in the formation of leaf blades, and hence it was under investigation as a component of fertilizers [66]. On this basis, it can be concluded that the tested ashes do not pose a threat to the environment in terms of examined metal and metalloid contents.

4. Conclusions

It was found that the properties of animal-origin biomass strongly depend on the farming style, not only on the animal species. Whether it is cow manure or chicken litter, the free-range raw materials showed different fuel and ash characteristics than industrial farming ones.

Free-range materials are characterized by higher ash contents. The great difference can be observed in chlorine concentration: Free-range samples of both cow manure and chicken litter contain chlorine at lower levels, comparable to plant-origin biomass, while

industrial farming samples are chlorine-rich (up to 1.02% of Cl). Free-range samples are characterized by the predominant content of silica in the ash, up to 75.6% in cow manure and 57.11% in chicken litter. The high concentration of silica in free-range ashes is caused by the presence of sand particles that were found in all free-range samples by SEM analysis.

The samples were classified by 11 "slagging indices". Similar to plant-origin biomass, the coefficients display mixed results when applied to animal-origin biomass. The ash fusion temperatures of industrial farming chicken litter can be considered very high since these samples were classified to have low deposition risk by indices that are based on AFTs (IT, ST and AFI). On the other hand, based on chlorine concentration, all industrial ashes were classified as highly risky.

The content of phosphorous, metals and metalloids was determined in ash samples to assess their potential for agricultural application together with the risk of their introduction into the environment. Ashes from industrial chicken litter contain more phosphorus than other ones. The concentrations of Hg, Cu, As, Ni, Cd and Pb in all samples are below the limits established in the EU Fertilising Products Regulation of heavy metals concentration in inorganic macronutrient fertilizers. The concentrations of Cr in all samples and Zn in industrial farming chicken litter are beyond the limits of UE Regulation. A possible explanation is an intentional addition of Zn into the poultry feed as a food supplement. Cr can be present in the feed as well; however, its concentration in animals' food is not regulated in the EU. Such ashes can be processed as an additive to mineral fertilizers in small amounts, taking into account their elevated Zn and Cr concentration.

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