Inorganic Elements of Mangium Stem (*Acacia mangium* Willd) from Different Provenances

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Abstract

This study aimed to investigate the ash content and concentrations of inorganic elements present in the stem of *Acacia mangium*. The tree samples (24 years) were collected from five different provenances (Sidei, West of Morehead, Daintree, Ellerbeck, and El Arish). Meanwhile, the disc samples were obtained from the trunk of each tree on the lower parts. The samples were collected from four radial positions (bark, sapwood, outer heartwood, inner heartwood), and the ash and insoluble acid contents were determined. Furthermore, the concentration of 5 elements (Ca, Mg, Fe, Mn, K, and Na) was measured by Atomic Absorption Spectrophotometry (AAS). The interaction of provenance and radial position factors affected ash and potassium contents. Also, acid insoluble ash and calcium contents showed a provenance factor effect. The barks obtained from the tree samples contained the highest concentrations of ash content and most of the elements. The wood and bark of El-Arish provenance showed the lowest (0.50~0.72%) and highest levels (4.75%) of ash content respectively. Furthermore, the highest amount of insoluble acid ash (3075 ppm) and calcium (4513 ppm) content was also measured in samples of El-Arish provenance, and radial position factor was a significant source of variation for Ca, Mg, Na, and Mn concentrations. Except Mg, the inner and outer portions of the heartwood mostly showed no significant difference in unprecedented element concentrations. Ash content was positively correlated with Ca in sapwood (r=0.39) and Mn in bark (r=0.54). In addition, moderate correlations were observed between Mg and Ca in heartwood (r=0.63) and bark (r=0.54) tissues. For ash and silica content, the comparatively low concentration on samples from El-Arish provenance are good options to improve wood quality for breeding programs.

Keywords: trace elements, silica, tree breeding, fast-growing, wood chemistry, mangium (*Acacia mangium*).

Introduction

Mangium (*Acacia mangium*) is one of the most important timber plant commodities in the tropics. In Indonesia, this species is planted on a large scale through the Forest Estate Timbers program due to its fast growth, good adaptability, high resistance to diseases, and multi-purpose uses. Primarily, the mangium wood is used by the pulp and paper industries, especially at a young age.

Furthermore, the rise in the consumption of wood products has tremendously increased the demand for mangium. The wood is used as an alternative for non-pulp products (furniture, veneers, sawn-timbers, and other products) by extending its rotation cycle to meet the commercial size of the tree. Meanwhile, several studies have focused on assessing the feasibility of mangium wood and bark for panel construction as well as adhesive production (Korai *et al.* 2000; Yano *et al.* 2003; Firmanti *et al.* 2007; Subyakto *et al.* 2003; Subyakto *et al.* 2005). The properties of this wood are undoubtedly affected by its inorganic or mineral components, for instance, the high silica contents cause deterioration of the cutting tools (Shmulsky and Jones 2011) and resistance to damage caused by insects as well as marine borers (De Silva and Hillis 1980). In addition, other major inorganic components cause wood adhesion (Kanazawa *et al.* 1978), blackening (Takahashi 1996; Minato and Morita 2005), and tree growth (Kuhn *et al.* 1997).

Regarding raw materials, few studies have measured the quality of mangium based on its origin or tree breeding. Furthermore, the difference in seed source and the influence of climate affect the properties of wood. Previous studies based on tree geographical or differences in provenance have compared chemical properties and fiber dimensions of mangium wood (Syafii and Siregar 2006; Raphy *et al.* 2011) the wood's physical and mechanical properties (Hadjib *et al.* 2007). In the tree breeding programs for the production of high-quality raw materials, it is important to consider the properties of wood as a basis of selection criteria. There is little information on the chemical properties of mangium wood, particularly with regard to breeding programs. In addition, the inorganic components of mangium wood is less explored. Previous reports have examined the color, anatomical, and various chemical properties of mangium wood (Lukmandaru *et al.* 2011a, 2011b; Lukmandaru 2012; Nugroho *et al.* 2012). Therefore, this research aimed to determine variations in the value of inorganic matter content based on differences in provenance and radial direction. In addition, the degree of relationship between inorganic substance parameters was also analyzed.

Materials and Methods

Plant Materials

The "Provenances Trial Site" for mangium is located in the Wanagama Educational Forest, Gunungkidul Regency,

Jogjakarta Province (110^0 30'38''~110^0 33' 03''E and 7^0 53' 25''~7^0 54'52'' S). The seeds were collected from several different provenances and seedlings were planted in 1984. The planting was conducted in a batch of five trees with a 4 x 4 m spacing in a full block design. Five straight trees (24 years, diameter range of 13-38 cm, with a tree height of 10-25 m), grown from the five provenances of *Acacia mangium* trees (compartment no. 17) were felled. The provenances were Sidei Papua (Indonesia), West of Morehead (Papua New Guinea), Daintree, Ellerbeck Red Cardwell, and El Arish (Queensland, Australia). The sample was a 5 cm thick disk cut at the base of the tree, and the bark of the stem was separated from the wood. Furthermore, each disc was subdivided into 4 sections in the radial direction i.e bark, sapwood, as well as outer and inner heartwood. Each section from two opposing radii was converted into wood powder by drilling and was combined to form a single sample.

Measurements of Ash, Insoluble Acid Ash, and Inorganic Elements Contents

To determine the ash content, the wood samples (2 g, oven-dry wood) were subjected to calcination in a muffle furnace around 600°C according to ASTM D-1002 (2002). The ash content is calculated on the basis of the initial weight percentage of the powder. It was then treated with 12 M HCl to dissolve the silica according to TAPPI (1992). To completely evaporate the silica in the solution, it was re-ignited in the muffle furnace at 600°C. The Shimadzu 6200 atomic absorption spectrophotometer (AAS) (flame emission) was used to determine the elements of ash content, namely calcium (Ca), magnesium (Mg), iron (Fe), manganese (Mn), potassium (K), and sodium (Na).

Statistical Analysis

An analysis of variance (two-way) was performed using SPSS version 10.0. The effect of provenance and radial direction on the measured parameters assayed as a normal data distribution was calculated in the general linear model (95 % confidence level). The Duncan multiple series tests were also applied for posthoc analysis. Also, correlation analysis (Pearson) was performed to evaluate the influence of silica and other elements on the ash content.

Results and Discussion

Ash and Acid Insoluble-ash Contents

The metals in the ash come in the form of various salts including oxalates, phosphates, silicates and other minerals (Sjostrom 1981). The ash content value obtained from this study (Table 1) (0.5 ~ 1.1%) was higher than the previous record (0.2%) and 0.6% for hybrid acacias (CABI 1996). Meanwhile, the high value is probably due to the older mangium trees used. The ANOVA of ash content showed that there were a significant provenance and radial position interaction (Table 2). On the contrary, the values of ash content between sapwood and heartwood were slightly different while the bark showed the highest values (Table 1). Bark samples had a greater content of ash than sapwood or heartwood, and this result was similar to the reports of Shanavas and Kumar (2003); Tsuchiya *et al*. (2010); Martinez-Pérez *et al*. (2015).

The values in the inner heartwood area reached 1.55% and were in the range of 1.0~1.5% in the samples of Daintree, Sidei, and Ellerbeck provenances (Table 1). Generally, the smallest average values were obtained in the samples of El-Arish provenance both in sapwood (0.57%) and heartwood (0.50~0.72%). However, the highest level (4.75%) was observed for bark at the same provenance. The amount of ash content that has declined from heartwood to sapwood was observed in Daintree, Sidei, and Ellerbeck provenances.

Measurement of insoluble acid ash content was used to determine the silicate and silica contents in wood (TAPPI 1992). Unlike the ash content, the insoluble acid parameter did not show interactions on both factors even though it had a significant effect. Furthermore, Daintree and bark tissue samples had the highest values among provenances and radial position respectively (Figure 1.) A high value is certainly not expected in woodworking since silica causes metal tools to become dull (Shmulsky and Jones 2011). ANOVA showed that genetic factors are affecting the value of the ash and insoluble acid contents since the trees are planted on relatively homogeneous sites. Previously, the provenance factor significantly affected color properties but not for extractive contents, pH values, and buffer capacities of mangium wood (Lukmandaru *et al.* 2011a, 2011b; Lukmandaru 2012). In addition, following the wood anatomical properties, Sidei and Daintree are more appropriate provenances among those examined for the *Acacia mangium* tree breeding programs in Indonesia (Nugroho *et al.* 2012). Due to low values of ash and silica contents, this finding suggests El-Arish provenance will improve wood quality in future breeding programs.

Table 1. Ash and inorganic element contents (% dry-wood weight) of *A. mangium* stem by provenance and radial position.

Provenances	Positions	Ash (%)	AIC (ppm)	Ca (ppm)	K (ppm)	Mg (ppm)	Na (ppm)	Fe (ppm)	Mn (ppm)
Daintree	Inner heartwood	1.26(0.18)c	940(592)	485(197)	145(66)g	178(51)	144(83)	nd	0.08(0.04)
	Outer heartwood	1.01(0.23)c	5800(275)	1296(432)	130(85)g	282(33)	168(67)	nd	0.05(0.01)
	Sapwood	0.93(0.17)d	910(178)	132(33)	252(0.4)f	287(52)	39(26)	nd	0.25(0.03)
	Bark	2.93(0.65)b	4000(868)	11746(5764)	250(0.8)f	377(62)	70(16)	196(328)	1.41(1.10)
Sidei	Inner heartwood	1.55(0.57)c	1290(815)	470(416)	208(28)fg	231(64)	152(26)	35(70)	0.11(0.05)
	Outer heartwood	1.06(0.22)cd	1860(688)	766(582)	311(235)e	246(84)	136(94)	26(42)	0.84(0.05)
	Sapwood	0.85(0.01)cd	337(175)	136(116)	252(548)f	287(52)	52(16)	501(1120)	0.62(0.88)
	Bark	2.70(0.45)b	4412(1506)	3919(4703)	210(78)fg	257(173)	61(4)	28(16)	0.99(1.06)
Ellerbeck	Inner heartwood	1.18(0.16)c	1287(979)	484(249)	164(75)fg	194(91)	159(31)	nd	0.11(0.07)
	Outer heartwood	1.10(0.15)c	2037(705)	542(387)	148(71)g	174(113)	126(50)	9(21)	0.06(0.02)
	Sapwood	0.69(0.21)d	1420(256)	1918(4093)	251(0.8)f	270(62)	35(24)	23(53)	0.23(0.07)
	Bark	2.84(0.28)b	4712(867)	4662(3269)	249(0.5)f	346(87)	38(27)	92(67)	1.06(0.53)
West of Morehead	Inner heartwood	0.68(0.08)cd	1010(483)	606(219)	40(15)h	139(69)	112(47)	2(1.87)	0.08(0.03)
	Outer heartwood	0.86 (0.23)cd	1300(1064)	623(406)	49(26)h	207(60)	105(26)	nd	0.08(0.01)
	Sapwood	0.75(0.13)cd	1220(315)	1759(3739)	251(0.5)f	278(50)	43(25)	0.80(0.83)	0.22(0.07)
	Bark	2.52(0.79)b	4025(567)	8132(6218)	248(1)f	329(48)	49(6)	54(37)	1.17(0.03)
El Arish	Inner heartwood	0.50(0.49)d	1366(802)	344(291)	240(113)f	184(148)	137(74)	9(12)	0.08(0.02)
	Outer heartwood	0.72(0.35)c	1375(742)	547(470)	186(134)g	110(94)	101(81)	10(24)	0.22(0.12)
	Sapwood	0.57(0.15)d	1600(141)	5852(6170)	240(0.5)f	266(42)	65(19)	36(29)	1.27(1.19)
	Bark	4.75(0.23)a	5960(1046)	11309(7772)	248(1)f	373(63)	45(4)	384(476)	0.52(0.84)

Remarks: AIA = acid insoluble ash content; Ca = calcium; K = potassium; Mg = magnesium; Na = sodium; Fe = iron; Mn = manganese. Mean of 5 trees (24 years), with the standard deviation in parentheses. The same letters on the same column are not significantly different at $p < 5\%$ by Duncan's test.

Table 2. Provenance and radial direction analysis of variance in ash and inorganic element contents

Source of variation	df	Mean square						
		Ash	AIA	Calcium	Potassium	Magnesium	Sodium	Manganese
Provenance (A)	4	0.4**	2397492**	30406691*	26745**	7052	1721	0.410
Radial position (B)	3	27.9**	62446559**	275166497**	55817**	109977**	45892**	3.680**
A x B	12	1.58**	901570	19560868	14745**	10028	1272	0.266
Error	74	0.1	533908	11449470	5756	6647	2521	0.268

Remark: AIA = acid insoluble ash content, ** Significant at the 1% level; * significant at the 5% level
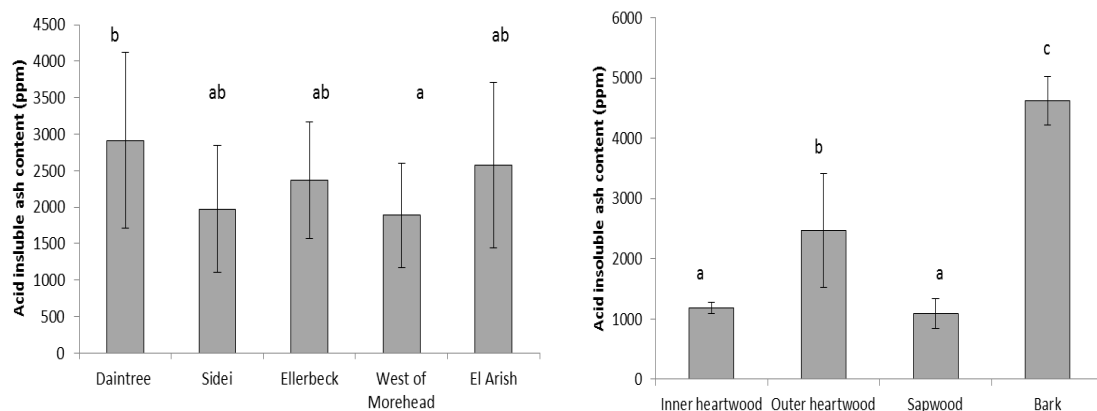

Figure 1. Acid insoluble ash content (ppm) of *Acacia mangium* stem by provenance and radial position. Mean of 5 trees (24 years), with the standard deviation in the error bar. The same letters are not significantly different at $p < 5\%$ by Duncan's test.

Inorganic Elements

The high content inorganic elements observed were Ca, K, and Mg, commonly found in wood (Fengel and Wegener 1984). Generally, Ca was the most abundant element followed by K or Mg while the least was Mn (Table 1), and Fe was not detected in several parts. High Ca levels were caused by the presence of Ca-oxalate crystals in sieve cells and longitudinal parenchyma (Fengel and Wegener 1984). The obtained values for the K concentration was lower but Ca, Mg, and Fe were in the range compared to those of teak wood (Lukmandaru *et al.* 2009).

The ANOVA of K content showed significant provenance and radial position interaction, indicating that their effects are varied (Table 2). Furthermore, the sapwood and bark regions exhibited a higher K concentration than the heartwood for samples from Daintree, Ellerbeck, and west of Morehead (Table 1). The maximum levels are obtained in the outer sapwood of Sidei provenance (311 ppm), while the lowest was found in the inner heartwood of West of Morehead provenance (40 ppm). Moreover, the ANOVA showed that a significant effect of the provenance factor was obtained in Ca content. According to Duncan's test, Ca contents in the El-Arish samples were significantly higher compared to those of Sidei provenance (Figure 2). Also, significant differences between the Ca content and the silica content were obtained in teakwood (Kjaer *et al.* 1999). Theoretically, the functions of K in plants is mainly for electrochemical role whereas Ca has a mechanical function in the cell wall (Okada *et al.* 1987). However, the exact economic significance of the Ca and K content is unknown. In the future, the wide range measured in this study should be considered in the breeding program. The radial positioning factor significantly influenced the content of Ca, Mg, Na, and Mn (Table 2), while Fe showed no normal distribution. Okada *et al.* (1993a, b) observed three patterns of radial nutrient distribution on wood. Type 1 showed element concentrations increased outward from the pith across the heartwood-sapwood boundary, while the pattern was reversed in Type 2. Furthermore, there was a peak in element concentration at the heartwood sapwood boundary in Type 3. The pattern Mg content was Type 1, Na, and K were Type 2 (Fig. 3), while Fe (Sidei provenance only) and Mn were Type 3 (Fig. 4). The highest levels of K, Mn, and Na in cortical tissue were observed with Duncan's test.

Systematic differences among the different radial directions were not observed for Ca content because of the less mobile element. Mg and Ca are adsorbed on negatively charged exchange sites or incorporated in the form of pectates or the lignin matrix (Meerts 2002). Na and K, which belong to the alkali metal in the periodic table, showed a similar radial distribution pattern, and a slightly different pattern was observed between Ca and Mg (alkaline earth metal). The radial distribution pattern of Fe, Ca, and Mn levels are in accordance with that of sugi wood but not for Na content (Okada *et al.* 1987). In *Robinia pseudoacacia* wood, the content of Ca, Mg, and Na increased from the heartwood to the sapwood (Passialis *et al.* 2008).

Generally, no significant differences were observed between the inner and outer heartwood parts. This is probably since there is no living tissue in the heartwood and no physiological reaction has occurred (Okada *et al.* 1987). Furthermore, the difference concentration in several inorganic elements is thought to be related to the heartwood formation such as phenolics formation and pH value changes. The high level of Na in the heartwood (Figure 3) may be related due to counter ions for phenolics (weak acid). In addition, high levels of K, Mg, and Mn in the sapwood are assumed to be related to their role as co-factors in enzymatic reactions in the cytoplasm (Kramer and Kozlowsky 1960; Okada *et al.* 1987). The concentrations of Mg increased significantly from inner heartwood towards bark which is probably due to the decrease in wood cation binding capacity due to the ageing of cells and a decrease of pectic material (Meerts 2002).
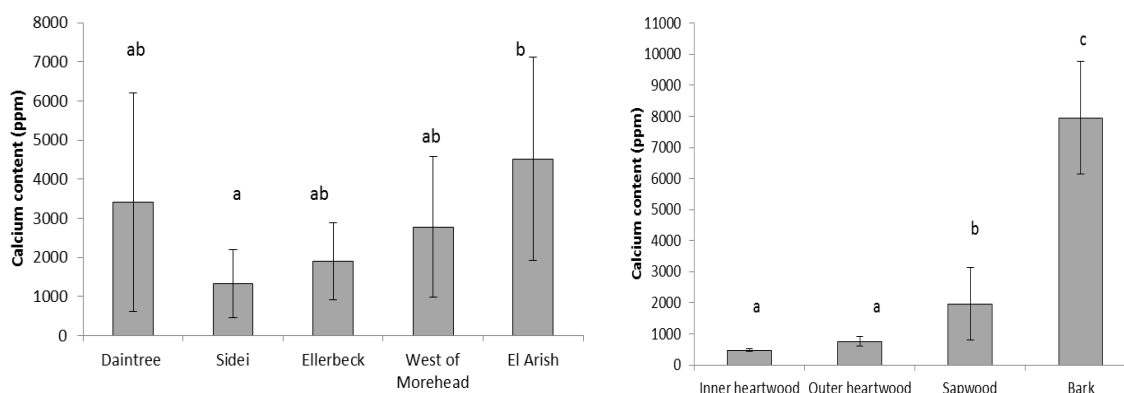

Figure 2. Calcium content (ppm) of *Acacia mangium* stem by provenance and radial position. Mean of 5 trees (24 years), with the standard deviation in the error bar. The same letters are not significantly different at $p < 5\%$ by Duncan's test.
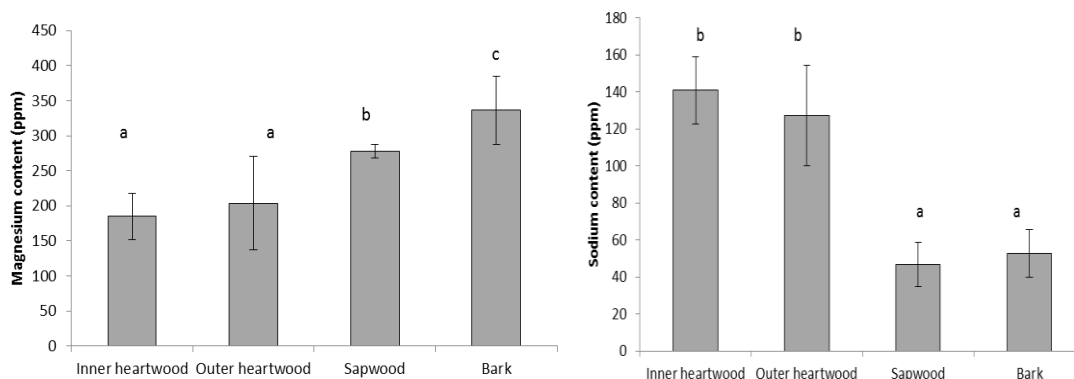
Figure 3. Magnesium and sodium content (ppm) of *Acacia mangium* stem by radial position. Mean of 5 trees (24 years), with the standard deviation in the error bar. The same letters are not significantly different at *p* < 5% by Duncan's test.
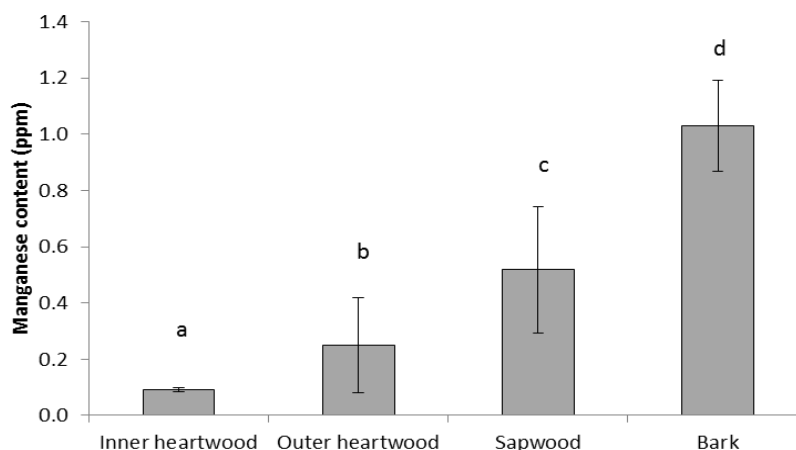

Figure 4. Manganese content (%) of *Acacia mangium* stem by radial position. Mean of 5 trees (24 years), with the standard deviation in the error bar. The same letters are not significantly different at *p* < 5% by Duncan's test.

Relationship between Extractive Compounds and Total Extractive Contents

The correlation between the parameters of each stem part is presented in Table 3-5. In the heartwood part, the strongest relationship was observed between Ca and Mg content (r=0.63**) among inorganic elements, and ash content correlated moderately with K content (r=0.30*). A negative moderate relationship was measured between ash and insoluble acid content (r=-0.41*) for the sapwood region. Only a few significant relationships were found for the inorganic element and silica in the same region, i.e. between insoluble acid ash and K content (r=-0.44*). In the bark part, moderate positive correlations were obtained between the ash and Mn contents (r=0.54*). Of the inorganic elements-silica, the strongest positive correlation was measured between insoluble acid ash and Fe contents (r=0.61**).

There was no common pattern in the correlation between ash and insoluble acid contents for all stem parts. Therefore, the variation of silica is independent of ash content, and this is contradictory to the results presented by Abasolo *et al*. (2001), where a strong correlation between ash and silica contents in several rattan species was obtained (r=0.96). Insoluble acid ash level moderately correlated with Fe level in sapwood and bark tissues but negatively correlated with K in the tissue. Silica affects the cuticular transpiration and CO_2 uptake of plants (Abasolo *et al.* 2001), while Fe is present in biologically more active parts of the tree. This correlation is interpreted to mean that Fe and silica may be more active due to the high number of living cells in sapwood and inner bark parts.

It is also noticed that positive moderate correlations were observed between Mg and Ca contents in heartwood (r =0.63**) and bark (r=0.54**) regions. Mg and Ca belong to the alkaline earth metal group (IIA). This correlation may be linked to the role of the two elements in cell and membrane production (Kramer and Kozlowsky 1960; Okada *et al.* 1987; Cutter and Guyette 1993). Furthermore, it should be noted that the values in the bark part are influenced by atmospheric deposition. However, it is not known why such a correlation was not observed in the sapwood region.

Table 3. Pearson's correlation among ash content and inorganic element contents in *Acacia mangium* sapwood

Content	Acid insoluble ash	Iron	Potassium	Calcium	Magnesium	Natrium	Manganese
Ash	-0.41*	0.09	0.39*	-0.32	0.01	-0.38	-0.36
Acid insoluble ash		0.42*	-0.44*	0.40	-0.25	-0.07	0.09
Iron			0.24	-0.04	-0.21	-0.01	-0.07
Potassium				-0.23	0.31	-0.26	-0.26
Calcium					0.32	0.32	0.00
Magnesium						0.14	-0.34
Sodium							0.34

Table 4. Pearson's correlation among ash content and inorganic element contents in *Acacia mangium* heartwood

Content	Acid insoluble ash	Iron	Potassium	Calcium	Magnesium	Natrium	Manganese
Ash	0.28	0.17	0.30*	0.00	0.26	0.19	0.11
Acid insoluble ash		0.08	0.14	-0.24	-0.19	-0.16	0.10
Iron			0.44**	-0.19	-0.16	0.06	0.17
Potassium				0.16	0.26	0.29	0.09
Calcium					0.63**	0.35*	-0.29*
Magnesium						0.42**	-0.35*
Sodium							-0.10

Table 5. Pearson's correlation among ash content and inorganic element contents in *Acacia mangium* bark

Content	Acid insoluble ash	Iron	Potassium	Calcium	Magnesium	Natrium	Manganese
Ash	0.44*	0.34	0.09	0.30	0.28	-0.15	0.54*
Acid insoluble ash		0.61**	0.11	-0.10	0.14	0.24	-0.22
Iron			0.11	-0.22	0.07	0.20	-0.27
Potassium				0,29	0.41	-0.12	0.21
Calcium					0.54**	0.22	-0.22
Magnesium						0.02	0.20
Sodium							0.10

Remark: ** Significant at the 1% level; * significant at the 5% level

Conclusions

The ash, silica, and inorganic element contents of mangium wood were measured to evaluate the effect of provenance and radial position factors. The ash content ranged 0.5~1.1%, and 2.5~4.7% for wood and bark respectively. A significant interaction was observed for ash content where the lowest level was found in the wood of El-Arish provenance. Furthermore, the amounts of insoluble acid ash content were 300-5800 and 4000-6000 ppm for wood and bark respectively, with provenance and radial position significant influencing factors. The highest amount was observed in El-Arish samples. The results of inorganic element measurement were Fe 0~500 ppm (wood) and 28~384 ppm (bark); K 40~311 ppm (wood) and 210~250 ppm (bark); Ca 130~5850 ppm (wood) and 3919~11746 ppm (bark); Mg 0~500 ppm (wood) and 28~384 ppm (bark); Na 35~65-168 ppm (wood) and 38~70 ppm (bark); Mn 0.05~1.27 ppm (wood) and 0.52~1.41 ppm (bark). The significant interaction between provenance and radial position factors was measured in K content. Ash content was negatively moderately correlated with insoluble acid on a moderate level in the sapwood. On a positive level with insoluble acid ash content, the bark was moderately correlated. Meanwhile, moderate correlations were calculated between Mg and Ca contents in heartwood and bark regions. In the sapwood region, the highest correlation degree was between insoluble acid ash and K contents. The comparatively low values of ash and acid soluble ash contents of El-Arish provenance make it is more suitable for improving wood quality by tree breeding.

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