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Mineral composition and ash content of six major energy crops

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Abstract

A major barrier to the growing of energy crops is the weak knowledge on their suitability for conversion plants, which greatly depends on chemical composition of raw materials. In this study, ash and mineral composition (C, N, Al, Ca, Cl, Fe, K, Mg, Na, P, S and Si) of major annual and perennial energy crops (switchgrass, miscanthus, giant reed, cynara, sweet sorghum and fibre sorghum) were analysed keeping leaves, stems and reproductive organs separate. As general, it resulted that biomass quality can greatly change depending on crop and, importantly, on biomass composition. Leaves were much more concentrated in ashes and minerals than reproductive organs and stems, in this order. Among the crops, cynara exhibited the clearly highest ash and mineral content, thus resulting in a major slagging, fouling and corrosion tendencies. Giant reed also showed a high leaf ash and mineral content, especially N and S. Nonetheless, its stems had a fourth of ashes and much less minerals, especially N, Si and Ca. Overall, this occurred in all stems, however, in cynara, and secondary giant reed, S and N were found to be above or proximate to recommended thresholds also in stems. Chlorine appears the most stumbling-block, always exceeding the limit, both in stems and leaves. It is perceived that, though leaves and reproductive organs may represent a significant biomass component, they gravely reduce the biofuel quality. Therefore, agricultural strategies aimed at increasing leaf or seed loss (e.g. delaying the harvest), though it will somewhat decrease the total yield, may be expected to considerably improve the suitability of these crops for conventional combustion plants.

Keywords: Miscanthus; Arundo; Panicum; Sorghum; Switchgrass; Giant reed; Cynara; Cardoon; Biofuels; Organs.

1. Introduction

According to the common European energy policy, biomass crops should increasingly contribute towards meeting the energy needs [1], with millions of hectares being expected to be allocated to dedicated crops in a very short-term [2]. So far, major efforts have been addressed to evaluate the potential yields of several dedicated crops under variable agro-techniques and environment [3,4,5,6]. Conversely, the quality of biofuels for thermo-chemical processes have not received much attention [7,8], and now it represents a major barrier to the growing of dedicated crops. The biomass quality can drastically lower the net energy output, both limiting the effectiveness of conversion plants [8], and decreasing the heating value. It was, in fact, demonstrated that heating values has been negatively related to ash content, with every 1% increase in ash concentration decreasing the heating value by 0.2 MJ kg^{-1} [9]. More than this, ashes and inorganic elements (e.g. alkali) realised during the combustion may cause a number of serious problems to the power plants, such as slagging, corrosion and fouling. The basic mechanisms describing these processes are now reasonably well understood [10]. In short, fouling leads to a decrease in the exchanger efficiency; slagging is related to the low melting point of deposits, which causes the formation of a glassy layer that must be removed. Finally, corrosion may be caused by the interaction between deposits and metal surface of the exchanger, which leads to an increase of the extra-costs in maintenance, whilst decreasing the plant life-span [11]. Importantly, the degree of fouling, slagging and corrosion is strictly related to ashes and minerals released during the combustion [8], a property which can substantially change among crops [6,12]. Therefore, classifying biomass crops as mineral composition will be helpful for understanding how the conversion technology can be adapted to different kind of biofuels, or how the properties of fuels might be modified, according to the conversion technology. For example, it is well-known how, during combustion, the volatile elements, such as S and Cl, can form sub-micron particles condensing as salts [13], which in turn, at elevated temperatures and in presence of K and Si, may lead the sticky deposit to grow-up rapidly [14]. Herbaceous crops are generally rich of K and Si, the first representing about 1% of the biomass dry weight and almost all potentially vaporizing during combustion. Because of its high melting point (1700 °C), Si would be not a problem in itself, however, the concurrent high presence of K or Ca, makes Si to easily react with them forming alkali silicates with a much lower melting points (about 700 °C) [13]. Again, other alkali elements, such as Na, Mg and their salts, chlorides, carbonates and sulphides, may form eutectics. Likewise, P can increase the slagging potential of deposits [13].

The ratios between K, Ca and Si should be also taken into great account because of their influence upon slagging. For example, Reumerman and van den Berg (2002) [11] showed as miscanthus having high Si/K and Ca/K ratios exhibited a less tendency towards slagging. It is therefore perceived that, irrespective of yield levels, biomass crops containing high Si and Ca, along with low K, should be better indicated for the energy end use. Nonetheless, it should be underlined that raw materials are also rather rich in Cl, a major factor in deposit formation. Chlorine may react with K thus leading to the formation of primary fouling compounds. Again, Cl also has a shuttle role in transporting alkali to surfaces, and its presence increases the corrosion of tubes used in both biomass power plants and heat exchanger [13].

The variable ash and mineral content within dedicated crops can be explained by genetic and environmental effects [15], as well as by the physiological and morphological differences of crops.

Leaves, stems and reproductive organs exhibited in fact different properties, leaves resulting generally much richer in ash content than the other organs [16,17]. Since biomass partitioning may drastically change depending on crops and agricultural strategies, or in a standing crop over the growing season [3], understanding the ash and mineral composition of different crops and at different organs may be very helpful in choosing the most appropriate agricultural strategy for each crop (e.g. harvest time). Therefore, in this research six energy crops (two annuals and four perennials) were characterized in term of their mineral composition and ash content, at different plant organs.

2. Materials and Methods

2.1. Plant material

Four perennial (*Miscanthus sinensis X Giganteus* Greef & Deuter, *Arundo donax* L., *Cynara cardunculus* L. and *Panicum virgatum* L.) and two annual crops (sweet and fibre sorghum, *Sorghum bicolor* Moench.) were characterized on the basis of their mineral composition and ash content, at different plant organs (leaves, stems and reproductive organs). Switchgrass (*Panicum v.*) was also investigated at 20 and 80 cm row-distances. Since in a parallel trial (unpublished data) comparing switchgrass varieties the biomass composition was found to significantly change from young (one or two years old) to more mature plants, the samples of perennial crops were collected from a fourth year plant.

Crops were arranged according to completely randomized blocks with four replications (about 400 m^2 each), in a plain soil at the experimental farm of the University of Bologna (Cadriano, 44° 33’ N, 33 m a.s.l.). The main soil physical and chemical characteristics are presented in Table 1. For each crop, the most conventional practice was adopted. During seedbed preparation all plots were fertilized with 31 kg ha^{-1} of P. In fibre and sweet sorghum, the N fertilization (urea) at a dose of 100 kg ha^{-1} of N was applied about 20 days after emergence. Plots were kept free of weeds until sown or plantation. Switchgrass and sorghum were sown on late April using a mechanical drill-machine

(Vignoli s.r.l.), while cynara was manually sown. Giant reed and miscanthus were hand-planted on early May by placing rhizomes into 150 cm row-spaced furrows. The average plant densities resulted: 13 plants m^{-2} for sweet and fibre sorghum; 2 plants m^{-2} for miscanthus, 1 plants m^{-2} for giant reed, 168 and 62 plants m^{-2} for switchgrass (20 and 80 cm row distances, respectively), 4 plants m^{-2} for cynara. For all the crops, irrigation and chemical products against pests and disease were not necessary. The annual crops and cynara were hand-harvested in September, while the other crops were harvested during wintertime (on early February). After the harvest, a sample of each crop and replication was split into three sub- samples including leaves, stems and reproductive organs (about 500 g each). Thereafter, samples were dried (60°C for 24 h), accurately grounded, and finally stored for the ash and mineral determinations.

2.2. Ash and mineral analysis

According to the ISO 1171-1981 (550 °C for 12 hours), the ash content was determined on a representative sub-sample of 3 g of each organ using a muffle furnace. Likewise, C and N concentrations were determined on a 3 g sub-sample by a CHN-elemental analyser (Carlo Erba - 1100) based on flash-combustion principle. Wet-digestion was also applied before mineral analysis using a microwave oven (Microdigest A-301, Prolabo). Briefly, a sample of plant material was placed into a PTFE-bomb together with 6 ml HNO_3 65%, 1 ml H_2O_2 30%, and 0.3 ml HF. After that, it was wet-digested. Organic matter was mineralized by a concentrated solution of HNO_3 and H_2O_2, while the less soluble inorganic compounds were attacked using HF. The use of HF in addition to HNO_3 is justified by the need to recover a higher amount of Si, HF being the only acid enabling to decompose silicates into a colloidal form [18]. Since HF was used during the analysis, glass vessels and spraying systems were carefully avoided, thus to prevent Si contamination [19]. Samples were then air-cooled and diluted in 20 ml of distilled water. Again, in order to prevent Si contamination from glasses, within 30 min after dilution, samples were transferred to a plastic recipient. Al, Ca, Cl, Fe, K, Mg, Na, P, S and Si were determinate by an inductively-coupled plasma atomic emission-spectrometry (ICP-AES), equipped with HF- resistant sample introduction system. The standard BCR-60 *Lagarosiphon major* by the Community Bureau of Reference (BCR, Belgium), was used as reference material for spot-checks during the analysis.

All data were subjected to statistical analysis according to the general linear model (GLM). When the statistical test revealed significant differences, the least significant Fisher's test (LSD) for $P \leq 0.05$ was used to separate means. Pearson's correlation test at $P \leq 0.05$ was used to assess the significance of correlation coefficients.

3. Results

3.1. Comparing leaves

Cynara and giant reed showed the highest ash content, about 50% higher than the other crops (Table 2). Along with sweet and fibre sorghum, giant reed also showed the highest N, and together with cynara, the highest S, too. Cynara exhibited the highest Al, Ca, Cl, Fe, Na concentrations, and along with the two sorghum types, the highest P. Alike switchgrass (at both row-spacings), cynara showed the lowest Si and Si/K ratio. Chlorine showed a very wide range of variation, resulting the lowest in sweet and fibre sorghum, and curiously, in switchgrass 80 cm row-spaced, as well.

Overall, the two sorghum types appeared very similar, as well as switchgrass at variable row-distances. The only differences between sweet and fibre sorghum were K, almost 33% higher in the sweet type, and Si, about 30% higher in fibre sorghum (Table 2). Switchgrass showed about a threefold Cl and a much lower Ca/K ratio at the narrower row-distance (Table 2).

3.2. Comparing stems

Once more, cynara exhibited the highest ash content, followed by fibre and sweet sorghum (Table 2). The latter also showed the highest N, along with giant reed. The other crops did not significantly differ in N, which ranged between 2 and 3 mg kg^{-1} (dry matter basis). Giant reed exhibited the lowest Ca, which was conversely exceptionally high in cynara, along with Na, S, P and Cl. Nonetheless, giant reed resulted in the clearly highest Al concentration, almost 90% higher than switchgrass (Table 2). Surprisingly, Cl greatly changed between switchgrass 20 and 80 cm row-spaced. Sweet and fibre sorghum had the highest K and Mg, while switchgrass the lowest (at both row distances), together with miscanthus. The lowest Si was found in cynara, while the highest one in sweet sorghum. The difference in Si between the leaves of two sorghum types were not confirmed in stems (Table 2).

3.3. Comparing reproductive organs

Reproductive organs may be a basic determinant of the biomass quality, representing up to about 30% and 35% of the total dry matter yield in sorghum and cynara, respectively [20,21]. For all crops, ash content was similar to that of stems, while N was much higher and approximated that of leaves. Alike leaves and stems, capitula exhibited a very high Ca, Cl and Na content. Unlike leaves and stems, K resulted much higher in cynara than in sweet and fibre sorghum. Again, Si was very low in cynara and very high in sorghum, especially in sweet one. Nonetheless, sorghum also exhibited a much higher Si/K ratio with respect to cynara (Table 2).

3.4. Relationships among minerals

A number of significant correlations has been found between different elements, both at a whole crop level and at a similar organs. For example, irrespective of crops and organs, ash content was found to be strictly related to C (-0.80**) and Ca (0.74**), and secondary to Na, Si and Cl (-0.58*, 0.50*, -0.47*, respectively). Equally, N was positively related to K (0.61*) and P (0.60*), and negatively to Si/K and Ca/K ratios (both -0.77**). Chlorine resulted negatively related to Si, Si/K and Ca/K (-0.55*, -0.47* and -0.41*, in this order). Again, K was highly related to P (0.93**), and to a lesser extent to Mg (0.63*). Phosphate was negatively associated to Si/K and Ca/K ratios (-0.69** and -0.77**, respectively), oppositely to what observed for Si (0.86** and 0.75**). The high correlation between Si/K and Ca/K is also noteworthy (0.96**).

As for single organs, only few striking correlations were found in leaves (Table 3). Among these, Si to Al, Ca, and Na, as well as between ash content and S.

Stems resulted in overall higher correlations between minerals. For example, ashes were highly and positively related to Ca, P, S, Na and Ca/K ratio, and negatively to C and Si/K ratio (Table 3).

Chlorine resulted strongly and positively related to Na, and to a lesser extent, to P and S. Na was also negatively related to Si, and positively to Ca/K ratio. The latter was positively and negatively associated to S and Si, respectively. Noteworthy, K was closely related to Mg.

The relationships between minerals in reproductive organs (panicle and capitula) were even more remarkable. For example, Cl was very closely associated to nearly all minerals, with correlation coefficients being over 0.80 for S, Na and K (positive relationships), and Mg and Si (negative correlations). Similarly, correlation coefficients over 0.90 were found between K and Mg, Na, S and Si (Table 3).

The relationships between leaves and stems on ash content resulted significant only when giant reed was not included into the analysis (Fig. 1). Finally, very few elements resulted correlated in leaves and stems (Fig. 1).

4. Discussion

Understanding the variation in chemical composition of different raw materials is strongly need to develop an effective biomass energy technology. Major problems, encompassing the reduction of process efficiency and the increase maintenance costs, may in fact arise from the use of low-quality sources [14]. We are aware of only few studies comparing the quality of dedicated energy crops [9,22,23,24]. Nonetheless, these studies report some contrasting results, both on quantitative and qualitative mineral compositions, thus suggesting the need of further *ad hoc* researches (Lewandowski et al., 2003 [23] for an extent review). For example, Miles et al. (1996) [14] reported an high ash and alkali content in switchgrass, thus to indicate this crop to be unsuitable for combustion in conventional boilers. In contrast, McLaughlin et al. (1996) [24] pointed out that switchgrass has typically a low alkali content and consequently a low slagging potential.

In the present study, it clearly resulted that biomass quality can drastically vary according to whether the crop and biomass partitioning are. For example, cynara exhibited a notable ash content, while sorghum and giant reed resulted more concentrated in N. Cynara also showed a high concentration in Ca, S and Cl, yet it exhibited the lowest Si content too. A high Si content was conversely found in both sorghum types. Moreover, the relationships between biomass organs was often insignificant (e.g. Ca, Si, Al), with ashes or minerals resulting, for example, abundant in leaves and scarce in stems, or *vice versa* (e.g. ashes in giant reed, Al in cynara and Si in fibre sorghum). As a consequence, if a crop is more or less suitable for combustion will not only depend on whether the crop is, but on biomass composition at harvest time, too. This may be highly relevant as biomass composition can be, to some extent, modified by pursuing strategic agricultural practices (e.g. delaying the harvest or using chemicals accelerating the leaf senescence). Furthermore, the unlike mineral composition of different organs should be taken into great account as literature commonly reports ash and mineral composition of crops as a whole, i.e. without distinguishing the different biomass components. Miscanthus, for example, is usually known to have a low (*c.* 700 °C) ash melting point [3,23,24,25], which is likely to be related to simultaneous presence of high Si, K and Ca, as Si in itself has a high melting point [13]. In the present study, Si, as well al Ca, resulted mostly concentrated in leaves, while K was equally distributed between leaves and stems. Therefore, it is perceived that agricultural strategies addressed to reduce leaf components might significantly increase the ash melting point and suitability of miscanthus. Nevertheless, this may be also true for the other crops. In fact, regardless of crops, leaves always showed the clearly highest ash content, almost double than stems, and about 50% higher than reproductive organs (Table 3). Likewise, leaves exhibited an overall much higher mineral concentration than other portions. Specifically, leaves showed the highest Al and Fe, and, along with reproductive organs, the highest N, Ca, Mg, S and Si. It is also true that leaves showed the highest Si/K and Ca/K ratios, thus to partially offset the negative effects the high Si and Ca [11]. It derives that, in a drying standing crop with a large number of leaves falling down, a significant better quality of biomass can be provided by delaying the harvest [26]. This is also consistent with recent findings on pyrolysis of switchgrass at variable stage of maturity [27]. Nonetheless, it should be also taken into account that leaf loss entails a lower marketable dry matter yield for farmers, up to about 20% in giant reed and sorghum [21,23]. Besides, crops are differently prone to preserve leaves during ageing. For example, it was observed that giant reed, miscanthus and cynara had a significant reduction of leaves in a post-frost harvest, while switchgrass has a moderate inclination in leaf loss [16]. Therefore, how delaying the harvest positively affects the biomass quality will greatly depend on environment and crop-specific dynamic of the biomass composition during the senescence.

In addition to leaf loss, mineral translocation from leaf tissues to rhizomes during crop drying may significantly improve the biomass quality. However, the extent of mineral translocation during crop ageing is still debatable, as literature reports contrasting results on this topic. For example, some authors [24,28], reported that in a number of perennial crops, the late harvest K-levels were strongly reduced with respect to those from an early harvest. In contrast, Sladden et al. (1991) [29] observed an opposite trend, while Monti et al. (2004) [30] reported the ashes to fall in late summer then rise again until approximating initial values. Dien et al. (2006) [22] observed the ashes of switchgrass to drop down until anthesis, whilst other elements (Ca, Si, P and Mg) increasing. This was however not corroborated by parallel findings on similar grasses [22].

In this study, a single harvest was performed for each crop, and thus the extent of mineral translocation could be not detected. However, remarkable differences in ash and N content are clearly visible in the leaves of giant reed and switchgrass or miscanthus, all three crops subjected to concurrent pos-frost harvest. Therefore, it appears that ash and mineral composition are much more crop- or biomass composition-dependent than on mineral translocation. Anyway, whatever will be the extent of mineral translocation, it runs in parallel with leaf senescence thus to further support the post-frost harvest from the energy standpoint.

We are aware of very few reports indicating recommended mineral thresholds to ensure low emissions and corrosion risks using conventional boilers [11,31]. According to these reports, stems resulted generally in a lower N and S concentrations than recommended (i.e. 6 and 1 mg kg^{-1}, respectively, [11]). The only clear exception was cynara for S, though giant reed also showed S and

N values proximate to the respective thresholds. Conversely, all crops exceeded the recommended Cl concentrations of 1000 $\mu g\ kg^{-1}$ [11]. However, Cl was also the elements having the highest variation coefficient, thus meaning that a crop can be easily found to be exceeding or having acceptable Cl values. So far, no clear explanation has been given about the inherent or environmental causes related to Cl variation. Importantly, in all crops leaves and reproductive organs, N, Cl and S visibly exceeded the indicated limits.

5. Conclusions

Cynara resulted the crop having the highest ash and mineral content and thus with major slagging, fouling and corrosion tendencies, according to other findings [11]. As general, the main problem in all crops resulted the high concentration of Cl, and secondary S, which increase the risks of corrosion and HCl-emission. Again, the highest Cl content was found in cynara, which imply that special measures have to be taken for this biofuel. In the case of giant reed, N resulted slightly lower than acceptable limit, therefore primary and secondary measures to prevent NO_x emissions may be required for this crop. Switchgrass (especially in spaced row-distance) and miscanthus showed the overall better biomass quality. Stems resulted much better than leaves and reproductive organs, and in most cases they showed acceptable mineral concentrations. Therefore, opportune agricultural strategies leading to biofuels with major stem component should be addressed. For example, post-frost harvest, though resulting in a likely lower total biomass yield, could provide a significantly better quality of feedstocks, both for leaves loss and mineral translocation during senescence.

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Table 1. Main physical and chemical characteristics of the soil.

Parameters	Units	Methods	Values
Sand	(g kg^{-1})	Bojoucos	270
Silt	(g kg^{-1})	Bojoucos	390
Clay	(g kg^{-1})	Bojoucos	340
pH		H_2O	7.2
SEC		meq 100g^{-1}	48.2
Organic matter	(g kg^{-1})	Walkey-Black	18
Total N	(μ g g^{-1})	Kjeldahl	1196
P-avail.	μ g g^{-1}	Olsen	20
K-exch.	μ g g^{-1}	$BaCl_2$ + Tea	265
Ca-exch.	μ g g^{-1}	$BaCl_2$ + Tea	4592
S	μ g g^{-1}	(Sulphate)	125
Mg-exch.	μ g g^{-1}	$BaCl_2$ + Tea	368
Na	μ g g^{-1}	$BaCl_2$ + Tea	48

Table 2. Ash and mineral concentration in leaves, stems and reproductive organs (capitula and panicula). Ash, N and C are expressed as g kg^{-1}, all the others as mg kg^{-1}.

Plant organ	Ash	N	C	Al	Ca	Cl	Fe	K	Mg	Na	P	S	Si	Si/K	Ca/K
Leaves															
Arundo d.	113 a	15.7 a	430 a	461 b	6167 bc	6986 ab	308 b	5080 c	2182 ab	159 b	803 b	3511 a	17232 b	3.4 bc	1.2 c
Cynara c.	117 a	9.6 bc	417 b	1781 a	27802 a	13143 a	655 a	4711 cd	1876 ab	11942 a	1459 a	3760 a	4267 c	0.9 c	6.1 a
Miscanthus s.	62 c	6.3 c	431 ab	595 b	5262 c	6701 ab	324 b	3265 cd	1291 b	193 b	396 b	867 b	16666 b	5.1 b	1.6 c
Panicum v. 20	76 b	7.4 bc	423 ab	543 b	6922 bc	9490 a	319 b	2126 cd	2706 a	326 b	774 b	991 b	15745 b	8.0 a	3.6 b
Panicum v. 80	70 bc	8.4 bc	428 a	435 b	8182 b	3617 b	283 b	1504 d	2626 a	317 b	578 b	1048 b	15036 b	10.1 a	5.5 a
Fibre *s.*	81 b	13.4 a	424 ab	483 b	9245 b	4737 b	236 b	8805 b	3086 a	195 b	1246 a	1105 b	19736 a	2.3 bc	1.1 c
Sweet *s.*	82 b	13.5 a	425 a	328 b	8359 b	3741 b	186 b	11661 a	2805 a	189 b	1273 a	1099 b	14858 b	1.3 c	0.7 c
mean	86	10.6	425	661	10277	6916	330	5307	2367	1903	933	1769	14791	4.4	2.8
Stems															
Arundo d.	32 bc	5.2 a	431 a	196 a	968 c	5608 c	102 a	5609 b	1027 b	130 b	320 bc	932 b	6223 a	1.1 b	0.2 b
Cynara c.	68 a	3.0 b	401 b	150 b	12190 a	18171 a	79 ab	6467 b	766 b	12807 a	1363 a	1740 a	889 c	0.2 c	2.1 a
Miscanthus s.	19 c	1.6 c	439 a	143 b	1730 bc	7406 c	61 b	3588 c	857 b	153 b	154 c	337 c	4531 b	1.3 ab	0.5 b
Panicum v. 20	26 c	3.0 b	435 a	137 b	1097 bc	13798 b	86 ab	3555 c	1020 b	870 b	404 bc	464 bc	5345 ab	1.5 ab	0.3 b
Panicum v. 80	23 c	3.3 b	440 a	111 b	1197 bc	4944 c	83 ab	2628 c	1171 b	870 b	248 c	443 bc	5301 ab	2.1 a	0.5 b
Fibre s.	41 b	2.6 bc	409 b	114 b	2643 b	6398 c	79 ab	12577 a	1903 a	193 b	702 b	817 b	5345 ab	0.4 c	0.2 b
Sweet s.	50 b	4.4 a	408 b	152 b	3446 b	7199 c	112 a	12991 a	2079 a	195 b	804 b	681 b	7013 a	0.5 c	0.3 b
mean	37	3.3	423	143	3325	9075	86	6774	1260	2174	571	773	4950	1.0	0.6
Reproductive organs															
Cynara c.	67 a	14.3 a	444 a	106 b	9960 a	9863 a	71 b	19325 a	1815 c	1340 a	2427 a	1708 a	474 c	0.0 b	0.5 a
Fibre s.	47 b	13.1 a	434 b	242 a	1824 b	6252 b	141 a	5587 b	2451 b	192 b	2150 a	1084 b	10671 b	2.0 a	0.3 b
Sweet s.	58 a	14.1 a	424 b	218 a	2417 b	5129 b	159 a	7125 b	2895 a	171 b	2620 a	1000 b	14321 a	2.0 a	0.3 b
mean	57	13.8	434	189	4734	7081	124	10679	2387	567	2399	1264	8489	1.4	0.4

Table 3. Significant (P≤0.05, Pearson's correlation test) correlation coefficients between minerals at different plant organs.

Plant organ	Ash	N	C	Al	Ca	Cl	Fe	K	Mg	Na	P	S	Si	Si/K
Leaves														
N	0.50													
C	-	-												
Al	-	-	-											
Ca	0.60	-	-	0.85										
Cl	-	-	-	-	-									
Fe	-	-	-	0.87	0.71	-								
K	-	0.60	-	-	-	-	-							
Mg	-	-	-	-	-	-	-	-						
Na	-	-	-	0.83	0.92	-	0.57	-	-					
P	-	-	-	-	-	-	-	-	-	-				
S	0.89	-	-	0.58	0.63	-	-	-	-	0.68	-			
Si	-	-	-	-0.74	-0.82	-	-0.54	-	-	-0.83	-	-		
Si/K	-	-0.53	-	-	-	-	-	-0.75	-	-	-0.66	-	-	
Ca/K	-	-	-	0.60	0.63	-	0.61	0.61	-	0.56	-	-	-0.63	-
Stems														
N	-													
C	-0.92	-												
Al	-	-	-											
Ca	0.85	-	-0.72	-										
Cl	-	-	-	-	0.68									
Fe	-	-	-	-	-	-								
K	-	-	-0.76	-	-	-	-							
Mg	-	-	-	-	-	-	-	0.78						
Na	0.76	-	-	-	0.94	0.77	-	-	-					
P	0.83	-	-0.76	-	0.72	0.66	-	-	-	0.72				
S	0.84	-	-0.74	-	0.88	-	-	-	-	0.84	0.67			
Si	-	-	-	-	-0.76	-0.63	-	-	0.51	-0.82	-	-		
Si/K	-0.79	-	0.87	-	-0.63	-	-	-0.70	-	-	-0.65	-0.66	-	
Ca/K	0.65	-	-	-	0.86	0.64	-	-	-	0.91	-	0.70	-0.80	-
Reproductive organs														
N	-													
C	-	-												
Al	-0.68	-	-											
Ca	0.71	-	0.66	-0.92										
Cl	-	-	-	-0.81	0.84									
Fe	-	-	-	-	-	-0.63								
K	0.69	-	-	-0.93	0.99	0.84	-0.58							
Mg	-	-	-0.76	0.72	-0.81	-0.79	0.69	-0.78						
Na	-	-	0.77	-0.88	0.96	0.86	-	0.94	-0.85					
P	-	0.79	-	-	-	-	-	-	-	-				
S	-	-	0.77	-0.87	0.95	0.88	-0.61	0.93	-0.91	0.97	-			
Si	-	-	-0.76	0.87	-0.91	-0.85	0.70	-0.90	0.95	-0.92	-	-0.95		
Si/K	-	-	-0.63	0.93	-0.92	-0.81	0.71	-0.94	0.84	-0.91	-	-0.89	0.93	
Ca/K	0.69	-	0.67	-0.71	0.86	0.71	-	0.78	-0.69	0.85	-	0.84	-0.78	-0.66

Figure caption

Relationships between leaves and stems on ashes, K, P and Si/K ratio. R, correlation coefficient; **, significant for P≤0.01 (Pearson's correlation test). G, giant reeed; M, miscanthus; S, switchgrass; FS, fibre sorghum, SS, sweet sorghum; C, cynara. In the top-left figure, giant reed was not included into correlation analysis. Units are: ashes, % (d.b.); P and K, μ g kg^{-1}.