

Ash from homestead fireplaces and wood as possible sources of minerals for livestock

By

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Declaration

I hereby certify that this research is the result of my own investigation. Where use was made of the work of others, it has been duly acknowledged in the text.

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CHAPTER ONE

1. LITERATURE REVIEW

1.1. Introduction

This investigation was prompted by an enquiry from a missionary in Mozambique who wanted to know if it is possible to use ash from fireplaces as a source of minerals to the livestock of resource-poor farmers in rural areas. A search through the literature covering animal nutrition did not supply much information, except for a comment in the book by Morrison (1959) that wood ash has a calcium (Ca) content of approximately two-thirds that of lime stone (CaCO_3). It was therefore, decided to conduct a survey on the composition of ash from fireplaces in rural areas in different regions of South Africa and this was followed by a survey of the ash in fire-making material used in South Africa, with emphasis on the mineral composition of ash from wood obtained from different tree species. As the investigation progressed, more literature was obtained on the topic of uses of ash in agriculture, though mainly in disciplines unrelated to animal nutrition. Information on indigenous knowledge and experience on the utilization of ash has also been obtained from various rural farming regions of South Africa. In the following review of literature relevant knowledge on the topic of the composition of ash and possible uses will be covered.

1.2. Homestead ash: Practices and indigenous knowledge in rural farming communities

Ash from homestead village fires in rural communities can originate from a number of fire making products. If available, wood from a mixture of tree species would be used. In certain areas cattle dung and maize cobs would be in abundance and be used. In others dry wood from fallen building structures and fencing poles would be used. Many people use newspapers, plastics and a few drops of paraffin to get the fire started. To a large extent, rural people would utilize what is available to them as long as it is dry to catch fire. The consequence is that a large variation in the composition of the ash could be expected between but even within locations. Furthermore, homestead fires are made on a soil surface in the lapa, or sometimes a piece of corrugated iron plate could be used on which to make the fire. This makes it easy for the ash to

be removed the following morning. It is therefore; quite likely that homestead ash may contain soil, wires, nails and discarded food and bones.

The discarded ash has been used for different purposes:

In some areas the ash is thrown into an outside hole-dug or pit toilets to reduce bad smell from the latrine;

Ash is spread on the land as part of fertilizing the soil;

It is also believed that ash would stop hick-ups in a person by tasting it two to three times with the tongue;

In Namibia and the Northern part of Limpopo Province such as Venda, Giyani and Musina, ash is mixed with water (“aswater” in Afrikaans) and given to a cow having problems of retaining the afterbirth.

Wood ash is used as tooth paste (it should work even better than the commercial products because it will neutralize all acid that corrodes teeth).

Some people use wood ash to white-wash their homes.

In the northern rural areas of Mpumalanga province, ash is also used as a replacement of liquid bath soaps to wash dishes and shine sauce pans.

Wood ash, an alkaline substance (Etiegni & Campbell, 1991), is used by the local people of South-Western Uganda to reduce tannin content in the red, bird resistant sorghum that is cultivated in that region. This traditional technology involves soaking sorghum grain in wood ash slurry and then allowing it to germinate for four (4) days. A modified study by Kyarisiima *et al.* (2004) was conducted on this traditional technology to reduce the negative effects associated with tannin. The modification involved the use of wood ash extract instead of wood ash slurry and a short germination period. The feeding value of the treated sorghum grain was assessed using broiler chicks.

It is also believed in the Northern region of South Africa (Bushbuckridge area) that a pregnant woman should brush her forehead with ash before attending any funeral ceremonies to avoid miscarriage.

According to Burford (1989) rural people are very knowledgeable on the various characteristics of woods for fuel, cattle feed and construction. Many farmers collect maize stover from their fields and store it in racks close to cattle pens in order to pen-feed the animals in the

dry season (Field observation). Some fodder trees that are often browsed by livestock in the tropics and sub-tropics are chopped or lopped and fed to livestock (Skerman, 1977; Le Houerou, 1980). These are often the sole sources of protein and energy for ruminants and are converted via this route into high-quality food for human consumption (Woodward & Reed, 1989).

Small-scale farming, low-input and agro-pastoral systems are found in all regions of Zimbabwe and largely confined to commercial farming areas (Anorld, 1991). The savanna type of vegetation in most of these areas has been opened by the cutting of trees for timber and wood-fuel, or was previously cleared of trees for the purpose of cultivation (Campbell *et al.*, 1991). Cattle, goats and chickens are their chief livestock. According to Sharland (2003), at the Mundri region in Zimbabwe, ash obtained from burning trees and bush is recognized as a way of improving soil fertility and is an important reason for using fire to clear the land. Spots with particularly high concentrations of ash such as where a large tree or a mound of rubbish has been burnt are regarded as ecologically significant and suitable for specialized crops.

Ash from domestic household fires, however, is seen in a different way even though it can provide depleted soils with an appreciable amount of nutrients (Sharland, 2003). When clearing new land for cultivation, the Moru of the Southern Sudan make extensive use of burning and the ash produced is highly valued (CRILEISA, 2002). Wood ash temporarily raises soil alkalinity making potassium and phosphate more available to crops (Sharland, 2003). According to Sharland (2003) the importance of potassium in the soil is difficult to teach, but the effect of wood ash is easy to see. In the past farmers were taught that all burning was bad. They rejected this teaching because they could see the beneficial effects that ash has on their traditional shifting agriculture. Since the Moru recognize wood ash and decomposed plant material sites as places suitable for cultivating ecologically specialized crops, advanced farming practices can be demonstrated using these established farming practices.

1.3 Properties of wood ash

There are numerous opinions as to what constitutes wood. No specific definition of wood is totally satisfactory but the one by Webster & McKetchnie (1980) that wood is “the hard fibrous substance beneath the bark in the stems and branches of a tree and shrub” xylem is as good as any. Wood is the hardest, fibrous substance that is found beneath the bark of the stems and branches in both trees and shrubs. It is plentiful and replaceable. It is made up of a number of substances. Cellulose constitutes 50% of wood by weight. Lignin makes up about 23- 33% of

softwoods but only about 16-25% of hardwoods (Golden Embers Marketing Pty Ltd, 2000). Generally the wood nearest the bark of the tree, called sapwood, takes part in the life activity of the tree. The water, minerals and materials needed for growth are moved through the sapwood of the tree (Golden Embers Marketing Pty Ltd, 2000).

Wood ash is the inorganic and organic residue remaining after the combustion of wood or unbleached wood fiber. The physical and chemical properties of wood ash vary significantly depending on many factors. The ash content and chemical composition vary among tree species and also depend on soil type and climate (Greene, 1988). Temperate-climate wood yields 0.1-1.0% ash, while tropical and subtropical wood yield up to 5%. Hardwoods, in general, contain more ash than softwoods; and the bark and leaves generally produce more ash than the inner woody parts of the tree (Internet In-service Training, 1995). On average, the burning of wood results in about 6-10% ash (Campbell, 1990).

Ash content is highly variable within a tree, being the highest in the foliage, and decreases in the bark, twigs, roots, branches and stems. Within the stems, ash is the highest in the pith, early wood (spring wood) and juvenile wood. Wood bark ash contains all the essential nutrients for tree growth except for nitrogen (N) (Imbeah, 1998).

Comparisons from the literature between industrial wood ashes are difficult to make because the moisture content; carbon (C) content and type of ash are seldom mentioned. The physical and chemical properties of ash collected from combustion systems vary significantly depending on the temperature of combustion, the type of fuel (species of wood and amount of bark), and where it was collected in the combustion system. Ash has a small particle size and low density. The ash has an average particle size of 230 μm (Etiegni & Campbell, 1990). Density varies with the C content in the form of organic matter. The greater the C content, the lower the density of the ash and the lower the concentration of elements in the ash. The C content can vary from 1% in fluidized-bed combustion systems to 70% in inefficient burners, with 5-30% being a typical range. The moisture content is also highly variable. Many ash collection systems commonly add water to cool the ash and reduce fugitive dust problems. Other ash collection systems use a wet-bottom furnace where the hot ash is dumped into re-circulated water, and the suspension is sent into a settling pond or waste treatment system. The leached ash residue is ultimately dredged from the settling pond, de-watered, and then land-filled (Etiegni, 1990).

In Table 1.1, wood ash was collected and mixed together then sifted to remove any charcoal and pieces of wood (NRC, 1983 and Imbeah, 1998). A sample of ash was taken for mineral analyses. Mixed varieties of grasses were cut and sun-cured for three days with turning at midday and 16:00. The sun-cured grass (hay) was manually chopped into 5-7 cm lengths over a piece of timber, using a cutlass. A sample of hay was taken and ground through a 0.5 mm screen for mineral analyses. The wood ash was made into a 20% (w/v) mixture with water to which 4% NaCl was added to improve palatability. The chopped hay were evenly spread on a concrete floor and the mixture was sprinkled on it using a watering can. The hay were then mixed by hand until all was uniformly moist. The treated hay was dried on a concrete floor in a shed, turning it at 09:00, 12:00 and 15:00 daily for four days. A sample of treated hay was taken and ground through a 0.5 mm screen for mineral analysis (Imbeah, 1998).

Table 1.1
Mineral compositions of bone meal, oyster shell, wood ash and hay

Component ^a	Bone meal ⁿ	Oyster shell ⁿ	Wood ash ^o	Untreated hay ^o	Treated hay ^o
Dry matter (g/kg)	970	990	989.4	888.6	854.2
Ash (g/kg)	-	-	825.5	94.4	228.7
Calcium (g/kg)	315.3	380	120.6	2.3	12.5
Phosphorus (g/kg)	142.2	0.7	10.6	2.5	3.1
Magnesium (g/kg)	6.4	3.0	23.4	6.3	7.3
Potassium (g/kg)	1.9	1.0	44.4	18.1	21.4
Sodium (g/kg)	40.0	2.1	41.3	9.4	22.5
Copper (mg/kg)	1.4	-	120.5	14.0	29.6
Zinc (mg/kg)	342	-	1618	66.5	256

^a Dry basis

ⁿ NRC, 1983; ^o Imbeah, 1998

Wood ash in Table 1.1 above appeared to be a good source of calcium (Ca), copper (Cu) and zinc (Zn) but a poor source of phosphorus (P) (Imbeah, 1998). Ramirez *et al.* (1992) reported the following composition of wood ash from mesquite wood (g/kg dry matter (DM)): P, 0.05; Ca, 172.7; potassium (K), 395.6; sodium (Na), 129.8 and magnesium (Mg), 87.6 compared to 10.6, 120.6, 44.4, 41.3 and 23.4, for P, Ca, K, Na and Mg respectively, in Table 1.1. Treating hay with 20% wood ash solution increased the mineral concentration considerably, especially

that of Ca, Cu and Zn in Table 1.1, in the ash content by 142%, Ca by 443%, Cu by 112% and Zn by 285%.

According to Ramirez *et al.* (1992) the mineral composition of wood ash varies depending on the species of trees from which the ash was obtained. Wood ash from village fires derives from a mixture of tree species and may vary from day to day and for different locations. Compared to oyster shell and bone meal (Table 1.1), the ash used appeared to be intermediate as a source of Ca and a good source of the trace elements Cu and Zn (Imbeah, 1998).

From an animal nutritional perspective, an analysis of the ash content is the chemical analysis that would provide the most information about the quality of the wood or bark from tree species. It is composed of major and minor elements needed by the tree for growth. The major elements are (g/kg DM): Ca, 70–330; K, 30-40; Mg, 1-2; P, 0.3-1.4; manganese (Mn), 0.3-1.3; and Na, 0.2-0.5 (Campbell, 1990). Ash-forming minerals are found in wood in very small quantities at concentrations of 1 to 30 g/kg. Essential trace elements for plant growth include Zn, boron (B), Cu, molybdenum (Mo) and others at concentrations of parts per million levels (Campbell, 1990).

A study was done by Fern *et al.* (1992) where ash was brought from a pulp mill and consisted mainly of residues of birch bark and wood. The ash was not fully burnt. It contained plenty of C and had a moisture content of about 40%. Based on the chemical analysis, the moisture content and the part of the ash not burnt, Veijalainen *et al.* (1984) estimated that one ton of this ash contained 1.0 - 3.0 kg P, 7 -11 kg K, 27 - 105 kg Ca and 38 - 102 g B /kg DM.

1.4 Historic uses of wood ash

Approximately 15% of wood ash is land-filled, 80% is land applied, and 5% is disposed of in some other way, mainly as a sewage sludge composting agent (Greene, 1988). In addition, ash has been granulated to yield a fertilizer and liming agent. From the 1700s through the early 1900s, wood was combusted in the United States to produce ash for chemical extraction. The wood ash industry in the Northeast actually generated \$2 million in 1810 (Campbell, 1990). The ash was mainly used to produce potash for fertilizer, but some also went into soap and glass manufacturing and into K cyanide which were used in the recovery of gold from tailings and low grade ores (Bradley, 1915). The K production process was unsophisticated and labour intensive (Bateman, 1919).

Carson & Weester (1980) evaluated a more sophisticated continuous-flow ash extraction system, but problems with ash settling deterred further development. They also considered using rain to leach potash from an ash landfill into a liner and leachate control system. Problems with clogging, soil solubilization and corrosion limited this approach. Even though these ash extraction processes failed, other variations yielded a valuable potash product and also reduced the alkalinity of the ash, making it more acceptable for land-filling. Until 1990's, ash was a valuable raw material, but from then ash wastes had a negative value due to its disposal costs (Campbell, 1990). For the most part, ash is either land-filled (90%) or land-applied. The disposal of wood ash is a growing problem as environmental regulations become more stringent and landfill sites become less available and more expensive (Campbell, 1990).

1.5 Wood ash and its uses for different agricultural practices

Ash has been used in a variety of agricultural applications as it is an excellent source of K, lime and other plant nutrients (Lerner & Utzinger, 1986; Naylor & Schmidt, 1986; Campbell, 1990; Etiegni, 1990). It is an economical and readily available source of alkaline material, which has been used successfully as a treatment of wheat straw to improve its digestibility (Nolte *et al.*, 1987). Such treatments could improve goat and sheep production in developing countries, (Ramirez *et al.*, 1992). Mineral concentrations of wood ash were reported by Nolte *et al.*, (1987) that they have lower values for K, Na and Mg and greater values for Ca and P. Ochetim (1988) suggested the use of wood ash as a source of minerals for poultry.

1.5.1. Source of fertilizer on agricultural land

Wood ash should not be viewed as a problem but as a valuable raw material containing elements concentrated by plants and the combustion process. It is well documented that wood ash is rich in Ca and has been used successfully as a fertilizer especially to ameliorate the acidity in soil (Demeyer *et al.*, 2001). It is a valuable liming agent and soil amendment that enhances agricultural productivity (Imbeah, 1998). One of the interesting possibilities of using the high-lime wood ash in agriculture is the potential for developing an alternative liming material that not only supplies lime but also provides P, K and trace minerals (Naylor & Schmidt, 1986).

Wood ash provides supplemental macro- and micro-elements needed for plant growth. The main characteristics of the ash material are dominated by Ca, silica (Si) and K, while straw ash contains more K than ash from wood and bark (Imbeah, 1999). Weber *et al.* (1985) studied the

effect of wood ash and NPK fertilizers on microbial activities over a three-year period in an intensively cultivated, acidic, N-rich peat soil planted with *Salix* sp. The wood ash increased all microbial activities that were examined, *viz.* N availability, mineralization, cellulose decomposition, N fixation, and denitrification. The recycling of ash back to agricultural lands can help improve soil productivity and also conserve valuable landfill space. Land application appears to be a safe and economic method for disposing of and utilizing wood ash (Campbell, 1990).

A study was conducted to determine the effects of applying wood ash to two soil types amended with partially-decomposed cattle and chicken manure on the uptake of nutrients, early growth and dry matter yields of maize (*Zea mays*) (Materechera & Salagae, 2001). A clay soil and a silt loam soil were used. Manure was applied to each soil type in pots at rates equivalent to 0.5 unit ha, and 15 unit ha while ash was applied to each of the manure treatments at rates equivalent to 0 and 2 unit ha. In both soils, the addition of chicken manure produced higher plant height, stem diameter, leaves per plant, DM yield and tissue concentration of protein, N and P than cattle manure. The responses of maize due to manure application were higher in the loam than in the clay soil.

Application of cattle manure produced responses, which were less than in the control in many cases. This was presumed to be due to microbial immobilization of nutrients. Generally, wood ash improved the responses of maize in the loam but not in the clay soil. The addition of wood ash to manure in clay soil reduced plant height, dry matter yield, plant tissue, protein and P content of maize compared to the control. In both soils, however, the addition of wood ash improved responses where cattle and not chicken manure was applied. In the latter, the increases in response due to manure rate were higher without ash than with ash. Within the cattle manure rates, wood ash produced better responses when 5 units ha manure was applied compared to 15 units ha. It is suggested that higher rates of wood ash application may have been necessary.

Dung ash plus area treatment of paja brava hay provides forage of an average quality comparable to alkali-treated straws, and the treated hay can be very useful security forage in the Arid Andean highlands for feeding strategies of livestock during the frequent periods of security (Genin *et al.*, 2002). This technical alternative seems particularly adapted to the economic conditions of the low-input subsistence farming systems found in this region. However, further investigations are needed in order to evaluate its feasibility and effectiveness in the local

livestock production systems, particularly in relation to labour availability, and to determine levels of land-use pressure to ensure the sustainability of the resource (Genin *et al.*, 2002).

Lerner & Utzinger (1986) performed a field study using ash from four different wood species, plus a species mix. The ashes had an average composition of 26% Ca, 7% K, and 1% P and an effective CaCO₃ equivalent range of 83-116%. A second greenhouse study examined the phytotoxicity of wood ash at high application rates on the growth and yield of snapbeans (Etiegni *et al.*, 1990). The alkalinity, K content and B content of the ash were examined as potential toxicants. The experiment demonstrated that the alkalinity was the most important growth limiting component in ash, but K was also an important limiting element.

Magdoff *et al.* (1984) evaluated land application of wood ash in a greenhouse and laboratory research project. Two soils were mixed with wood ash, limestone and a limestone-ash mix (90:10). Plant growth, nutrient uptake and soil chemical changes were measured during the growth of maize and lucerne. Ash gave better growth responses than limestone. The effect of over-liming was reduced when ash was added with the limestone, probably due to the extra nutrients in the ash. The study demonstrated that wood ash could be used as an effective liming material by following the currently recommended guidelines for limestone. Magdoff *et al.* (1984) recommended that crops should not be planted immediately after ash application, as ash absorbs herbicides and pesticides and could cause concentrated alkaline conditions before neutralization by the soil. Magdoff *et al.* (1984) also recommended that because of ash variability the CaCO₃ equivalent should be measured routinely.

Weber *et al.* (1985) studied the effect of wood ash and NPK fertilizers on microbial activities over a three-year period in an intensively cultivated, acidic, N-rich peat soil planted with *Salix sp.* The wood ash increased all microbial activities that were examined: N availability, mineralization, cellulose decomposition, N fixation and denitrification. Lumme & Laiho (1988) examined the effect of conifer bark ash on the growth of fast growing willow (*Salix aquatica*). The ash was considered to be a good P, K and Mg fertilizer and a liming agent. The elements in the ash were released more slowly than those in the fertilizer, showing a higher release in the second growing season.

The ashes from biomass fuels contain only trace amounts of heavy metals, which make them fairly easy to dispose of. They are found to be good fertilizers, and can be used as mineral nutrient for forest and agricultural soils (Olanders & Steernari, 1995). The composition of the ashes varied between different plants depending on the combustion method and on the growing

conditions where the bio-fuel was taken. The main constituents are the same though. However, it is essential to have a thorough knowledge of the composition before the ashes are utilized (Berry *et al.*, 1985).

1.5.2. Industrial uses

From the 1700's through the early 1900's, wood was combusted in the United States to produce ash for chemical extraction. Recently, ash has been considered a waste product instead of a resource, as the demand as a raw material dropped. Today, approximately three million tons of wood ash is produced annually in the United States (Internet In-service Training, 1995). Wood ash has been used as a binding agent, as glazing base for ceramics (McWhinnie, 1979), a road base, an additive in cement production and an alkaline material for the neutralization of waste. In Europe, ash is used as a feedstock for cement production, a soil amendment on forest lands and a road-base material (Campbell, 1990). Campbell (1990) suggested that ash could be used to cover landfills or added to landfill leachates to reduce the metal and organic content of leachates. Ash has been used effectively in north-eastern Europe as a bulking and odour control agent in composting of municipal sewage sludge in aerated static piles (Campbell, 1990).

Several ash disposal and utilization methods were evaluated in the late 1980's as environmental concerns increased. Land application appears to be one of the best methods for ash disposal, recycling the nutrients taken from the land during harvests back to the land (Gray *et al.* 1988). Wood ash is used to lime acidic agricultural and forest soils and replace micro- and macro elements removed during plant growth and harvesting. Ash has a low fertilizer equivalent (NPK ratio of 0:1:2), but it can be used as an excellent substitute for lime and limestone to neutralize acidic soils and to add Ca, P and Mg (Naylor & Schmidt, 1986). Liming with wood ash may also reduce the toxic effect of Al and Mn in acidic soils. Campbell (1990) further suggested that ash will probably be sold in future as a liming agent and soil amendment.

The vitality of trees was greatly improved by ash fertilization, (Fern *et al.*, 1992). The effect of wood ash fertilization on Scottish pine growth has generally been higher than commercial PK- fertilizers on drained peat-lands in Finland (Silfverberg & Huikari, 1985). Soil changes due to ash fertilization were most evident in the topsoil. Ash fertilization improved the biological properties of the organic soil by increasing microbial activity, the number of total

bacteria, specifically those of nitrifying kind and the amount of mycorrhizae. This has been reported by Silfverberg & Huikari (1985).

Pulp and paper industries utilize enormous quantities of timber resources annually for producing paper products. Since a portion of the tree is unusable in production operations, residuals such as the bark must be managed through other methods. Burning such residues, known as hogged fuel, in wood-fired boilers for production of steam and electricity is economical, environmentally sound and energy conserving (Naylor & Schmidt, 1986). Combustion of wood produces a highly alkaline ash (pH = 9 - 13.5). Ash generated from burning the hogged fuel is collected. Deposition of the boiler ash along the fly ash from air pollution control represents the final step of this resource recovery. When ash is produced in industrial combustion systems, the temperature of combustion, cleanliness of the fuel wood, the collection location and the process can also have profound effects on the nature of the ash material. Therefore, wood ash composition can be highly variable depending on geographical location and industrial processes (Internet In-service Training, 1995). Bark contains much higher ash content than wood, as indicated by the 1-3% ash content in hog fuel (Campbell, 1990).

Since the oil crisis in the 1970s that was followed by rapidly rising energy costs, Americans have sought energy sources of lower costs. However, the pulp and paper industry has used wood waste as fuel on a wide scale since the 1960's and has recognized that wood can be an important economical and readily available source of energy (Naylor & Schmidt, 1986). There is also a need to adequately recognize that ash residual from wood burning can be an important source of crop nutrients and lime for agricultural uses. With the increasing use of wood as a fuel especially in rural areas and the subsequent need to dispose of the ash, it is important to reconsider the use of wood ash for agricultural purposes and to put such use on a quantitative basis (personal opinion and observation).

The research has used alkalinity and the absorbent nature of the ash to neutralize acidic wastes. Gray *et al.* (1989) evaluated the treatment of landfill leachate with wood-coal ash. Naylor & Schmidt (1986) evaluated wood-ash liming characteristics and micro- and microelement availability in soil. An industrial wood ash, equivalent to a 0-1-3 NPK fertilizer, was mixed with two soil types in pots at application rates of 0, 2.24, 4.5, 9.0, 17.9, and 35.9 metric tons/ha. After two months of incubation, the extractable P, K and Ca and the pH of the ash were linearly related to the rate of ash application. The ash increased the exchangeable

concentration of K, Ca, Mn and Mg. The exchangeable iron (Fe) and aluminium (Al) decreased because of the rise in soil pH. Hay yields and protein content increased at all application rates compared to the control. The application rate had little impact on the trace metal composition of the lucerne. In general, ash appeared to be a good soil amendment and liming material, even at high application rates.

So far, most investigations have only reported the elemental composition of different ashes but little has been said about the actual compounds and the formation reactions of the ashes during combustion. To understand what occurs during combustion it is essential to investigate what compounds exist in the ashes and what reactions occur in their formation (Olander & Gunners, 1994). Since minerals are concentrated in the bark layer of the tree, the ash content of wood chips normally depends on the bark content of the mixture. Many ash-forming inorganic species are associated with organic compounds in the fuel.

During combustion the organic structures are decomposed and the ash formers are released. Some of them for example, alkaline earth metals leave the combustion zone as solid particles, while the alkali metals are transported in vapour form as chlorides, hydroxides or oxides. These species can react with SO_2 in the combustion gas and form sticky sulphate particles which readily adhere to heat exchange surfaces and form hard deposits. Combustion of wood produces a highly alkaline ash (pH = 9 - 13.5). There is also a possibility of vapour-phase CaO condensing on surfaces and reacting further with SO_2 to form CaSO_4 (Steenari & Lindquist, 1989).

An ultimate analysis of the ash samples obtained at different combustion temperatures indicated that Ca, K, Mg, Si and P were the major components. For the most part, the metal content increased with temperature; but K, Na and Zn content decreased with temperature, probably due to the low boiling and decomposition points of their carbonates and oxides (Etiegni & Campbell, 1990). Ash yield and chemical composition changed with temperature, and thus combustion temperatures could affect the value of wood ash and its potential applications.

Paper mill wood-derived ash contains P, K, Ca, Mg, and trace minerals derived from the burning of the hogged fuel. These crop nutrients, present also in commercial fertilizers, are essential to the maintenance of soil fertility (Yearbook of Agriculture, 1938).

Ash is composed of many major and minor elements needed by the tree for plant growth (Table 1.2). Since most of these elements are extracted from the soil and atmosphere during the

tree's growth cycle, they are common elements in our environment and also essential elements in the production of crops and forages (Risse & Harris, 1994).

Table 1.2
Range in elemental composition of industrial wood ash samples and ground limestone

ELEMENT	WOOD ASH ^o (range)	LIMESTONE
Macro (g/kg)		
Calcium	15 (2.5-33)	31
Phosphorus	0.53 (0.1-1.4)	0.06
Magnesium	1.0 (0.1-1.4)	0.06
Potassium	2.6 (0.1-13)	0.13
Sodium	0.19 (0-0.54)	0.07
Nitrogen	0.15 (0.02-0.77)	0.01
Manganese	0.41 (0-1.3)	0.05
Iron	0.84 (0.2-2.1)	0.29
Aluminium	1.6 (0.5-3.2)	0.25
Micro (mg/kg)		
Arsenic	6 (3-10)	-
Boron	123 (14-290)	-
Cadmium	3 (0.2-26)	0.7
Chromium	57 (7-368)	6.0
Copper	70 (37-207)	10
Lead	65 (16-137)	55
Mercury	1.9 (0.5)	-
Molybdenum	19 (0-123)	-
Nickel	20 (0-63)	20
Selenium	0.9 (0-11)	-
Zinc	233 (35-1250)	113
Other Chemical Properties (%)		
CaCO ₃ Equivalent	43 (22-92)	100
pH	10.4 (9-13.5)	9.9
% Total solids	75 (31-100)	100

^o Mean and Ranges taken from analysis of 37 ash samples

Risse & Harris, 1994, Internet In-service Training, 1995

1.5.3. Treatment of animal feed

Wood ash has been used to treat straws to improve their digestibility and mineral contents (Nolte *et al.*, 1987; Ramirez *et al.*, 1992). Such treatments could improve goat and sheep production in developing countries (Ramirez *et al.*, 1992). Alkaline treatments of high fibre roughages have been investigated extensively, and there are numerous reviews of their effect in incrementing the feeding value for ruminants (Jackson, 1978; Wanapat *et al.*, 1985). The most common alkalis used are NaOH, Ca(OH)₂ and urea-ammonia. Nolte *et al.*, (1987) found that treatment of wheat straw with 30% solution of wood ash for six hours increased digestibility of DM, organic matter (OM), neutral detergent fibre (NDF) and acid detergent fibre (ADF) in goats. Ramirez *et al.* (1992) confirmed these results and showed that the DMD of diets containing maize stover treated with a 20% wood ash increased by up to 20% in sheep, compared to a control group.

Wood ash and animal urine are readily available low-cost products that can be used to improve fibre digestibility of straw in a manner comparable to NaOH treatment. Therefore, crop residue treated with 20% solution of wood ash, 20% wood ash plus urea or with urine could economically supply a major portion of the energy and protein needs in ruminants during winter seasons (Ramirez *et al.*, 1991). Sorghum straw is a lignocellulostic crop residue produced in considerable amounts in some sorghum grain-producing regions.

However, in areas where feed for animal production is limited, most producers use sorghum straw as animal feed. The low digestibility and nutritive value of sorghum straw limits animal intake and cannot support growth of adult ruminants without adequate supplementation (Males, 1987). Another problem connected with the utilization of straw as a fuel is that straw ash usually melts at a rather low temperature, thus producing cakes of sintered ash which can be difficult to remove. The firing of wood chips is not often hampered by ash melting (Steenari & Langer, 1988). Wood ash is also considered economical as an alkaline source.

Kyarisiima *et al.* (2004) conducted a study to investigate the effects of wood ash treatment on the nutritional value of high tannin sorghum. High tannin sorghum was either soaked in wood ash slurry and then germinated for four days or soaked in wood ash extract and germinated for 28 hours or germinated after soaking in water. Chemical composition of the grain thus treated was determined. The feeding value of the wood ash extract treated grain was evaluated in a three-week experiment where sorghum replaced maize in broiler starter diets. Treatment of high tannin sorghum with wood ash extract was effective in reducing the tannin level and did not

lower the nutritive content of the grain, unlike the treatment that involved the use of wood ash slurry. There was no significant difference in feed intake between the maize based diet and the diet that contained wood ash extract treated sorghum. There was a significant improvement in growth rate of chicks that were fed on a diet that contained treated sorghum. This was also reflected in the improvement of the digestibility of diets that contained treated grain. The treatment of high tannin sorghum with wood ash extract improves its nutritive value.

1.6 Bioavailability of metallic forms in various mineral sources

The availability of Ca from CaCO_3 and oyster shell, two commonly used Ca supplements, was 72 and 68%, respectively (Weaver *et al.*, 1987). Several studies showed that when CaCO_3 and oyster shell of similar particle size were fed, there were no detectable differences between the two sources. It was suggested by Weaver *et al.* (1987) that the oxalate content of spinach is the factor reducing Ca availability. Ninety five percent or more of the feedstuffs that are considered to have relative low Ca bioavailability values for both non-ruminants and ruminants in comparison to CaCO_3 include aragonite, bone meal, calcium gluconate, dicalcium phosphate, ground eggshell, ground CaCO_3 , ground oyster shell, calcium sulphate, non-fat dry milk and tricalcium phosphate (Joseph & Soares, 1995).

Heavy-metal concentrations are typically low. Also, wood ash is substantially different from coal ash, which has a lower alkalinity but higher Si, Al, Fe and heavy-metal content (Campbell, 1990). The alkalinity of wood ash depends on the carbonate, bicarbonate and hydroxide content. Carbonate and bicarbonates predominate below 500 °C, whereas oxides become more prevalent above 1000 °C where most of the industrial wood-fired boilers operate (Naylor & Schmidt, 1986). Ash composition will also change during storage and under varying environmental conditions as carbon dioxide (CO_2) and moisture react with ash to form carbonates, bicarbonates and hydroxides, as shown in Table 1.3.

Table 1.3

Combustion, hydration and carbonation reactions of wood and ash components using Ca salts as an example

CRYSTALLINE FORM		
Wood + O ₂	→	Charcoal + CaO + K ₂ O + MxOy + CO ₂ +H ₂ O
CaO + H ₂ O	→	Ca(OH) ₂
Ca(OH) ₂	→	CaCO ₃ + H ₂ O
CaCO ₃ + H ₂ O + CO ₂	→	Ca(HCO ₃) ₂
K ₂ O + H ₂ O	→	2 KOH
2 KOH + CO ₂	→	K ₂ CO ₃ +H ₂ O

Etegni & Campbell (1990); Naylor & Schmidt (1986)

1.7 Objectives of the study

Many regions within different provinces of South Africa (SA) are largely dominated by resource-poor livestock farmers whose animals depend on poor veld grazing throughout the year. The question, therefore, was if there could be alternative affordable sources of mineral elements that may be used in livestock nutrition.

Therefore, this study was designed:

- (a) To determine the potential of traditional homestead ash from fireplaces produced under rural farming conditions as a source of minerals for livestock.
- (b) To determine the mineral concentration in the ash from the main source of fire-making material, wood and bark from different tree species, including *Acacia karoo*.

CHAPTER TWO

2 MATERIALS AND METHODS

2.1 Introduction

This investigation encompassed two aspects:

A) The determination of the mineral element composition of ash from fireplaces at homesteads in rural areas.

B) The determination of the mineral element composition of the ash of fire-making material in rural homesteads. Since the mineral composition of ash from homesteads in different regions varied tremendously, this study was extended from collecting only wood from trees to the analysing of other possible sources of fire-making material in rural areas, viz. cattle manure and maize cobs.

To get an indication of variation in mineral composition in ash between tree species, wood samples from different tree species were collected and analysed. Wood samples from one tree species that is widely distributed throughout the country were collected from different locations to get an indication of geographical variation in the mineral composition within a tree species.

2.2 Sample collection

2.2.1 Homestead Ash

Ash from fireplaces at homesteads was collected in different subsistence farming regions of SA, viz. the bushveld areas of Limpopo (LP), Mpumalanga (MP) and the north-eastern KwaZulu-Natal (KZN) Provinces, as well as from the former northern and southern Transkei (ST) and Ciskei (CK) in the Eastern Cape (EC) Province. Samples were collected from five (5) homesteads per regions.

Between 200 and 500 g ash were collected in plastic shopping bags and delivered to the University of Pretoria (UP) Nutrilab of the Department of Animal & Wildlife Sciences at UP.

2.2.2 Wood from tree species

The wood from eight different tree species was collected from different regions in SA, namely: - the LP, MP, KZN, Northern Cape (NC) and Gauteng (GP) Provinces. Since many of

the tree species grow only in specific geographic regions, no attempt was made to balance for region of origin in the collection of the wood. Wood from the tree species presented in Table 2.1 was collected: These samples were collected during years 2001 and 2002, and time of the year was not accounted for.

Table 2.1

List of tree species with their scientific, common and African indigenous names

Scientific name	Common name	African indigenous name
<i>Acacia karoo</i>	Sweet Thorn	UmuNga (Z & X)
<i>Acacia erioloba</i>	Camel Thorn	Môgôtlhô (Se)
<i>Acacia sieberiana</i>	Paperbark Thorn	umKhamba (Z)
<i>Sclerocarya birrea</i>	Maroela	Marula (S), umGanu (Z)
<i>Strychnos medagascariensis</i>	Black Monkey Orange	UmKwakwa, UmNconjwa (Z) AnKwakwa (T)
<i>Combretum apiculatum</i>	Red Bush willow	UmBondwe, OMnyama (Z)
<i>Peltophorum africanum</i>	Weeping/ African Wattle	UmThobo, Isehle, Isikhabamkhombe (Z)
<i>Dichrostachys cinerea</i>	Sickle Bush	uGagane, UmThezane (Z)
<i>Trichilia dregeana</i>	Forest Mahogany	Umkhuhlu (Z & X)

Z: IsiZulu; X: IsiXhosa and S: SeSotho, T: XiTsonga

For each species, except for *A. karoo*, wood was collected from three different locations. Samples were usually taken from more than one tree per location and these samples were pooled per location. Location was classified as trees from the same vicinity, e.g. from La Montagne in Pretoria.

To get an indication of variation in composition between locations, wood samples from *A. karoo* were collected from eight different locations.

Samples per tree of approximately 30 cm long were obtained from growing trees, using an axe or a portable handsaw. The samples varied in thickness, though samplers were asked to cut branches of about the thickness of a man's arm. The samples were placed in plastic bags and delivered to the laboratory for preparation.

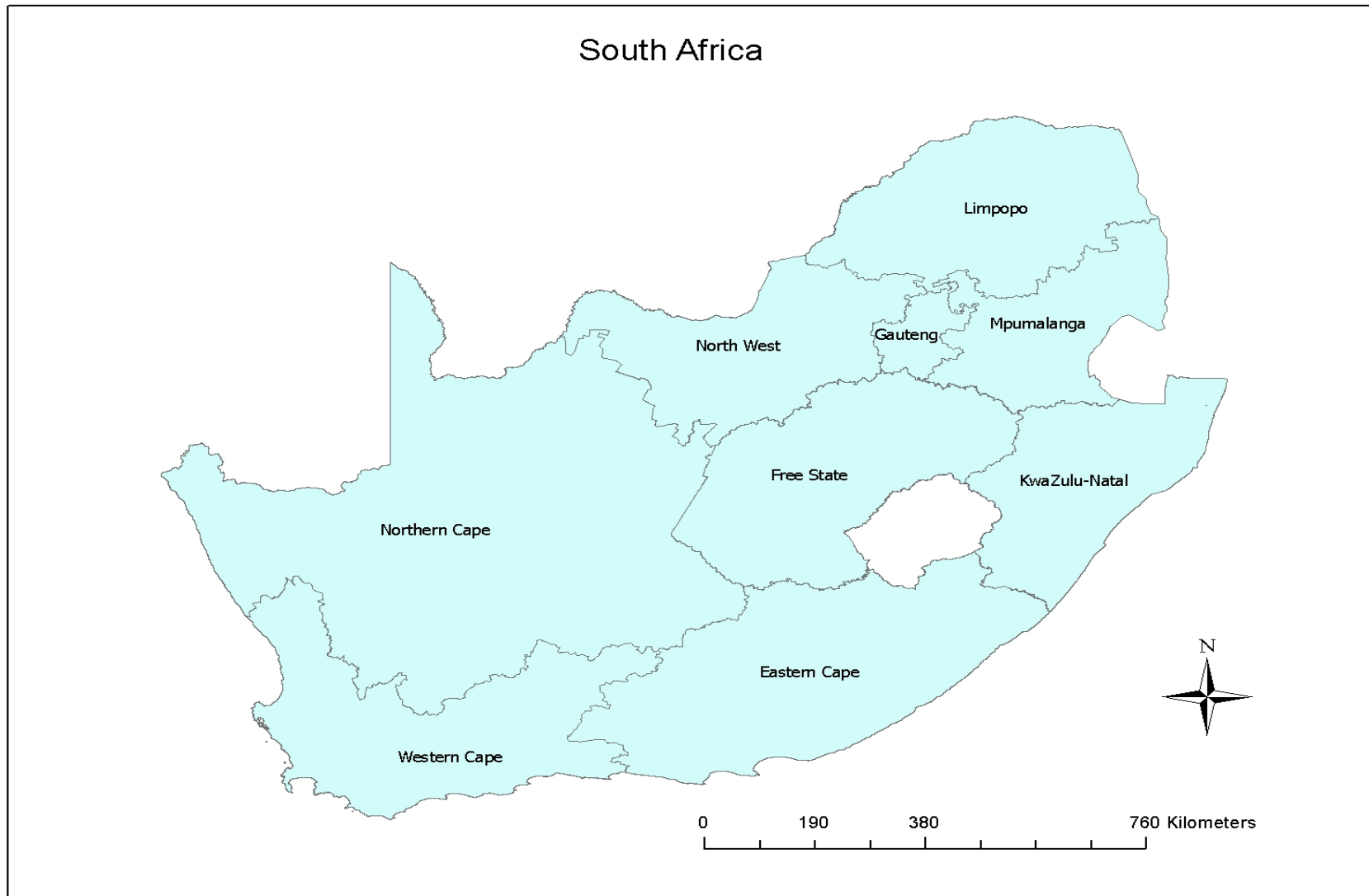


Figure 2.1: Map to show some of the provinces/ regions for Republic of South Africa where samples were collected.

2.2.3 Maize Cobs and Cattle manure

The maize cobs, after removal of the kernels, were collected from three locations in subsistence farming areas *viz.* Isomo, Pedi, Mqunduli and from three commercial farms *viz.* a farm near Thabazimbi, the UP Experimental Farm at Hatfield and that at Miertjie le Roux near Rayton.

Fresh cattle manure samples were collected in subsistence farming areas in the five districts of Northern KZN province *viz.* Nongoma, Hlabisa, Mahlabathini, Mtubatuba, Mondlo/Vryheid (figure 2.2, figure 2.3, Table 2.2 and Table2.3); EC Province (CK), and from the Free State (FS) region. The manure was kept in a cooler box, and delivered to the laboratory where the samples were dried.

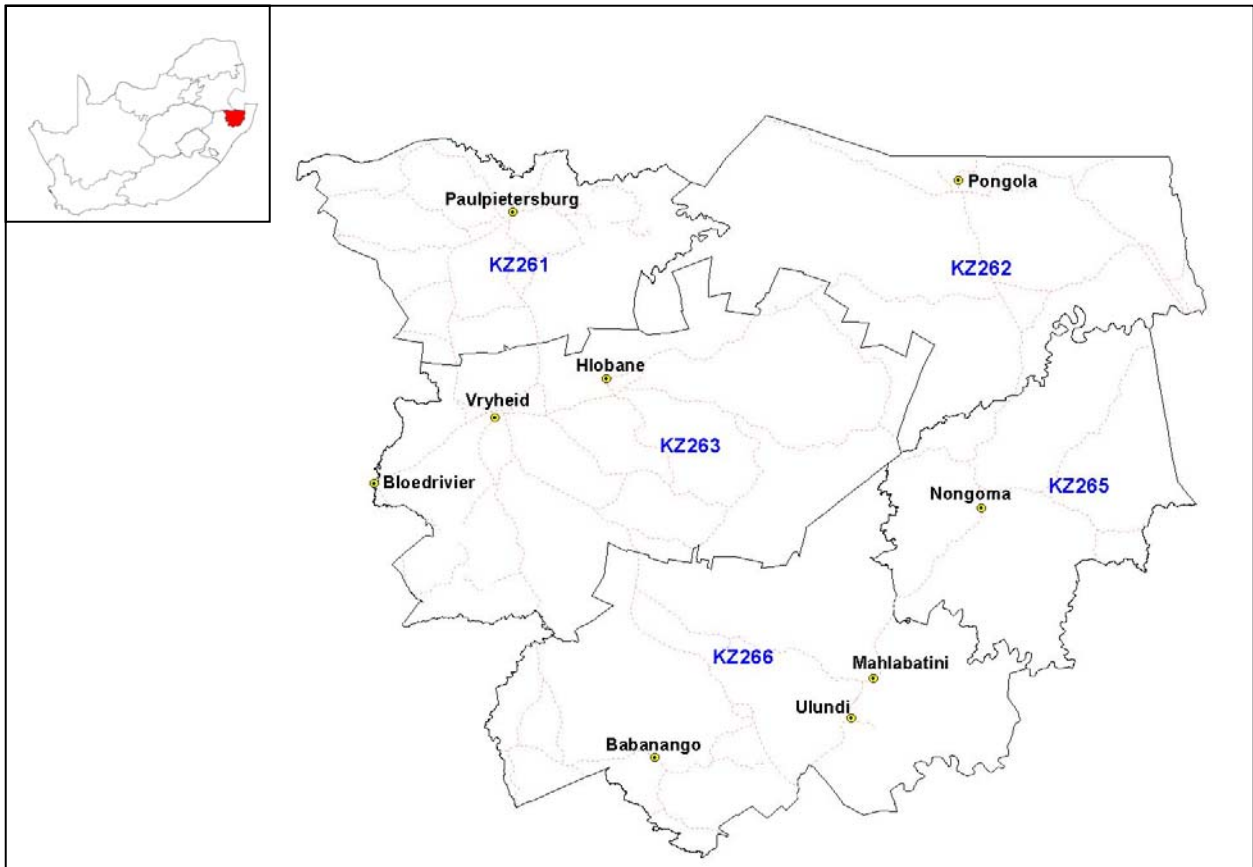


Figure 2.2: Zululand (DC 26) District Municipality in the Northern KZN Province showing subsistence farming areas where fresh cattle manure samples were collected.

Table 2.2
New names of local municipalities and the previous old names

NUMBER	NEW LOCAL MUNICIPALITY NAME	OLD MUNICIPALITY NAME
KZ261	EDumbe municipality	Paulpietersburg
KZ262	UPhongolo municipality	Pongola
KZ263	Abaqulusi municipality	Vryheid*
KZ265	Nongoma municipality	Nongoma*
KZ266	Ulundi municipality	Ulundi and Mahlabathini*

* Areas where samples were collected

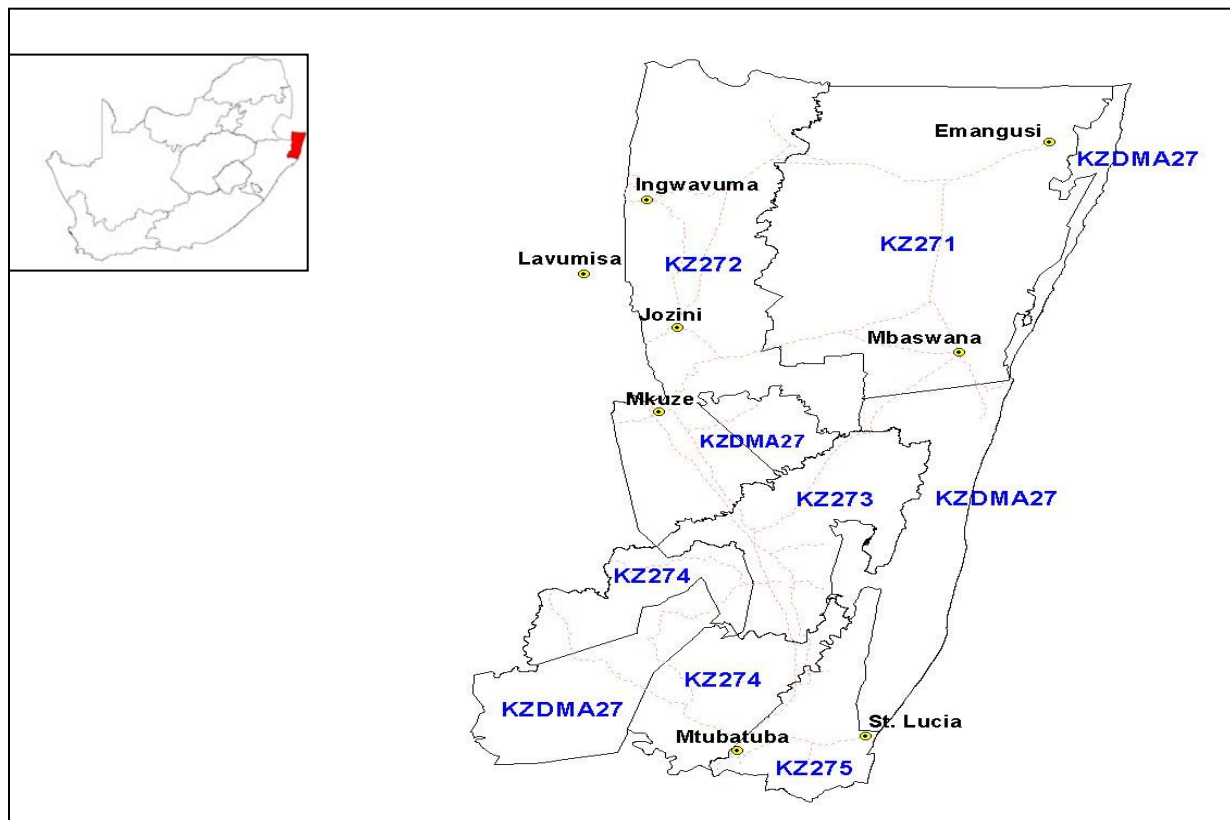


Figure 2.3: Umkhanyakude (DC27) District Municipality in far Northern KZN Province showing subsistence farming areas where fresh cattle manure samples were collected.

Table 2.3
New names of local municipalities and the previous old names:

NUMBER	NEW LOCAL MUNICIPALITY NAME	OLD MUNICIPALITY NAME
KZ271	Umhlabuyalingana	Emangusi
KZ272	KZ 272 Municipality	Nqutu
KZ273	Umzinene	HluHluwe
KZ274	Hlabisa*	Somkele
KZ275	Mtubatuba	Mtubatuba

* Areas where samples were collected

2.3 Sample preparation

Homestead ash: The ash was sifted through a kitchen sieve to remove coarse coal particles and contaminants, and ashed to determine ash content.

Wood: The wood samples from the tree species were sawed into smaller lengths, then chopped into small pieces and dried for seven days at 100 °C in a forced-air drying oven. The bark could then be separated. The wood and bark were burned separately in the open air on tinfoil, set alight with methylated spirits. The residue was further combusted at 500 °C for 8 hours in a muffle furnace after the burning. A constant volume of bark per species from the different locations was pooled because the quantity of ash in many locations was very small.

Maize cobs: The maize cobs were chopped and milled. Whole samples were ashed overnight in a furnace at 550 °C. The residue was collected and well mixed.

Cattle manure: The manure was dried in a drying oven and then ashed (as above).

2.4 Chemical analysis

2.4.1 Dry matter (DM) content

The DM content was determined as recommended by the AOAC (1990). A gram of ash was weighed into a porcelain crucible then placed in an oven at 105 °C for 16 hours. Thereafter, the crucibles were put into a desiccator containing silica gel for 30 minutes to cool before being weighed. The DM was calculated as follows:

$$\% \text{ DM} = \{A / B\} \times 100$$

Where: A = Dry matter

B = Wet sample mass

2.4.2 Ash content

After DM determination the crucibles were placed in a cold furnace. The temperature was set at 600 °C for a minimum of four hours. Afterwards, the furnace muffle was allowed to cool down to at least 250 °C. The crucibles were then placed in a desiccator for 30 minutes and weighed. The ash content of the samples was calculated as follows:

$$\% \text{ Ash} = \{A / B\} \times 100$$

Where: A = Ash mass

B = Wet sample mass

2.4.3 Organic matter (OM)

The OM content of the original samples and the ash was determined by combustion in the muffle furnace at 500 °C for eight hours. The OM content was calculated as follows:

$$\text{OM} = \text{DM (g/kg)} - \text{Ash (g/kg)}$$

The OM content was reported as in g/kg DM.

2.4.4 Minerals determinations

The following analyses for minerals concentrations were determined in all samples: Cu, Mn, Fe, Zn, P, K, Mg, Ca, Na, Al and Si. Samples were digested using wet digestion. Samples of between 0.5 - 1.0 g were soaked in 25 mL nitric acid for 10 minutes, with distilled H₂O in a block digester at 230 °C. They were therefore, removed to be cooled down for 5 minutes. Perchloric acid (10 mL) was added; digested for 30 minutes and then shaken.

The concentrations of Cu, Mn and Fe were determined using the Varian Atomic Absorption Spectrophotometer 50 after dissolving ash in hydrochloric acid (HCl). The minerals, Zn, Mg and Ca, were determined on the Perkin Elmer 2380 Atomic Absorption Spectrophotometer pp Ay II with a dilution of 0.1 % lanthanum chloride (LaCl₃). The GBC atomic absorption spectrophotometer 905 was used to determine the concentration of K and Na. The concentration of P was determined using a Technicon Auto Analyser II with colour reagent molybdovanadate. The concentrations of Si and Al were both measured, using the ICP-AES.

An internal laboratory standard sample with known concentrations of all the minerals analysed, was included in every digestion and the standard was kept in the refrigerator at all times. The macro-minerals; P, K, Mg, Ca, Na and Si were reported in g/kg DM while the micro-minerals; Cu, Mn, Fe, Zn and Al were reported in mg/kg DM. The minerals were calculated as follows:

$$\text{Macro-minerals:} \quad \% = \{\text{ng/kg} \times \text{D/M}\} / 1000$$

$$\text{Micro-minerals:} \quad \% = \{\text{ng/kg} \times \text{D/M}\} / 1000$$

$$\text{Where:} \quad \text{D} \quad = \quad \text{dilution factor while M} \quad = \quad \text{sample mass}$$

Because of the high cost of the analyses, pooled samples within groups were prepared to measure the crystalline forms of the metals in the samples. This was done to get an indication of the metal composition of the ash using the standard Powder x-ray diffraction (XRD) technique at room temperature on a Siemens D-501 automated diffractometer using a Cu target ($\lambda = 1.5406 \text{ \AA}$) operated at 40kv and 40 mA (Chung, 1974).

The instrument was equipped with a diffracted beam graphite monochromator, divergence slit of 1°, receiving slit of 0.05° and scintillation counter. A sample spinner was used. The sample was step scanned from 5° to 70° 2 θ with steps of 0.04° with a fixed counting time of 1.5s at a mean temperature of 25 °C. Quantities have been calculated assuming all phases in the samples are crystalline and using published reference intensity ratios. The scans were interpreted using Eva – software by Bruker axs. It is also important to mention that this is a wide confidence level semi-quantitative analysis and errors could be as high as 10%.

Table 2.2
 Settings of the standard Powder x-ray diffraction technique at room temperature

Instrument	Siemens D-501
Radiation	Cu $K\alpha$ (1.5418)
Temperature	25°C
Specimen	flat-plate, rotating (30 RPM)
Power Setting	40 kV, 40 mA
Soller slits	2 (diffracted beam side)
Divergence slits	1
Receiving slits	0.05
Monochromator	secondary, graphite
Detector	scintillation counter
Range of 2θ	5 - 70
Step width	0.042 θ
Time per step	1.5 seconds

2.5 Statistical analyses

An analysis of variance with the ANOVA model was used to determine the significance between different samples, e.g. homestead ash, maize cobs and cattle manure for the balanced data (SAS, 2001). An analysis of variance with the GLM model was used to determine the significance between different sample locations and interactions e.g. different tree species including *A. karoo* for the balanced data (SAS, 2001). Bark samples per tree were pooled and differences in composition between species could not be analysed statistically. Because the wood samples varied in thickness, it was considered meaningless to determine the ratio of wood to bark in the species. Least Square Means and standard deviations (SD) were calculated. Significance of difference (5%) between means was determined by multiple comparisons using Fischer Test (Samuels, 1989).

CHAPTER THREE

3 RESULTS

The objective of the study was to conduct a survey on the composition of ash from fireplaces in rural areas in different regions of South Africa. Methods used included wet digestion of samples, the use of Varian Atomic Absorption Spectrophotometer and other methods as outlined in chapter 2. This section outlines findings based on the samples collected and analyzed.

3.1 Minerals

3.1.1 Homestead ash

The concentrations of OM and mineral found in ash collected from rural homestead fires are presented in Table 3.1. It was found that all samples contained a small amount of OM, between 1.7 and 6.5 g/kg. The Ca concentrations in the samples from the northern provinces, that is KZN, LP and MP, were significantly ($P < 0.001$) higher (248 and 183 g/kg DM) than those from the EC region (8, 37 and 45 g/kg DM). In comparison, the Ca concentrations in the homestead ash from the three northern bushveld regions of SA (LP, MP and KZN) differed slightly, between 248 and 183 g/kg DM in Table 3.1.

From the XRD test (Tables 3.16 and 3.17), the Ca was mainly in the form of calcite (CaCO_3). Ash from the three regions in the EC contained only between 8 to 45 g Ca/kg and 8 to 16.2 g P/kg ash. Furthermore, Ca and P concentrations were found to be similar at 8 g/kg dry ash in the Northern Transkei (NT). High concentrations of Si in the latter samples at 331 (CK) and 252 g/kg dry ash (ST) were observed (Table 3.1) and were in the form of quartz (SiO_2) (Table 3.17) (CK: 60% and NT: 79%), respectively.

3.1.2 Minerals composition of *Acacia karoo*

The comparison of Cu content in the bark samples across the different locations showed no significant difference (Table 3.3). However, a significant correlation occurred in wood of KZN and bark of LP ($P < 0.037$); and bark of MP and wood of KZN ($P < 0.012$); bark of NC and wood of KZN ($P < 0.006$).

A significant correlation ($P < 0.05$) of Fe content in bark was observed only in samples of MP against GP and LP regions (Table 3.4). While the comparison between the bark and wood samples showed a significant correlation ($P < 0.05$) within those of GP and LP against other

locations; and the bark against bark samples of MP, GP and LP. The correlation of Zn and K in both wood and bark across the locations were insignificant.

A significant correlation at ($P < 0.05$) of P in Table 3.5 was observed in wood against bark of GP, LP and NC when compared with all other locations. The correlation for Mg within bark samples was insignificant while that within wood samples was significant only for LP against MP and KZN ($P < 0.05$). However, a significant correlation ($P < 0.05$) was observed in wood against bark of GP and LP when compared to all the other locations. An interesting significance ($P < 0.05$) for Ca was observed in the comparison of wood against bark for all the locations with the exception of GP and LP (Table 3.7). Although Na varied significantly in comparison particularly of wood against bark samples, those of LP showed a significant correlation over all the locations as depicted in Table 3.8.

Although bark and wood could not be compared statistically in other trees, those of *A. karoo* were compared since samples were collected in most of the regions of the country. The results of the micro and macro mineral concentration in bark and wood of *A. karoo* are presented in Table 3.9. The Cu and Fe concentrations in bark ranged from 20 to 124 mg/kg DM; 41.8 to 150 mg/kg DM respectively; while the wood ranged from 175 to 3256 mg/kg DM; 259 to 1000 mg/kg DM respectively and showing a similar significant difference ($P < 0.05$). The Mn and Zn concentrations in bark ranged from 75 to 716 mg/kg DM; 64 to 823 mg/kg DM respectively; and 70 to 269 mg/kg DM; 85 to 416 mg/kg DM in wood respectively. However, there was no significant difference.

The P concentration was 13.1 and 3.0 g/kg DM for wood and bark respectively and they both showed a significant difference of $P < 0.05$ while the Ca concentration was 240 and 320 g/kg DM for wood and bark respectively, showing a significant difference of $P < 0.05$. The Mg concentration was 350 and 150 g/kg DM for wood and bark respectively.

3.1.3 Minerals content of different tree species

The results of the micro and macro mineral concentrations in both wood and bark, and also in pooled bark of different tree species are presented in Table 3.10 and Table 3.11, respectively. The Cu concentrations ranged from 87 (*S. birrea*) to 5.2 mg/kg DM (*A. sieberiana*); Fe from 503.0 (*S. birrea*) to 95.0 mg/kg DM (*A. sieberiana*) and Zn from 187.0 (*D. cinerea*) to 29.0 mg/kg DM (*A. erioloba*). However, there were no significant differences between tree species. The Mn concentration ranged from 2032 (*P. africanum*) to 14.5 mg/kg DM (*S. birrea*) and were significantly different ($P < 0.01$).

The concentrations of Mg and Ca ranged from 25.4 (*S. madagascariences*) to 3.1 g/kg DM (*T. dregeana*) and 98.9 (*P. africanum*) to 13.6 g/kg DM (*D. cinerea*), respectively. The difference within the samples was similarly significant at $P < 0.01$ in both minerals. The P concentrations ranged from 20.3 (*T. dregeana*) to 2.6 g/kg DM (*S. madagascariences*) and the variation in this mineral within samples thereof, was significant at $P < 0.05$. The K and Na concentrations ranged from 140 (*A. karoo*) to 14.0 g/kg DM (*A. erioloba*) and 34.0 (*P. africanum*) to 0.3 g/kg DM (*A. erioloba*), respectively.

The mineral concentrations of single pooled bark samples of each different tree species were not analysed statistically (Table 3.11). The concentrations of Cu and Zn were the same at 56 mg/kg DM in *S. birrea*. Equal P concentrations of 1.8 g/kg DM were also observed in both *A. erioloba* and *A. sieberiana*. A slightly different Ca concentration of 320 g/kg DM from that of *A. karoo* and *A. erioloba* was observed in *C. apiculatum* while that of *A. sieberiana*, *S. birrea* and *S. madagascariences* ranged very closely and with almost the same concentrations, viz. 318, 314 and 313 g/kg DM respectively (Table 3.9 and Table 3.11).

The highest macro mineral concentration was that of Ca at 337 g/kg DM in *D. cinerea* when compared with the bark of all different tree species including *A. karoo*, while the lowest was found to be that of Na at 1.0 g/kg DM in *A. Erioloba*. Compared with micro mineral concentrations, the highest was obtained in Fe at 2070 mg/kg DM for *A. sieberiana* while Zn was the lowest at 15 mg/kg DM in *S. madagascariences*. The Fe and Cu concentration ranged almost equally at 39.5 (*A. sieberiana*) and 39.1 mg/kg DM (*D. cinerea*), respectively.

Although bark from different tree species could not be compared statistically due to limited samples, the differences were still observed, the same as in *A. karoo*. The bark showed more or less the same pattern as that of *A. karoo*.

Table 3.1

 Mean (\pm S.E.) organic matter (OM) and of micro and macro minerals concentrations in ash from rural homestead fire places

REGION*	MICRO (mg/kg DM ash)					MACRO (g/kg DM ash)						
	Cu	Mn	Fe	Zn	Al	OM	P	K	Mg	Ca	Na	Si
LP	95.0	191	3850	2124	3582	31.0	6.8	50.9	28.2	248	6.8	50.0
	± 32.0	± 130	± 735	± 2427	± 1230	± 14.0	± 2.3	± 23.2	± 12.4	± 50	± 3.3	± 32.0
MP	89.0	104	5853	308	5488	45.0	8.5	52.5	25.4	183	6.7	137
	± 58.0	± 60.0	± 3131	± 255	± 1511	± 18.0	± 4.2	± 9.3	± 9.4	± 52.0	± 4.2	± 67.0
KZN	193	208	10551	619	6360	65.0	12.2	64.4	55.9	197	13.3	71.0
	± 22.0	± 32.0	± 2947	± 241	± 1176	± 23.0	± 0.5	± 10.1	± 34.2	± 1.1	± 3.0	± 17.0
CK	135	171	13887	644	7954	61.0	12.2	7.0	14.7	37.0	4.5	331
	± 21.0	± 20.0	± 1374	± 243	± 259	± 13.0	± 1.0	± 0.7	± 0.8	± 2.8	± 0.4	± 22.0
ST	141	198	12881	429	7752	53.0	16.2	9.9	20.4	45.0	5.0	252
	± 14.0	± 30.0	± 7142	± 44.0	± 576	± 17.0	± 2.2	± 2.4	± 2.9	± 9.1	± 0.9	± 142.0
NT	41.0	190	6077	321	-	17.0	8.0	13.5	9.98	8.0	2.1	-
	± 12.0	± 34.0	± 1203	± 60.0		± 4.0	± 3.0	± 6.7	± 2.4	± 5.1	± 0.3	

*Five samples per region; LP, Limpopo; MP, Mpumalanga; KZN, KwaZulu-Natal; CK, Ciskei; ST, Southern Transkei and NT, Northern Transkei

Table 3.2

 Micro and macro mineral concentrations in ash from the wood and bark of *A. karoo* collected in different locations

LOCATIONS	<i>n</i>	MICRO (mg/kg DM ash)				MACRO (g/kg DM ash)				
		Cu	Mn	Fe	Zn	P	K	Mg	Ca	Na
Wood										
GP	3	62.2 ^c	495.9 ^c	792.4 ^a	172.9 ^b	11.5 ^b	66.0 ^a	39.0 ^a	280	8.4
LP	3	82.2 ^b	413.5 ^c	479.2 ^b	227.7 ^a	11.7 ^b	236 ^a	45.8 ^a	200	12.2
MP	3	85.3 ^b	237.5 ^a	492.7 ^b	193.9 ^a	16.2 ^a	95.6	29.2 ^b	259	7.0
KZN	3	105.6 ^a	115.8 ^b	363.9 ^b	192.6 ^a	16.5 ^a	131 ^b	27.5 ^b	220	9.4
NC	3	80.1 ^b	113.4 ^b	363.5 ^b	208.3 ^a	9.6 ^b	92.7 ^b	31.9 ^b	240	5.5
Bark										
GP	3	65.0 ^b	290.1 ^a	1551.5 ^b	189.9 ^a	2.9	23.0	17.7 ^b	309	5.1
LP	3	53.4 ^b	349.1 ^a	1492.5 ^b	121.9 ^b	3.2	39.2	21.9 ^b	292	6.0
MP	3	41.6 ^b	196.6	414.3 ^c	164.9 ^a	2.7	25.2	9.8 ^a	347	4.5
KZN	3	84.8 ^b	94.8 ^c	660.6 ^c	111.5 ^b	4.1	31.6	14.2 ^b	335	5.7
NC	3	35.0 ^a	183.5 ^b	827.9 ^a	98.4 ^b	2.3	23.2	13.7 ^a	330	4.8

 Superscripts ^{a-b-c} within columns denote a significant variation between wood and bark at $P < 0.05$

GP, Gauteng; LP, Limpopo; MP, Mpumalanga; KZN, KwaZulu-Natal and NC, Northern Cape

Table 3.3

The correlation (r) between Cu concentrations in ash of *A. karoo* collected at different locations, and between wood and bark

LOCATIONS		Copper (mg/kg DM)									
		GP LP MP KZN NC					GP LP MP KZN				
SAMPLES		Bark					Wood				
LP	Bark	0.62									
MP		0.32	0.62								
KZN		0.40	0.19	0.08							
NC		0.21	0.44	0.78	0.045						
GP	Wood	0.91	0.71	0.39	0.34	0.25					
LP		0.47	0.23	0.09	0.91	0.06	0.40				
MP		0.39	0.19	0.07	0.99	0.04	0.33	0.90			
KZN		0.96	0.04	0.01	0.38	0.01	0.08	0.33	0.40		
NC		0.52	0.27	0.11	0.84	0.07	0.45	0.93	0.83	0.29	

GP, Gauteng; LP, Limpopo; MP, Mpumalanga; KZN, KwaZulu-Natal and NC, Northern Cape

Table 3.4

The correlation (r) between Fe concentrations in ash of *A. karoo* collected at different locations, and between wood and bark

LOCATIONS		Iron (mg/kg DM)									
		GP LP MP KZN NC					GP LP MP KZN				
SAMPLES		Bark					Wood				
LP	Bark	0.89									
MP		0.02	0.02								
KZN		0.06	0.08	0.59							
NC		0.12	0.15	0.37	0.71						
GP	Wood	0.11	0.13	0.41	0.77	0.94					
LP		0.02	0.03	0.89	0.69	0.44	0.49				
MP		0.03	0.03	0.86	0.71	0.46	0.51	0.97			
KZN		0.01	0.02	0.91	0.51	0.31	0.35	0.80	0.78		
NC		0.01	0.02	0.91	0.51	0.31	0.35	0.79	0.78	0.99	

GP, Gauteng; LP, Limpopo; MP, Mpumalanga; KZN, KwaZulu-Natal and NC, Northern Cape

Table 3.5

The correlation (r) between P concentrations in ash of *A. karoo* collected at different locations, and between wood and bark

LOCATIONS	SAMPLES	Phosphorus g/kg dry ash					GP	LP	MP	KZN	
		GP	LP	MP	KZN	NC					
		Bark					Wood				
	Bark	-									
		0.93									
		0.95	0.88								
		0.74	0.80	0.69							
		0.87	0.81	0.92	0.62						
	Wood	0.02	0.02	0.02	0.04	0.016					
		0.02	0.02	0.017	0.04	0.014	0.95				
		0.001	0.001	0.0009	0.002	0.0007	0.18	0.21			
		0.0009	0.001	0.0008	0.002	0.0006	0.16	0.18	0.93		
		0.07	0.08	0.06	0.13	0.5	0.59	0.55	0.07	0.06	

GP, Gauteng; LP, Limpopo; MP, Mpumalanga; KZN, KwaZulu-Natal and NC, Northern Cape

Table 3.6

 The correlation (r) between Mg concentrations in ash of *A. karoo* collected at different locations and between wood and bark

LOCATIONS	SAMPLES	Magnesium g/kg dry ash												
		GP	LP	MP	KZN	NC	GP	LP	MP	KZN				
		Bark					Wood							
GP	Bark	-												
LP		0.54												
MP		0.27	0.09											
KZN		0.61	0.27	0.53										
NC		0.57	0.24	0.58	0.94									
GP	Wood	0.006	0.02	0.0004	0.002	0.001								
LP		0.0006	0.002	<.0001	0.0002	0.0001	0.32							
MP		0.11	0.29	0.01	0.04	0.03	0.18	0.02						
KZN		0.17	0.43	0.02	0.07	0.06	0.11	0.01	0.80					
NC		0.05	0.16	0.004	0.02	0.01	0.32	0.05	0.70	0.53				

GP, Gauteng; LP, Limpopo; MP, Mpumalanga; KZN, KwaZulu-Natal and NC, Northern Cape

Table 3.7

The correlation (r) between Ca concentrations in ash of *A. karoo* collected at different locations and between wood and bark

LOCATIONS	SAMPLES	Calcium g/kg dry ash					GP	LP	MP	KZN
		GP	LP	MP	KZN	NC				
		Bark					Wood			
GP	Bark	-								
LP		0.53								
MP		0.18	0.05							
KZN		0.35	0.13	0.67						
NC		0.45	0.17	0.54	0.86					
GP	Wood	0.33	0.72	0.03	0.06	0.09				
LP		0.0009	0.004	<.0001	<.0001	0.0001	0.009			
MP		0.08	0.25	0.004	0.01	0.02	0.41	0.05		
KZN		0.004	0.02	0.0002	0.0004	0.0007	0.03	0.52	0.17	
NC		0.02	0.07	0.0009	0.002	0.004	0.15	0.17	0.51	0.46

GP, Gauteng; LP, Limpopo; MP, Mpumalanga; KZN, KwaZulu-Natal and NC, Northern Cape

Table 3.8

 The correlation (r) between Na concentrations in ash of *A. karoo* collected at different locations and between wood and bark

LOCATIONS	SAMPLES	Sodium g/kg dry ash					GP	LP	MP	KZN
		GP	LP	MP	KZN	NC				
		Bark					Wood			
GP		-								
LP		0.46								
MP	Bark	0.59	0.20							
KZN		0.65	0.77	0.32						
NC		0.80	0.32	0.77	0.47					
GP		0.009	0.05	0.003	0.03	0.005				
LP		<. 0001	<.0001	<. 0001	<. 0001	<. 0001	0.003			
MP	Wood	0.12	0.39	0.04	0.26	0.07	0.23	0.0002		
KZN		0.001	0.01	0.0004	0.004	0.0008	0.41	0.02	0.05	
NC		0.75	0.67	0.39	0.89	0.57	0.02	<. 0001	0.20	0.003

GP, Gauteng; LP, Limpopo; MP, Mpumalanga; KZN, KwaZulu-Natal and NC, Northern Cape

Table 3.9

 Mean micro and macro mineral concentrations (LSM \pm SE values) of ash from wood and bark of *A. karoo*

PARAMETERS	MICRO MINERALS (mg/kg DM)					MACRO MINERALS (g/kg DM)				
	<i>n</i>	Cu	Mn	Fe	Zn	P	K	Mg	Ca	Na
Wood										
Mean	15	83 ^a	275	498 ^b	199	13.1 ^a	124 ^a	35 ^a	240 ^b	8.5 ^a
		± 32.6	± 245.5	± 256	± 98.5	± 0.57	± 14	± 1.1	± 4.3	± 0.28
Minimum		41.8	64.9	259.7	85.1	4.6	23.1	175	126	4.5
Maximum		150.4	823.6	1000	416.9	25.4	620	55	300	13.6
Bark										
Mean	15	56 ^b	222	989 ^a	137	3.0 ^b	28 ^b	15 ^b	320 ^a	5.0 ^b
		± 25.2	± 168.6	± 789.7	± 59.0	± 0.14	± 1.31	± 0.67	± 3.1	± 0.089
Minimum		20	75	175	70	1.73	16.5	70	250	4.0
Maximum		124.7	716.4	3256.5	269.7	7.63	67	28.1	350	7.0

 Superscripts ^{a-b} within columns denote a significant difference between wood and bark at $P < 0.05$

LSM, Least square means; SE standard error

Table 3.10

Mean micro and macro mineral concentrations (LSM and SE values) in the ash of wood from different tree species

TREE SPECIES	n	MICRO (mg/kg dry ash)				MACRO (g/kg dry ash)				
		Cu	Mn	Fe	Zn	P	K	Mg	Ca	Na
<i>A. karoo</i>	15	83.0 ±32.6	275 ±245	498 ±256	199 ±98.0	13.1 ^a ±5.7	124 ±140	34.6 ^b ±11.0	241 ^b ±43.0 ^b	8.5 ±2.8
<i>A. erioloba</i>	3	96.0 ±83.0	117 ±54.0	584 ±264	173 ±29.0	8.2 ^b ±3.1	59.4 ±13.8	25.5 ^b ±4.5	237 ^b ±49.0	2.2 ±0.3
<i>A. sieberiana</i>	3	70.0 ±5.2	315 ±145	541 ±95.0	96.9 ±44.0	6.1 ^b ±4.1	109 ±57	69.1 ^a ±5.3	243 ^b ±41.0	5.7 ±0.6
<i>S. birrea</i>	3	134 ±87.0	196 ±14.5	617 ±503	131 ±106	15 ^a ±13.5	122 ±86.5	62.6 ^a ±13.7	215 ^b ±86.5	8.2 ±1.5
<i>S. madagascariences</i>	3	94.0 ±32.9	3809 ±1161	736 ±197	129 ±57.5	9.7 ^b ±2.6	146 ±54.7	74.0 ^a ±25.4	191 ^a ±83.7	8.3 ±1.5
<i>C. apiculatum</i>	3	48.0 ±17.6	549 ±244	230 ±108	257 ±174	6.0 ^b ±5.4	68.9 ±43.9	31.6 ^b ±15.6	318 ^b ±44.5	6.6 ±1.1
<i>P. africanum</i>	3	102 ±15.4	1527 ±2032	452 ±396	93.0 ±39.0	6.7 ^b ±3.7	154 ±38.9	25.7 ^b ±9.6	211 ^a ±98.9	28.0 ±34
<i>D. cinerea</i>	3	76.0 ±24.0	138 ±50.5	548 ±102	185 ±187	17.4 ^a ±20.0	119 ±45.1	15.9 ^b ±11.4	279 ^b ±13.6	5.8 ±1.9
<i>T. dregeana</i>	3	73.6 ±11.7	256 ±95.0	739 ±358	197 ±112	31.5 ^a ±20.3	148 ±20.5	61.2 ^a ±3.1	92.8 ^a ±28.2	8.8 ±3.3

 Superscripts ^{a-b} within columns denote a significant variation on wood of the different tree species at P < 0.05

LSM, Least square means; SE standard error

Table 3.11

Mean micro and macro mineral concentrations (LSM and SE values) in the ash of bark from the different tree species

TREE SPECIES	n	MICRO (mg/kg DM)				MACRO (g/kg DM)				
		Cu	Mn	Fe	Zn	P	K	Mg	Ca	Na
<i>A. erioloba</i>	1	45.0	274	4432	139	1.8	14.0	6.5	328	1.0
<i>A. sieberiana</i>	1	39.5	123	2070	79.0	1.8	19.8	24.7	318	4.9
<i>S. birrea</i>	1	54.9	889	714	56.0	3.2	35.1	21.4	314	4.9
<i>S. madagascariences</i>	1	30.0	1693	397	15.0	11.4	41.9	32.1	313	5.8
<i>C. apiculatum</i>	1	97.7	986	1977	215	3.2	38.6	25.7	322	7.9
<i>P. africanum</i>	1	84.6	1706	59.7	194	9.4	93.7	28.0	283	7.7
<i>D. cinerea</i>	1	63.5	205	39.1	156	5.4	37.8	14.9	337	5.0
<i>T. dregeana</i>	1	45.0	309	1049	234	8.4	82.8	19.5	283	4.9

Single samples were analysed and the statistical analyses was impossible to be done due to pooled bark samples.

LSM, Least square means; SE standard error

3.1.4 Correlations between mineral concentrations

The correlation coefficients of the minerals within wood of the nine tree species *A. erioloba*, *A. sieberiana*, *S. birrea*, *S. madagascariences*, *C. apiculatum*, *P. africanum*, *D. cinerea* and *T. dregeana*; and *A. karoo*, within bark and wood are presented in Table 3.12 and Table 3.13, respectively. A highly significant correlation ($P < 0.01$) within wood was observed between concentrations of K, Ca and Mg, Ca both at ($r = 0.001$); Mn and Na ($r = 0.002$), P and Ca ($r = 0.006$) in different tree species; Mn and Fe ($r = 0.008$) and; K, Ca ($r = 0.001$) in both bark and wood of *A. karoo*.

There was a significant correlation ($P < 0.05$) observed between Fe and Mg ($r = 0.045$), Zn and P ($r = 0.011$) wood of various tree species; Mn and K ($r = 0.046$), Zn and K ($r = 0.025$), P and Ca ($r = 0.040$) in bark and wood of *A. karoo*. A similar significant correlation was also observed among Mn, Mg ($r = 0.017$) and ($r = 0.012$); Ca, Na ($r = 0.016$) and ($r = 0.044$) at both Table 3.12 and Table 3.13 respectively. No correlation was found at all between Cu and the rest of the minerals in both tables; and among Fe and Mg with the rest of the minerals in Table 3.13 only.

Table 3.12

The correlation coefficients (r) between mineral concentrations in wood ash over different tree species

MINERALS	MICRO MINERALS				MACRO MINERALS			
	Cu	Mn	Fe	Zn	P	K	Mg	Ca
Mn	0.018							
Fe	0.216	0.061						
Zn	-0.199	-0.170	-0.011 ^b					
P	0.163	-0.175	0.306	0.404 ^a				
K	0.0259	0.155	0.304	0.287	0.248 ^a			
Mg	0.191	0.379 ^a	0.323 ^a	-0.062 ^b	0.166	0.189		
Ca	-0.151	-0.278	-0.198	-0.078 ^b	-0.434 ^b	-0.533	-0.529	
Na	0.097	0.486 ^b	-0.251	-0.121 ^b	-0.129	0.184	0.001	-0.385

 Superscripts ^{a-b} within columns denote a significant variation on wood ash over different tree species at P < 0.05

Table 3.13

 The correlation coefficients (r) between mineral concentrations in ash within the wood of the *A. karoo*

MINERALS	MICRO MINERALS				MACRO MINERALS			
	Cu	Mn	Fe	Zn	P	K	Mg	Ca
Mn	-0.312							
Fe	-0.318	0.711 ^b						
Zn	-0.479	0.393	0.286					
P	0.068	0.277	0.169	0.109				
K	-0.275	0.521	0.365	0.574 ^a	0.471 ^b			
Mg	0.181	0.632	0.304	0.108	-0.091	0.147		
Ca	-0.0830	-0.307 ^a	-0.075	-0.437 ^b	-0.535 ^a	-0.787 ^b	-0.334	
Na	-0.104	0.339	0.091	0.139	0.208	0.327 ^a	0.453	-0.527

 Superscripts ^{a-b} within columns denote a significant variation on ash within wood of *A. karoo* at P < 0.05

3.1.5 Maize cobs and cattle manure

The mineral concentration of ash in maize cobs from commercial vs. communal farms was (g/kg DM): 99.3 and 82.0 Ca; 198.0 and 198.0 Mg; 83.0 and 26.0 Na, and in mg/kg dry ash; 586.0 and 415.0 Fe; 175* and 403* Zn (*P < 0.01), 246.0 and 210.0 Cu; 541.0 and 497.0 Mn, respectively and is presented in Table 3.14. Similar Fe concentrations were observed *viz.* 198.0 g/kg DM from both commercial and communal regions. Basically, all mineral concentrations were the highest in the commercial region with an exception of Mg which was similar at 198.0 g/kg DM in both regions; and Zn (175.0 and 403.0 mg/kg commercial and communal, respectively). In all micro mineral concentrations Fe was the highest at 586.0 mg/kg while Zn was the lowest at 175.0 mg/kg, both in commercial region.

The results of the mineral concentrations in cattle manure are shown in Table 3.15. The concentration of Fe was very high and ranged from 17123.0 mg/kg (Nongoma) to 102240.0 mg/kg (Hlabisa) while Cu showed very low concentrations which ranged between 0.001 mg/kg (FS) and 3.8 mg/kg (Mahlabathini). Amongst the macro minerals concentrations, K appeared to be the highest at a range of 120.0 g/kg DM (cow dung homestead ash) and 350.0 g/kg DM (FS) while Ca was the lowest at a range of 1.0 (Nongoma) and 5.1 g/kg DM (cow dung homestead ash). Although the cattle faeces were not collected at the same localities as the homestead ash, their mineral concentrations corresponded fairly well with that of the homestead ash from the EC in terms of comparisons.

Table 3.14

Mean ash and mineral concentrations of maize cob ash collected in communal farming areas vs. samples collected in commercial farming areas

COLLECTION AREA		MICRO (mg/kg dry ash)					MACRO (g/kg DM)		
	<i>n</i>	Ash (g/kg DM)	Cu	Mn	Fe	Zn	Mg	Ca	Na
Commercial	3	12.5	260	602	588	269	198	126	175
		14.0	185	399	487	125	182	117	40
		20.5	293	621	683	132	213	55.0	34.0
Mean		15.7	246	541	586	175	198	99.3	83.0
		±4.3	±55.34	±123.1	±9.801	±8.119 ^a	±0.155	±0.387	±0.797
Communal	3	14.3	282	576	423	410	239	87.0	35.0
		24.0	176	450	544	400	145	116	25.0
		19.3	173	466	278	399	209	42.0	17.0
Mean		19.2	210	497	415	403	198	82.0	26.0
		±4.9	±62.08	±68.59	±13.32	±0.608 ^b	±0.481	±0.373	±0.091

 Superscripts ^{a-b} within columns denote a significant variation at P < 0.01

Table 3.15

Mean ash and mineral element concentrations in ash in cattle manure (dry basis) collected in communal grazing and commercial farming areas

REGION	Ash (g/kg DM)	MICRO (mg/kg)				MACRO (g/kg)				
		Cu	Mn	Fe	Zn	P	K	Mg	Ca	
Northern KZN	NND	15.8	1.3	13.4	17123	3.2	92.0	278	100	1.0
	NMA	16.3	3.8	10.9	30883	5.9	119	186	170	47.0
	NHL	18.6	1.2	9.87	102240	7.8	92.0	120	140	12.0
	NMT	16.6	2.5	13.4	22368	10.1	127	158	190	12.0
	NV	15.7	2.5	11.5	48598	0.001	118	206	120	3.0
EC	CK	19.8	0.01	6.0	20738	1.4	101	251	60.0	6.0
FS	--	14.2	0.001	6.5	52622	12.8	185	350	60.0	6.0

COMMUNAL: KZN, KwaZulu-Natal; NND, Nongoma; NMA, Mahlabathini; NHL, Hlabisa, NMT, Mtubatuba; NV, Vryheid; CK, Ciskei; EC, Eastern Cape

COMMERCIAL: FS, Free State

3.1.6 Crystalline forms

The results of the crystalline form of the different minerals from different regions are shown in Table 3.16. and Figure 3.1. and 3.2. while Table 3.17. and Figures 3.3, 3.4, 3.5,3.6, 3.7 and 3.8 show those of *A. karoo*, *A. sieberiana* and *C. apiculatum* for both wood and bark. The CaCO₃ was higher in LP at 85.9% and as low as 2% in NT while the SiO₂ in NT was higher at 79% followed by CK and ST at 60 and 36%, respectively. Generally all the crystalline formation occurred in LP and KZN more than in other regions. These are also indicated by Figures 3.1 and 3.2 which show that CaCO₃ was counted to be > 40 00 Lin in KZN and > 50 00 Lin in LP, respectively.

Anhyrite occurred only in EC to a maximum of 13% while 2% of K₂SO₄ occurred only in MP. The CaCO₃ of the wood was high at 94.7% for *C. apiculatum* and lowest in *A. karoo* at 70.7% while that of the bark was similar for the two *Acacia. spp* at 97.1% and low at 93.6% for *C. apiculatum* . Amongst the crystalline forms of minerals; CaCO₃ was observed to be the highest in both wood and bark (70.7 and 97.1%) while the others were below 10%. Furthermore, CaCO₃ was also observed to be high (70 00 > 80 00 Lin) in all the barks as compared to all the wood of the species except that of *C. apiculatum* as shown in Figures 3.4, 3.6, 3.7 and 3.8. Natrite was observed only in wood of *A. sieberiana* at 5.3%.

Table 3.16

Crystalline forms of minerals in homestead ash, pooled per region, using X-ray diffraction (XRD) analysis (expressed semi-quantitatively as percentages of total*)

CRYSTALLINE FORM	LP	KZN	MP	EC		
				CK	ST	NT
Calcite (CaCO₃)	85.9	76.0	70	17	15	2
Quartz (SiO₂)	3.8	5.4	7	60	36	79
Hematite (Fe₂O₃)	0.7	1.7	-	-	-	-
Portlandite (Ca(OH)²)	1.3	1.8	2	-	-	-
Lime (CaO)	0.7	1.4	-	-	-	-
Siderite (Fe(CO₃))	0.7	1.8	1	-	3	-
Dolomite (CaMg (CO₃)₂)	1.4	1.7	-	-	-	-
Sylvite (KCl)	1.5	2.7	1	-	-	-
Manganese Flouride (MnF₂)	0.3	0.7	-	-	-	-
Albite (Ca, Ca)Al (Si, Al)₃O₈	3.6	3.2	-	-	-	-
Arcanite (K₂SO₄)	-	-	2	-	-	-
Wuestite (Fe_{.9712}O)	-	-	-	-	-	-
Halite (NaCl)	-	-	-	-	-	-
Anhydrite	-	-	-	-	13	5

LP, Limpopo; KZN, KwaZulu-Natal; MP, Mpumalanga; EC, Eastern Cape; CK, Ciskei; ST, Southern Transkei and NT, Northern Transkei

Table 3.17

Crystalline forms of minerals in the ash in wood and bark of different tree species, using X-ray diffraction (XRD) analysis (expressed semi-quantitatively as percentages of total*)

CRYSTALLINE FORM	<i>A. karoo</i>		<i>A. sieberiana</i>		<i>C. apiculatum</i>	
	Wood	Bark	Wood	Bark	Wood	Bark
Calcite (CaCO ₃)	70.7	97.1	71.8	97.1	94.7	93.6
Quartz (SiO ₂)	-	0.5	-	0.4	-	0.3
Hematite (Fe ₂ O ₃)	1.2	-	-	-	0.7	0.7
Portlandite (Ca(OH) ²)	4.7	0.9	3.6	-	2.1	1.3
Lime (CaO)	-	0.6	-	0.5	0.4	0.2
Siderite (Fe(CO ₃))	0.7	-	0.8	-	0.3	0.4
Dolomite (CaMg (CO ₃) ₂)	-	0.5	-	-	0.7	0.7
Sylvite (KCl)	1.6	0.4	1.1	0.4	-	0.3
Manganese Flouride (MnF ₂)	0.4	-	0.5	-	-	0.2
Albite (Ca, Ca)Al (Si, Al) ₃ O ₈	9.9	-	5.7	-	1.0	1.4
Arcanite (K ₂ SO ₄)	2.9	-	5.5	0.8	-	0.8
Wuestite (Fe. ₉₇₁₂ O)	0.5	-	-	-	-	-
Halite (NaCl)	-	-	1.5	-	-	-
Serpentine	4.2	-	2.1	-	-	-
Natrite	-	-	5.3	-	-	-

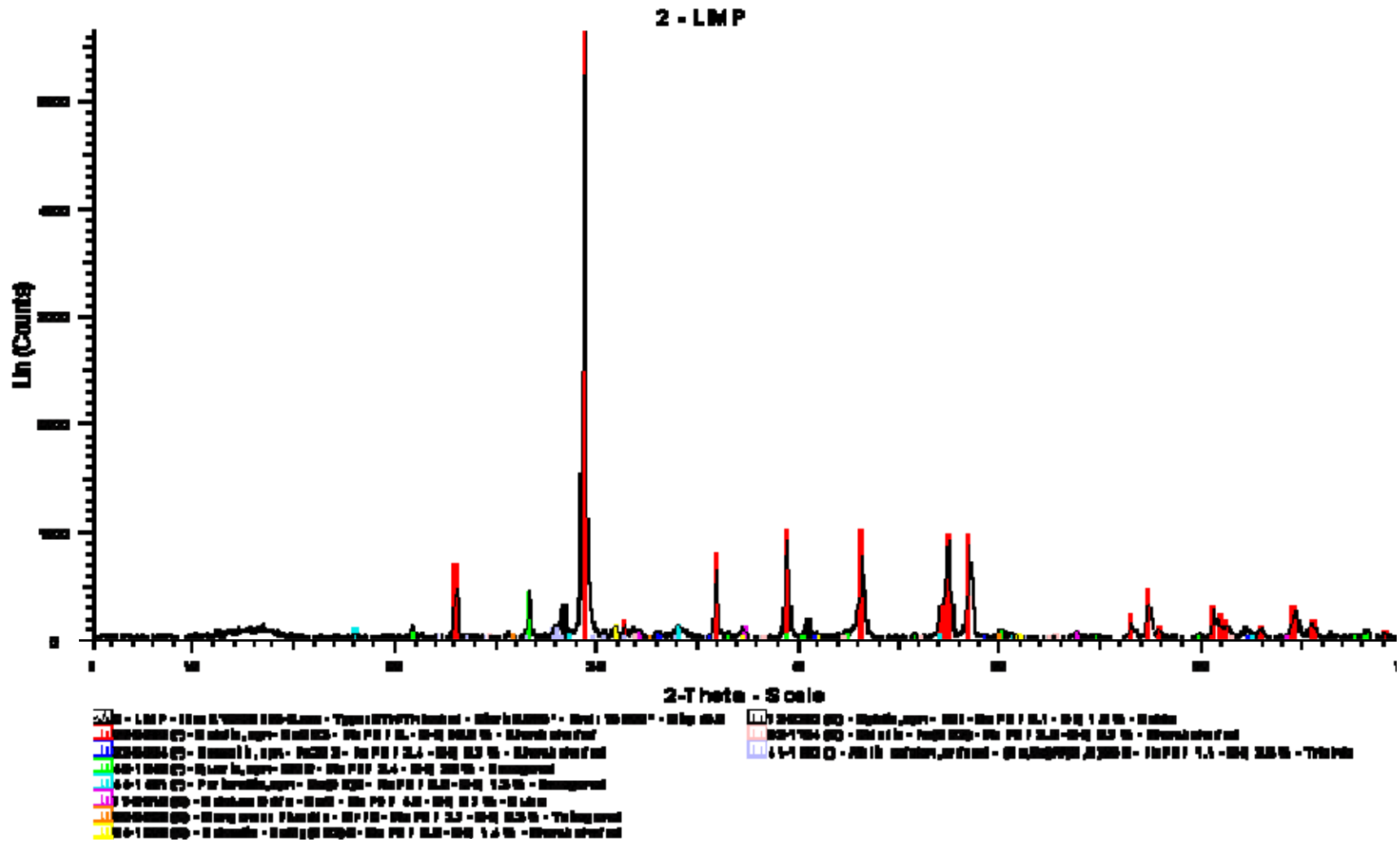


Figure 3.2: The crystalline form of minerals in homestead ash pooled in Limpopo

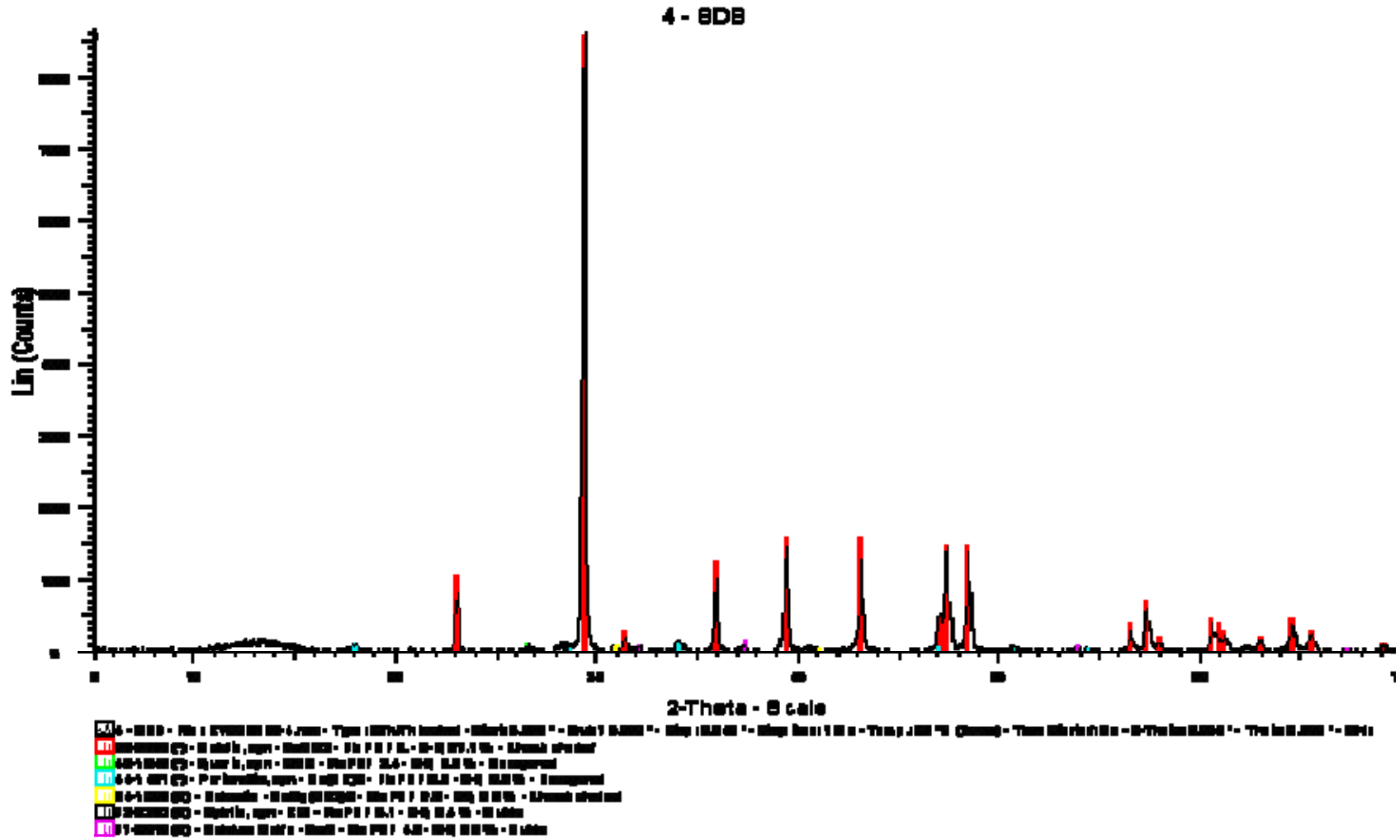


Figure 3.4: The XRD analysis for crystalline mineral form ash of in bark of *A. karoo*

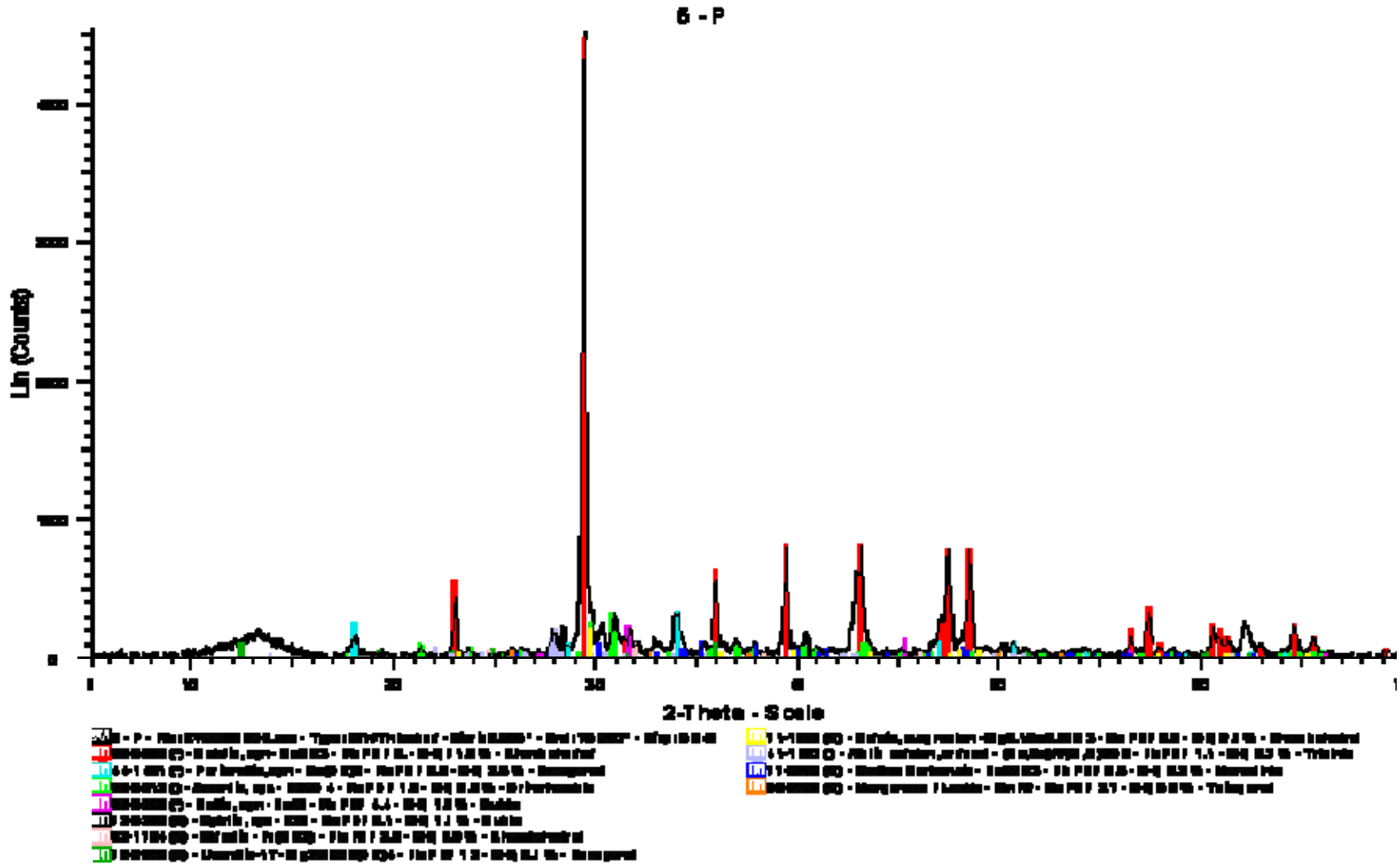


Figure 3.5: The XRD analysis for crystalline mineral form in ash in *A. sieberiana* wood

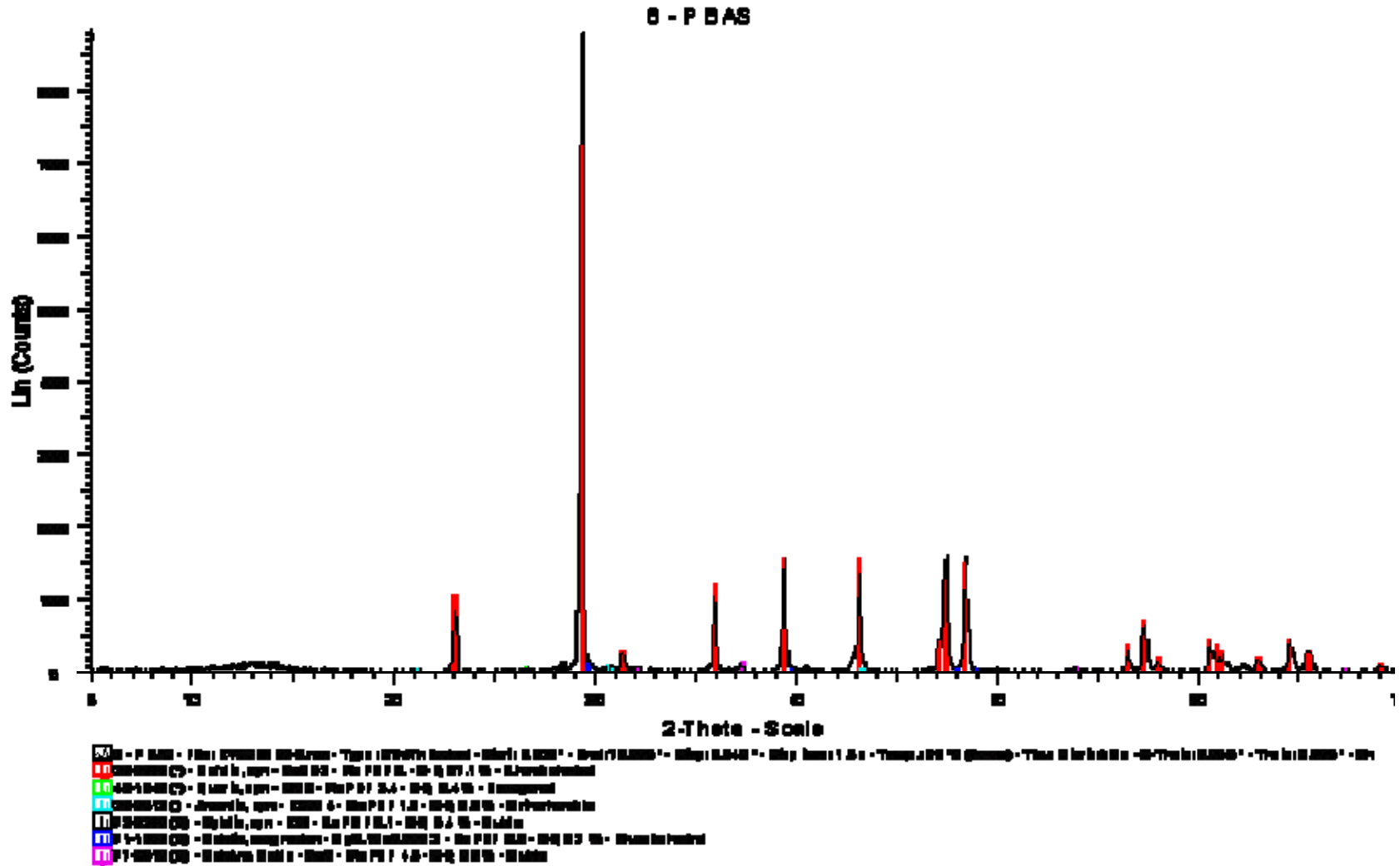


Figure 3.6: The XRD analysis for crystalline mineral form in ash of bark of *A. sieberiana*

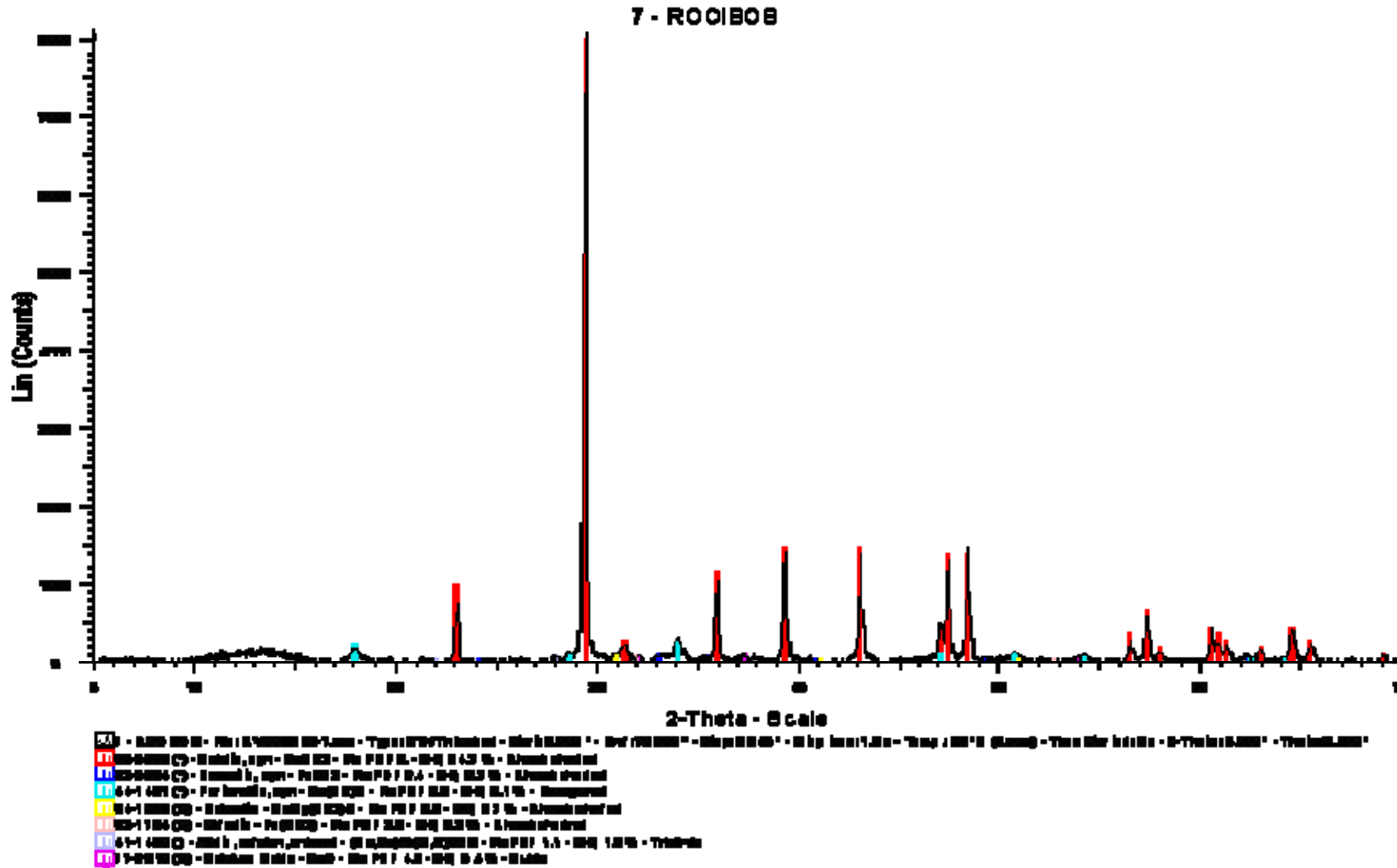


Figure 3.7: The XRD analysis for crystalline mineral form in ash of wood of *C. apiculatum*

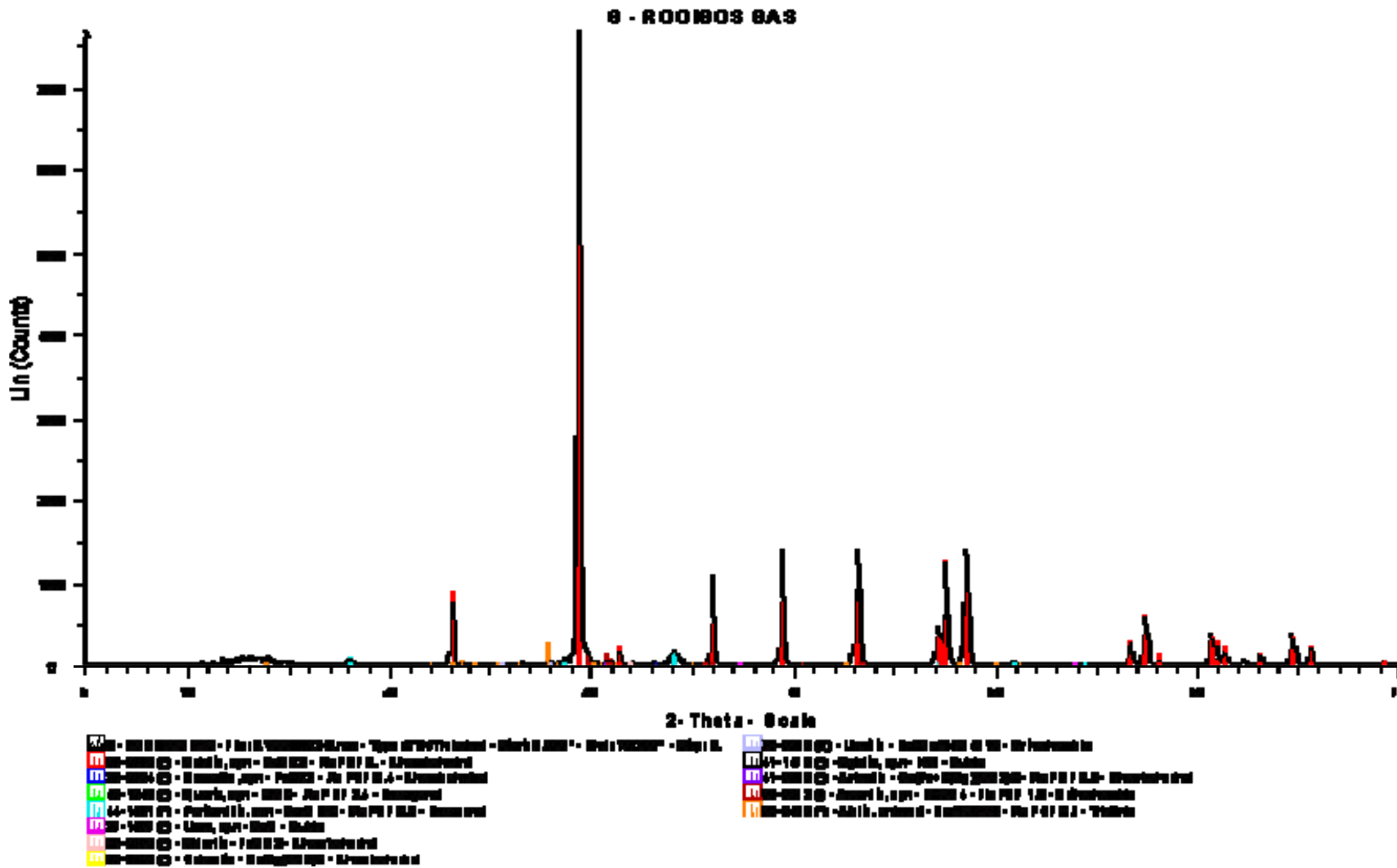


Figure 3.8: The XRD analysis for crystalline mineral form in ash of bark of *C. apiculatum*

CHAPTER FOUR

4 DISCUSSION

An interesting result from this investigation was that homestead ash collected from different rural areas in South Africa differed widely in mineral composition. The obvious conclusion would be that people used different material for fire making in different regions. In the savanna / bushveld regions in the northern parts of the country wood from trees and bushes are obviously being used, with the composition of the homestead ash corresponding quite well with the mineral composition of wood ash.

Homestead ash from the Transkei and CK regions of the EC Province contained only between 8 and 45 g Ca/kg ash compared to over 180 g/kg in ash from the northern provinces. It could be concluded that different fire making materials with different chemical compositions have been used in these regions of the EC. In the Transkei and CK regions of this province the land has been largely denuded of trees, and other sources of fire making materials were obviously used, such as maize cobs and cattle manure. The investigation was therefore extended to measure the mineral composition of ash from cattle manure and maize cobs.

The mineral composition of ash in maize cobs from commercial and communal farms is presented in Chapter 3. In Table 4.1 the composition of maize cobs and cattle manure from communal farming areas is highlighted to compare them with those of the homestead ash from these regions.

Table 4.1

Average mineral element composition in the ash (dry basis) in maize cobs and cattle manure collected in communal grazing areas vs. the composition of the homestead ash collected in the Eastern Cape

MINERALS	Ca	P	Mg	K	Na	Fe	Zn	Cu	Mn
	g/kg					mg/kg			
Maize cobs: Communal farms									
	8.2	-	19.8	-	2.5	414915	403148	210	497
Cattle manure: Communal farms									
	45.5	11.0	14.4	19.2	12.2	44200	391	107	-
Eastern Cape: Homesteads									
	29.8	12.1	15.0	10.1	3.9	10948	465	106	186

The Fe plus Zn concentration constituted about 82% of the elements in the ash of maize cobs. It is therefore most unlikely that maize cobs could have been the source of the homestead ash from the EC. Although the cattle manure was not collected at the same localities as the homestead ash but in the same region, the mineral composition corresponded fairly well with that of the homestead ash from this region. This suggests that cattle manure was probably an important source of fire making material in the EC and could explain the differences in composition of homestead ash between the EC and the northern provinces of SA. However, it is known that maize cobs are also widely used as fire making material in many regions of SA such as in the FS Province.

Irrespective of its mineral composition, to answer the question of whether ash from homestead fireplaces in communal farming areas could be used as mineral supplements to livestock, it could be concluded that ash from homesteads tends to vary tremendously in mineral composition, depending on the material used to make the fires. Even within a region or homestead it must be recognised that ash from homestead fires would derive from a mixture of tree species and may vary from day to day and in different locations. This has been pointed out by Nolte *et al.* (1987), as well. Therefore, before considering the feeding of the ash, the user / advisor should at least have some idea of what the potential composition of the ash would be.

A further problem with the use of homestead ash is that it may contain foreign material such as unburned pieces of wood and charcoal, bones, rocks, nails and wire, glass and other contaminants. These coarse materials can be removed through the sifting of the ash. Whether this is feasible will depend on the availability of, for instance, a kitchen sieve, and whether the user of the ash is prepared to take the trouble of sifting the material or using his/her kitchen utensils for that purpose.

Impossible to remove would be soil contaminating the ash. Soil in ash could originate from the soil on which the fire was made and included while collecting the ash, or from the fire-making material itself. The exceptionally high Si content of the ash originating from the EC in the present study leads to some speculation of its source. It is significant that, without exception, all samples from this region contained high concentration of Si, while samples from the northern provinces contained substantially lower Si concentrations. Contamination through soil at the fire-making sites is therefore, probably not the main reasons for the high Si levels in the EC samples. It was concluded that cattle manure was the main source of fire making material in this region.

Almost each patch of cattle dung would probably land on the soil after defecation by the animal. Some soil would therefore, be collected with each patch of manure. However, the fact that the Si was so consistently present in all ash samples could also imply that the soil intake by cattle in the area could have been very high. Those rural grazing areas are frequently overgrazed, forcing grazers to pick food quite close to the soil, with a likelihood of taking in some soil (Fries *et al.*, 1982; Ammerman *et al.*, 1984). Unfortunately the Si content of the manure samples collected from those areas was not determined in the present study.

A further risk when using ash from fire places is that burned materials that contain toxic substances which would end up in the ash might have been used, e.g. toxic elements from wood treated with chromated Cu arsenate to preserve it (Jones, 2006), waste plastics, metal or other synthetic substances containing toxic metals (Reilly, 1991).

The ash content of the wood from the trees analysed, corresponded well with reports in the literature that ash from tropical and subtropical trees (hard wood) contains more than 1% ash, while trees from temperate regions contain from 0.1 to 1% ash (Campbell, 1990). Bark contains substantially more ash than the wood itself, as verified in the present study. In a fire-making situation the bark and wood would probably not be separated, and the percentage of ash could be expected to be well above one. That would depend on the proportion of wood to bark, thus, amongst other reasons, the thickness of the logs or branches used, and this would not be consistent between fires.

Although it has been reported in the literature that the mineral composition of wood would vary depending on soil type and climate (Ellis, 1962; Ramirez *et al.*, 1992; Greene, 1988 and Nolte *et al.*, 1987)) no clear regional differences could be observed in the *A. karoo* samples collected in different parts of South Africa, though the P levels in the ash from the NC (Kuruman / Vryburg districts) was lower than in the samples from the other areas. However, three samples per region were probably too few to reflect any differences except if the differences were substantial.

The Ca concentration in the wood samples from the different tree species varied between 93 to 318 g/kg dry ash. However, the 93 g/kg in *T. dregeana* is really an outlier compared to the Ca from the other species where the second lowest was the 191 g/kg in the ash from *S. madagascariences*. The Ca in the bark ranged from 283 to 337 g/kg ash, with the *T. dregeana* again being the lowest. The Ca content in the ash from homesteads in the northern regions of the country was 248 (LP), 183 (MP) and 197 (KZN) mg/kg.

The values of the last two were lower than in most wood samples, suggesting that other sources of fire making material were probably used together with wood. Imbeah (1999) reported that ash from wood fires collected from houses in Papua New Guinea contained 121 g Ca/kg ash, while Campbell (1990) stated that wood ash in general contains between 80 and 330 g Ca/kg.

As an aside: It is interesting to note that the r between Ca concentrations and the concentrations of the macro-nutrients in the ash were negative (most of them significant) in both the analyses of the different tree species (Table 3.12) and that of *A. karoo* (Table 3.13) collected in different regions. That means that the higher the Ca contents in ash, the lower the concentrations of the other macro-elements in the ash. Correlations between Ca and the micro-elements were negligibly small.

The crystalline forms of the elements in the ash from both the homesteads in the three northern provinces and the trees analysed, showed that the ash consisted mainly of CaCO_3 (“calcite” - the term used by the geology laboratory), in accordance with Demeyer *et al.* (2001), with small proportions of other mineral salts containing Ca and the other elements. In the ash of the three tree species analysed, CaCO_3 constituted 70.7 to 94.7% of the ash in the wood and 93.6 to 97.1% in the bark. It could be concluded that ash from trees consists predominantly of CaCO_3 or “feed lime”, in animal nutrition terms (Bredon *et al.*, 1987). Taking into consideration that CaCO_3 contains 40% Ca, and that the bark ash contained 31% Ca and wood ash 24% Ca, then approximately 77.5% of the ash in bark was CaCO_3 , and 60% in the wood. These values are lower than those obtained from the XRD technique that determined the crystalline forms of the elements. This is probably a reflection of the semi-quantitative nature of the XRD technique.

The other macro-elements are present in wood ash in relatively low concentrations, except for K where the concentration in wood ash ranged from 69 to 154 g/kg and in bark from 19.8 to 93.7 mg/kg ash. As indicated in the Chapter 1 (Lerner & Utzinger, 1986; Naylor & Schmidt, 1986; Campbell, 1990; Etiegni, 1990), wood ash was considered an excellent source of potash (K). An inconsistency in the present study is that according to the chemical analyses of the ash, the K concentrations are fairly high in the ash. However, according to the crystalline forms of the ash (Table 3.16), K was present only in small proportions in the crystalline forms, sylvite (KCl) and arcanite (K_2SO_4). This is probably a reflection of the semi-quantitative nature of the XRD technique. The similar concentrations of Ca and P as observed in the XRD test results from NT may imply an imbalance in the Ca:P ratio.

From an animal nutrition perspective, wood ash should be an excellent source of Ca. In the form of CaCO_3 the Ca would probably be highly available to the animal. However, only a limited number of feedstuffs available in rural situations have a serious deficiency of Ca and would need to be supplemented. Cereal grains and their by-product are typically deficient in Ca (Bredon *et al.*, 1987), but probably not available in these regions for animal consumption. However, cassava roots contain very low levels of Ca (Oke, 1978; Smith, 1988) and the non-fibre carbohydrates in cassava are high in amylopectin, compared to maize, and are more suitable in ruminant nutrition than in human diets (Oke, 1978). Therefore, in subsistence situations where cassava can be produced, wood ash would form an excellent Ca supplement where cassava roots are fed to livestock

A major deficiency of the fodder available to grazing animals in the tropics and subtropics is phosphate (Du Toit *et al.*, 1940). In general, that is one of the primary reasons for supplying mineral supplements to livestock, i.e. to provide P. Unfortunately wood ash contains a very low concentration of P, and is thus not suitable for use as a mineral supplement in most grazing situations in the tropics and subtropics.

The concentrations of the micro-elements in wood ash are quite high. However, if used as a supplement, wood ash would probably form only a very small proportion of the total diet, probably well below 5%. Such a small quantity of wood ash would contain very little of the trace elements. Even at trace element concentrations in ash as high as 1000 mg/kg ash, as was the case for Fe, Mn and Zn in some samples, only 1 mg of the element would be supplemented at an inclusion rate of 1% ash. A further uncertainty would be whether the elements in ash are highly available in the forms present in the salts (Demeyer *et al.* 2001). According to Table 3.16, the largest proportion of Fe was present as hematite (Fe_2O_3) and Mn as manganese fluoride (MnF_2).

It is well documented that wood ash is rich in Ca and has been used successfully as a fertilizer especially to ameliorate the acidity in soil (Demeyer *et al.*, 2001). Campbell (1990) suggested that land application appears to be a safe and economic method for disposing of and utilizing wood ash. An indirect benefit of using ash from wood as a fertilizer would be that a rise in pH of acidic soils would increase the availability of elements such as P, Mg and Se to plants (Reid & Horvath, 1980), and therefore an increased supply to the animals consuming them.

Maize cobs from the commercial and communal farms contained 58.6% and 41.5% Fe and 17.5% and 40.5% Zn, respectively. This suggests a different scenario on the utilization of ash from maize cobs, though this would not be discussed further.

Except for the Fe concentration, the mineral concentrations in the cattle manure from the communal grazing areas in the EC (Table 3.15) were less than 50% of that in manure from steers in feedlots (converted to an ash basis) in the United States of America, as reported by Fontenot (1991). Even though cattle manure could be a potential source of P, the concentrations in the homestead ash collected in the EC were still very low, too low to be considered a potential source of supplemental P for grazing livestock.

Alternative uses of ash could be considered. Ramirez *et al.* (1991, 1992) reported improved digestibility and increased mineral content in sorghum straw and maize stover soaked in 20% or 30% wood ash solutions for 6 hrs. Soaking sorghum straw, maize stover or rice straw for a few hours to increase their mineral content is a type of technology that can be adopted at the village level. However, application to the soil as fertilizer would probably be the most successful way of utilizing ash from homesteads in the rural village situation.

CHAPTER FIVE

5 CONCLUSION

1. It is not recommended that ash collected from homestead fireplaces in rural areas be used as a mineral supplement in diets for livestock. Apart from a wide variation in composition between locations, there is a possibility that the ash could be contaminated with a variety of undesirable substances such as soil, pieces of wood, pieces of iron, etc.
2. If fireplace ash is to be used for specific purposes, it is advisable to establish what kind of fire-making material was used. That would give the user an idea of what the composition of the ash is likely to be, and for what it can be used. However, such ash should preferably be used for purposes other than the feeding of animals, e.g. as a fertilizer to ameliorate the pH of acid soils, or even to alkali-treat low-quality roughage.
3. Since wood ash is rich in Ca, it could be used to supplement deficiencies in diets that contain ingredients known to be deficient in Ca. A good example of these would be cereals and cereal by-products, if available for animal nutrition. Cassava roots and root products, on the other hand, are products that are low in Ca and are widely utilized in many developing countries as animal feed. Diets containing cassava could successfully include wood ash as a Ca source instead of feed lime. However, it seems advisable that the ash is prepared specifically for the purpose of being used as a feed ingredient, rather than being collected from homestead fireplaces.
4. If the usually cheap source of Ca, feed lime, is not readily available, for instance in remote rural areas, wood ash should be an excellent source of Ca in farm animal diets. Laying hens have high Ca requirements relative to other chickens and farm animals, and would probably benefit from additional Ca when on a free-ranging, scavenger type of diet. However, to get animals to consume the ash which is a fine powder, could be a problem.
5. Although wood ash contains other mineral elements, their concentrations are too low to contribute much to the mineral content of a diet, especially because the ash, as a supplier of Ca, would probably be included in diets at levels of <5%.

6. It is acknowledged that the investigation in the present study on the possible alternative sources of fire-making material in the Transkei and Ciskei was rather exploratory. However, the alternatives gave such dramatically different results, and explained the differences sufficiently that no further efforts were made to obtain more material to analyse. Further investigations could be undertaken to explain the differences in the composition of ash from homesteads in different regions. However, the information would be of little practical significance and probably not worth pursuing.

7. Since the primary deficiency problem in herbivores in the subtropics and tropics is P, in theory ash from cattle dung should be a source of P. Unfortunately this does not look very promising, considering the low P content of the ash from cattle dung samples analysed in the present study.

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