Wood Ash use in forestry A Review of the Environmental Impacts

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Introduction

Following a brief introduction to the geographical history of wood ash production and research, this report is separated into three main sections. Section A systematically addresses all those factors that affect the chemical composition of wood ash; Section B discusses the potential physical and chemical environmental implications of recycling wood ash and Section C, the biological response.

A brief history of wood ash use : data sources

- Finland dry wood ash has been used as soil ameliorant for second rotation forestry on drained peat bog sites. Research data, from 1935 to the present, exists from extensive field monitoring. Key papers: Hakkila (1989), Korpilahti *et al.* (1998).
- Sweden ash is produced from energy generation (biomass fuel stations). There has been wide ranging research on ash recycling to forest sites on peats and podsols under the auspices of SkogForsk since the 1970's.

Key paper: Högbom & Nohrstedt, SkogForsk Report 2 (2001).

Denmark – ash is produced from community energy projects using mixed organic fuels such as straw, woodchip, green waste and tree thinnings. This results in ash of variable chemical content with heavy metals and dioxins, particularly in fly ash which is not routinely separated out.

Key paper: Serup, H (ed)Wood for Energy Production (1999). Report of the Centre for Biomass Technology – Möller and Ingerslev (2001).

USA – ash is derived from paper industry waste and power generation. Nationally 90% of this goes to landfill. This proportion falls in the Lakes region to 44%, and in NE States only15% is landfilled, as the remaining eighty percent is land applied and 5% added to sewage composting. Research since 1980's evaluating detrimental effects of leachate from landfill sites has resulted in renewed trials of ash as a fertiliser for agricultural crops and forestry, particularly on sandy soils.

Key papers: Greene (1988), Campbell (1990) and Vance (1996).

Section A: Wood ash – the raw material : factors affecting wood ash chemistry

1. Effects of the fuel type and burn process.

There are major differences between the ash chemistry derived from different burning processes: e.g. bottom ash, fly ash and hog fuel ash. A glossary of some of these processes and products is given below:

- **Hogged fuel** a term used in America to include all wood residues, such as bark strippings from the paper industry, wood fines/shavings from the furniture and timber chipping.
- **Bark Boilers** used commercially in the US to burn all the above plus coal, natural gas, waste plant sludge, tyres and paper packaging. Ash residues, which may be 0.5% to 6.0%, generally increase as the percentage of wood decreases.
- Combustion plants hot gases from wood chip combustion are used to raise steam for a generator.
- **Gasification plant** combusts wood in restricted O₂, and uses these gases to drive a generator. This gives higher efficiencies to the system and produces less ash.
- **Grate fired ash** That which has been burned on a perforated metal grate bed in situ in the burner (common in the US).
- Bottom ash associated with ash falling into a fluidised bottom bed (CFB) for delivery to settling ponds.
- Fly ash- fine airborne ash that is retrieved from washings of chimneys and extraction systems. Average ash particle size from a mixed boiler is ~230µm (Etiégni & Campbell, 1991).

Circulating Fluidised Bed ash (CFB) is generally easily separated into bottom and fly ash, whereas grate fired ash usually includes a mixture of bottom & fly ash (80 & 20%).

Burning hogged fuel results in an ash with a very variable macronutrient content (Someshwar, 1996). The proportion of bark in the boiler particularly alters the Al and Si content due to sand collected during logging. Mean ash content data from eight typical US industrial bark boilers and six US paper mills furnaces taken from Muse (1993) and Campbell (1990) are given in Table 1. Note the overall high pH. The wide variation in element concentrations in Table 1 were also confirmed in Finland by Hakkila (1989) in a survey of six bark fired power plant boilers.

| | | residue/bark ash mpbell, 1990) | Pulp & paper mill a (Muse, 1993) | | | |
|----|-------------|-----------------------------------|-------------------------------------|------------|--|--|
| | Median g/kg | Range | Median g/kg | Range | | |
| 41 | 20.0 | 15.9-32.0 | 9.1 | 8.0-14.5 | | |
| Ca | 132.0 | 73.5-331.4 | 165.5 | 77.5-235.0 | | |
| Fe | 15.1 | 3.3-21.0 | 5.1 | 4.2-7.3 | | |
| K | 29.3 | 16.6-41.7 | 25.7 | 13.1-37.1 | | |
| Mg | 14.7 | 7.1-22.4 | 10.7 | 4.3-22.4 | | |
| Mn | 6.7 | 3.3-12.7 | 3.2 | 0.0-7.3 | | |
| Na | 2.4 | 1.5-5.4 | 1.0 | 0.6-1.8 | | |
| Р | 7.9 | 3.3-13.6 | 3.9 | 0.3-7.2 | | |
| S | 5.6 | 4.4-6.8 | 2.0 (mg/kg) | 0.8-6.0 | | |
| pН | 12.7 | 11.7-13.1 | 12.4 | 11.9-12.8 | | |
| Ċ | | | 254.5 | 69.2-493.0 | | |

| Table 1. | Comparison o | of ash chemistry | from bark and | pulp mill wood residue |
|----------|---------------------|------------------|---------------|------------------------|
| | 1 | • | | 1 1 |

2. Effects of tree components on ash chemistry

Hakkila (1989) gives the most detailed summary of the major differences in elemental composition between various ashed segments of the tree. This is taken from both published sources and his own laboratory research. He concludes that branch and root wood are generally richer in elements than stem wood, and that bark and foliage have concentrations between five and ten fold greater than stem wood. Note the particularly high values of Ca in bark ash, and also Mn, Al and S.

Foliage concentrations of Ca, Mg and Fe are known to increase with leaf age (Waring and Schlesinger, 1985) whereas initial concentrations of N, P and K decrease with foliage age as elements are withdrawn preceding leaf abscission and leaching by rainfall removes mobile elements. Calcium content increases with leaf age as calcium pectate deposition increases in cell walls, and calcium oxalate increases in the cell vacuoles.

The following general trends for major elements appear to hold good from Hakkila's summary:

| | Stem wood | Stem bark | Branch | Foliage |
|---------------|-----------|---------------------|-----------------------|-------------------------|
| Values in % | | | | |
| Р | 0.02 | - | Increases 2 to 4 fold | Increases 7 to 10 fold |
| Κ | 0.05-0.15 | - | 0.15-0.2 | 0.4-1.2 |
| Ca | 0.1-0.5 | 0.5-0.9 | - | 0.5-1.2 |
| Mg | 0.02-0.04 | 0.05-0.15 | - | (soft) 0.1 – (hard) 0.2 |
| Values in ppm | | | | |
| Mn | 30-200 | 150-1000 | - | 500-1000 |
| Fe | 20-100 | (root bark 150-500) | - | - |
| Zn | 10-80 | irreg .increases | increase | increase |
| S | 80-120 | 300-400 | - | 500-1000 |
| Al | 20-60 | increase | increase | increase |
| B, Cu, Mn | <20 | <20 | <20 | <20 |

 Table 2.
 General trends for major elements in wood ash

See also Table 4. N levels are commonly < 0.1%, and rarely reported.

3. Effects of tree species on ash chemistry.

Someshwar (1996) has summarised data from five American authors to show the effects of species composition on the resulting wood ash chemistry. Some of this is generalised to tree type, e.g. pine, oak etc, but there is even less specific data comparison from Europe. Hakkila (1989) has summarised data from Finland for a generalised category of hardwoods (including *Alnus incana, Betula* spp, and *Populus tremula*,) and softwoods, including *Pinus sylvestris* and *Picea abies*). Few other Scandinavian authors state the tree types used in their experiments, but as most of the ash used in experimental work in Scandinavia comes from commercial energy plants, it could be assumed to be a mix of conifers (possibly with some birch). For example, Lumme and Laiho (1988) specify bark ash proportions in their experiments as 70% from spruce and 30% from pine.

In Table 3 below the available data for stem wood (*without bark*) for conifers and hardwoods is taken from the USA sources (Misra *et al.*, 1993 and Mingle & Boubel, 1968).

| | Conifers | | | Broadleaves | | | | | | | |
|-------------------|--------------------|-------------|-----------------------|--------------|------------|------------------------|---------------|------------------|------------------------|--|--|
| Macro elements | Pinus banksiana | Pinus sp | Tsuga heterophylla | Betula sp | Acer sp | Populus tremuloides | Populus sp | Quercus rubra | <i>Quercus</i> (white) | | |
| Al | 33.3 | 4.7 | 11.1 | 0.0 | 20.1 | 1.4 | 3.5 | 6.8 | ND | | |
| Ca | 387.4 | 290.5 | 421.7 | 466.0 | 401.7 | 211.7 | 256.7 | 365.8 | 313.5 | | |
| Fe | 35.0 | 5.8 | 9.1 | 20.3 | 11.9 | 2.6 | 3.2 | NM | 0.9 | | |
| Κ | 22.5 | 162.4 | 25.3 | 36.3 | 31.9 | 112.5 | 79.3 | 60.8 | 102.5 | | |
| Mg | 33.2 | 70.3 | 79.0 | 25.3 | 117.0 | 35.5 | 90.9 | 52.0 | 75.7 | | |
| Mn | 39.0 | 40.4 | 19.0 | 47.0 | 27.0 | 1.4 | 4.5 | 14.9 | 1.4 | | |
| Na | 23.0 | 0.6 | 8.2 | 9.6 | 16.3 | 0.6 | 23.0 | 0.8 | ND | | |
| Р | 12.2 | 8.4 | 9.2 | 12.6 | 4.8 | 11.8 | 9.5 | 15.6 | 5.6 | | |
| S | 10.4 | 10.7 | 5.6 | 12.8 | 5.6 | 7.0 | 10.2. | 18.0 | 12.1 | | |
| Si | 74.8 | ND | 46.7 | 14.0 | 46.3 | 1.1 | ND | ND | 1.3 | | |

Table 3. Mineral concentrations in wood ash from specified source types (mg/kg)

ND = Not detected NM = not measured

Hakkila (1989) concludes that variation amongst species is large, but as Table 4 shows, hardwoods generally contain more inorganic elements than softwoods (see K and P levels) and much less Ca and Si. There are notable differences between pine species (two orders of magnitude-Table 3) in such elements as Fe, Na and K, and a similar but less pronounced pattern among oak species. However, the poplar species are more consistent, and show great differences in their concentrations of Ca compared to other broadleaves (two thirds that in *Quercus sp*, and a half of *Betula* and *Acer*). This could result in a lower pH in the ash from short rotation coppice, but as yet no data has yet been found for the ash chemistry from willow species.

 Table 4. Comparison of elements in ash from various component parts of hard and soft woods (From Hakkila 1989)

| Element (%) | Р | K | Ca | Mg | Mn | Fe | Zn | S | В | Cu |
|--------------------|-----|------|------|-----|-----|-----|------|-----|------|------|
| Softwood stem | 2.4 | 12.4 | 22.4 | 4.3 | 2.9 | 0.8 | 0.32 | 2.3 | 0.05 | 0.04 |
| Hardwood stem | 4.2 | 20.4 | 19.0 | 3.6 | 0.8 | 0.5 | 0.4 | 2.1 | 0.05 | 0.04 |
| Softwood stem bark | 2.8 | 9.8 | 28.5 | 2.8 | 1.7 | 0.2 | 0.3 | 1.2 | 0.04 | 0.02 |
| Hardwood stem bark | 3.4 | 12.2 | 27.1 | 2.2 | 0.6 | 0.6 | 0.4 | 1.1 | 0.06 | 0.04 |
| Softwood whole | 2.7 | 12.0 | 22.8 | 3.8 | 2.5 | 0.7 | 0.3 | 2.0 | 0.05 | 0.04 |
| Hardwood whole | 3.9 | 18.0 | 21.4 | 3.3 | 0.7 | 0.5 | 0.3 | 1.8 | 0.05 | 0.04 |

Calcium and potassium elements are commonly bound into oxides during the burning process, and appear as both OH and CO₃ compounds (Campbell, 1990)

4. Effects of burn temperature

American authors have noted differences in the ash quality and quantity of domestic wood stoves and commercial boilers which commonly fire at below 1200 °C and above 2000 °C respectively (Naylor & Schmidt, 1986). In particular the higher temperatures of the burn result in an increased volatilisation and loss of K. Detailed studies in 1991 (Etiégni & Campbell) used Lodgepole pine, and in 1993 Misra *et al.*, examined the change in composition of ash from five species, fired from 500°C upward to 1400°C. Bark and stem wood investigated separately in the latter study included the following species: *Pinus ponderosa (Dougl), Populus tremuloides, Quercus alba, Quercus rubra* and *Liriodendron tulipifera*.

Conclusions:

Ash production:

In the Etiégni (1991) study the percentage of ash production decreased by 45% over the temperature range of 538 - 1093 °C. In the study by Misra *et al.* (1993), a mass loss of between 23 and 48% was recorded up to a maximum temperature of 1300 °C, according to species. Mass loss significantly increased at temperatures above 650°C and appeared to occur in pine, aspen and white oak in two steps. This was attributed to decomposition of carbonates of calcium, in which CaCO₃ changes between 650 and 900°C, and K to K₂CO₃ at higher temperatures.

General chemical changes:

The mass of K, S, B, and Cu show decreases with burn temperature, but this is less definite for Na and Zn.

The mass of Mg, P, Mn, Al, Fe and Si do not change with temperature (relative to Ca, which is assumed to be constant) (Misra *et al.*, 1993). No analysis for N was recorded. However, Etiégni and Campbell (1990) measured a decline in carbonate content from 63% to 51% as temperature increased to 1093°C. Carbonates of Ca and K are formed at low temperatures (< 900°C) in a quiescent atmosphere, whereas CaO, MgO and metal oxides were the main identified compounds present at 1300°C in an oxidising atmosphere. Ash composition is much modified by the presence/absence of Si, Mn, Fe or Al, all of which may form acidic oxides combining with the alkali compounds to form sintered ceramic- like deposits in the ash. These elements have synergistic effects on one another, for instance at burn temperatures above 900°C molten potassium carbonate and sulphate adhere to cooler metal surfaces and trap other solid particles, such as the oxides of Ca and Mg. Potassium volatilisation begins at 800-900°C, and sulphur at 1000-1200°C resulting in losses of between 63 and 90% K and 7-55% S. (See Figures 1a and b for graphs for pine, aspen and oak on the following pages)

Carbon content of ash

Unburned C concentrations in commercial boilers in eastern USA form commonly 7-50% (av. 26%) of the ash (Someshwar, 1996). Studies in Sweden indicate that conventional grate boilers can produce ash with similar high quantities, but that Circulating Fluidised Bed (CFB) boilers are more efficient and allow fly ash to be cleared out for potential retrieval of carbon.(Tollin et al, 2000). The lowest ash volumes quoted in American literature (5%) come from boilers with inclined, sliding pinhole grates (Etiégni *et al.*,1991). Apart from indicating an inefficient burning process and creating unneccessary bulk, proportions of C over 20% create problems to ash agglomeration and chemical hardening. This adds extra cost to handling, transportation and spreading.

Recommendations:

Combustion at temperatures below 900°C results in the maximising of K content in bottom ash and a minimum amount of metal compound formation. From the perspective of furnace design, this also produces the cleanest burn. CFB boilers appear to create the lowest proportions of carbon.

5. Microelements and heavy metal production

Someshwar (1996) has summarised data on trace and heavy metal production from other American authors with ash analyses from wood combustion boilers (using hogged fuel) from 26 separate sample case studies. The summary data for concentration ranges follow below in Table 5.

Table 5. Median values of selected heavy metals in wood boiler ashes (from Someshwar, 1996)

| Concentration | < 3mg/kg | <25 mg/kg | < 50 mg/kg | < 110mg/kg | >300 gm/kg |
|---------------|----------|-----------|----------------|------------|------------|
| Element | Se, Hg | Cd, Co | Mo, Ni, As, Cr | Pb, Cu, B | Zn, Mn |

Zinc and Mn always occur in the greatest concentrations (median levels of 329 and 3485 mg/kg respectively) with a very wide deviation of value about the mean (Table 6).

Table 6.Average concentrations of 26 wood boiler ash analyses in USA in mg/kg
(Someshwar, 1996)

| | As | В | Cd | Cr | Co | Cu | Pb | Mn | Мо | Hg | Ni | Se | Zn |
|------|------|-------|-----|------|-----|------|------|------|------|-----|------|------|-----|
| Mean | 23.2 | 119.9 | 5.0 | 39.0 | 8.7 | 75.3 | 65.6 | 4370 | 14.9 | 0.4 | 23.5 | 0.10 | 443 |
| SD | 20.5 | 71.2 | 4.9 | 30.1 | 5.1 | 44.5 | 40.2 | 2621 | 27.0 | 0.8 | 21.0 | 0.2 | 417 |

These overall concentration ranges appear to hold across a variety of boiler types, as investigated in a study by Väättila *et al.* (1994), who looked at the effects of adding paper mill sludge to three different wood ash burners in Finland. Out of these, the Grate boiler burn produced the highest levels of Cr, Cu ,Ni and Pb from identical mixes, and the Circulating fluidised Bed boiler produced the least. The third design, a Bubbling Fluidised Bed boiler, produced less of the above metals, but higher concentrations of Zn and As.

However, a detailed study by Miljoeffekter (1983) quoted in Hakkila (1989) presents a comparison of heavy metal analyses from both bottom ash and fly ash samples which reflect very different concentrations. This phenomena is well known from other European experiences (e.g. Denmark), and is due to vaporisation of metals in the combustion process (particularly at higher temperatures), which then condense around small particles or on cooler surfaces. Hakkila concludes that the more effective the systems of filtration of the gases during combustion, the higher the proportion of heavy metals will be in the fly ash. Note particularly the increased levels in Cd, As, Mn, Cr and Pb in the fly ash, but higher range of Zn concentration in the bottom ash in Table 7 below.

| Table 7. | Heavy metal content in botto | m and fly ash (after Hakkila | , 1989) in mg/kg |
|----------|------------------------------|------------------------------|------------------|
|----------|------------------------------|------------------------------|------------------|

| | | v | | | | v | (| | , 8 | 8 | |
|--------------------|-------|---------|-------|--------|--------|------|-----------|--------|---------|--------|---------|
| Element | As | Cd | Со | Cr | Cu | Hg | Mn | Ni | Pb | V | Zn |
| Ash type Bottom | 0.2-3 | 0.4-0.7 | 0-7 | >60 | 15-300 | <0.4 | 2500-5500 | 40-250 | 15-60 | 10-120 | 15-1000 |
| Fly | 1-60 | 6-40 | 3-200 | 40-250 | ~200 | 0-1 | 6000-9000 | 20-100 | 40-1000 | 20-30 | 40-700 |

Further comment on environmental effects of heavy metal ash content appear in Sect B3.

6. Organic Compounds

Polyaromatic hydrocarbons (PAHs)

Data quoted by Someshwar from Diebel *et al.* (1992) indicate that the types of PAHs found in wood ash are those of the two and three ring constituents, which are less toxic than the four and five ring compounds. Naphthalene proved the most plentiful in his study (1.6 mg/kg), but many compounds were below detection levels in the samples. In a recent study in Switzerland wood ash derived from a pure burn at 550 - 650 °C was added to mineral soils, and monitored for both PAH and PCB compounds (Bundt *et al.*, 2001). The wood ash was found to have high concentrations of PAHs (the sum of 20 types equated to 16.8 mg/kg). However, the PCB addition to soils from the wood ash was low (totalling 14 types which equated to $3.4\mu g/kg$). The exact nature of the wood burned was not recorded.

7

Polychlorinated biphenyls (PCB)

Samples from wood ash samples tested for an electricity generation company (1990) (quoted in Someshwar, 1996) showed no trace of the above organic compounds in either the bottom, multicyclone or electrostatic precipitator ash. Tests for chlorobenzines and chlorophenols were also negative (data from Someshwar's review in 1996). Large inputs of PCBs into the natural environment were recorded in western countries between the 1950 and 1970, with consequent high concentrations in vegetation and soil sinks (Harrad *et al.*, 1994). However, the absorption by organic matter (Bundt *et al.*, 2001) and the breakdown rate in soils, combined with volatilisation of these compounds back to the atmosphere, appears to limit uptake of PCBs by trees.

Dioxins and Furans (PCDD/Fs)

PCDD/Fs are not expected to leach out of wood ash, due to its absorbent nature, and are expected to be immobilised. In North America, Diebel's report (1992) included analyses of PCDD/Fs in the wood ash from five wood boilers, and found TEQs (Toxic EQuivalents expressed in terms of the most toxic isomer (2,3,7,8-TCDD)) between 0.013 to 1.1 ng/kg – i.e. very low levels.

PCDD/F levels were monitored in wood ash samples included in a USA National Dioxin survey of combustion sources and their products under the USEPA, which was reported by Kuykendal *et al.*(1989). In the ten ash samples from wood boilers tested the levels of PCDD/Fs in six were all at the non-detect, or very low level. However, in three bottom ash and one scrubber water discharge, very high levels were found. These particular boilers had been fired with salt laden wood after carriage by sea. This same effect after combustion of salt laden wood was reported by Luthe & Prahacs (1993) from Canada, with *flyash*. TEQ's ranged from 340 to 4020 ng/kg. *Bottom ash*, however, had undetectable levels of TEQs.

On a domestic scale, several studies report on the incidence of PCDD/F compounds in grate ash and chimney soot. Someshwar (1996) quotes data from five separate studies of wood burning stoves and smoke emissions from 1983 - present, and includes data from a NCASI report (1991-94), all of which showed negligible PCDD/Fs in grate ash, but more in chimney soot where cooling of the smoke occurs.

Other authors in Europe have reported TEQs from *fly ash* samples that are slightly higher than those in inland USA, with levels ranging from 22 to 390 ng/kg – an average of 164 ng/kg (Välttilä *et al.*, 1994; Pohlandt & Marutzky, 1994). However, *bottom ash* from the same boilers showed TEQ levels from 0-0.66 ng/kg, confirming that PCDD/Fs do not adhere to coarse ashes. Chlorine levels in the bark fuels (Finland) ranged from 110 - 250 mg/kg, which is higher than most inland wood residues burnt in the USA. These levels of chloride (>0.03%) have the potential to create higher levels of PCDD/Fs in the ash (Someshwar,1996). These synergistic effects causing PCDD/Fs are not yet fully understood - but it is *possible* that the more oceanic climate of Western Europe may be a factor operating in the slightly higher local occurrence of these compounds recorded in wood ash.

7. Radioactive elements

There are several studies providing general inventories of radionuclides in 'natural systems' (see Simkiss, 1993 for the UK, Bunzl & Kracke 1988 in Bavaria). Some specifically address trees (Momoshima, & Bondietti, 1994) others soils (Thiry & Myttenaere, 1993; Schimmack *et al.*, 1994), and a few studies trace radioactivity through the lumber industry (Ravila & Holm, 1994; Krosshavn *et al.*,1995). It is expected that ashing wood concentrates any radioactive elements such as those in the U and Th series, radiocesium and radiostrontium.

Two Scandinavian papers have in particular investigated the increased fall out associated with the Chernobyl incident (1986) as it becomes apparent through the harvesting and ashing of trees. The Swedish Radiation Protection Institute advise that no wood-ash with activities exceeding 5 kBq/ kg should be applied in forests. Throughout a north – south transect of Sweden the background levels of radioactivity range from 0-40 kBq/m², due to Chernobyl fall-out, with most of the activity associated with the soils rather than the vegetation. Experiments by Högbom & Nohrstedt (2001) remeasuring activity at afforested field sites, some 5-8 years after deposition of ash with a concentration of 0-4 kBq/kg , concluded that there was no statistical difference between 6 sites which had added ash and the background variability monitored in the controls. The activity of ¹³⁷Cs was still greatest in the soils compared to the tree components by a factor of three. But at the seventh site,

radioactivity significantly decreased in all compartments. This they attributed to the synergistic effect of K concentration in the ash with ¹³⁷Cs in the humus layer of the soil.

A more detailed examination of a range of radioactive elements, both in background fall-out and in ash additives, was completed by Ravila and Holm in 1996 at the Skogaby site, known to have received little or no Chernobyl fall-out. This included analysis of soil water, soil cores and roots, tree parts and a reassessment of the radioactive status of ash granules from treatment plots which had been laid on the forest floor in 1989. Over three winters (1992-1994) samples were assessed for ¹³⁷Cs ,⁴⁰K ,²¹⁴Pb, ²¹⁴Bi, ²²⁶Ra and ²³⁹U. The occurrence of radionuclides remained strongly in the forest soils, though radiostrontium (not caesium) was found in the intrasoil lysimeters. For the tree canopies, stems and branches the radio activity was statistically similar for both radiostrontium and radiocesium in the control and treated plots in the first two winters. In the third winter, however, small increases in radiocesium activity in the wood xylem were detected in the plots treated with ash. The spatial occurrence of these samples within the treated plots matched the uneven distribution of ash granules mapped on the forest floor, and the authors attributed the tree increases to this factor. They thus concluded that most of the change in the radiation field above the ashed plots was associated with a suite of volatile radionuclides, such as ⁴⁰K, and ¹³⁷Cs. The level of volatile ⁴⁰K within the trees themselves is unlikely to change into the future, as that uptake is biologically limited, but no estimate of the likely change in ¹³⁷Cs is made. Whilst the aim of burn technology is to allow as few particles as possible to escape into the atmosphere, it is likely that most radionuclides from trees previously growing in higher fallout areas, will be trapped in the bottom ash of wood boilers.

Taken together, these two studies seem to indicate that the levels of radioactivity added through using ash on forest floors are not any greater than the naturally occurring levels from background fallout, and may well be decreased over time in the soil due to the ash K content.

8. Physical considerations - To granulate or not to granulate?

The disadvantages of loose dry wood ash have been well investigated by Scandinavian and American researchers due to inherent handling difficulties comprising

- health risks to operators of fine airborne particles potential silicosis (see Hakkila, 1989)
- the difficulty of spreading the ash evenly, necessitating slow delivery rates (Wilhoit & Qingyue, 1996 Spreader performance evaluation)
- Deleterious effect on ground vegetation (Kellner and Weibull, 1998)

The preparation of wood ash into granulated form appeared to have arisen from the consequences of the washing down process in wood boilers, which has now become formalised and refined.

Examples of three common preparation methods existing in Sweden are given below:

| Crushed ash – | Bottom ash is taken from the CFB (circulating fluidised bed) station (Perstorp, Sweden). The ash residue is moistened to 30% water, allowed to harden for 4 weeks and then dried out. This is called the 'Self hardening process' (Nilsson and Lundin, 1996 and Korplahti <i>et al.</i> , 1998). The hardened as is then crushed and sieved for fractions under 5mm. |
|--------------------|--|
| Granulated ash (A) | Bottom ash from the CFB (Eskilstuna, Sweden) is mixed with water and then rolled to form balls 4-20 mm in size. These are then dried until the water content is < 5% (Kellner & Weibull, 1998 Uppsala). |
| Granulated ash (B) | Wood ash (source unspecified) with admixture of dolomite (ETEC) used as a binder. The residue is ground to uniform size, mixed with water, and passed through a drum granulator (2 rotating parallel cylinders), then dried. Optimal size 0.5-4.0mm. (Svantesson, LIC thesis, Lund University. Pers Comm. to S. Morgan, TDB) |

Table 8 below gives the specifications for ash produced by three ash types. Notable chemical change occurs in the decreasing amount of Ca as the processing becomes more involved, but there is an increasing amounts of P.

Note the increased sand proportions in crushed and granulated ash (x2), possibly from using bark from conifers, which is lost by settlement from loose ash.

| Ash type | Ca | Mg | K | Na | Р | S | Zn | SiO ₂ |
|------------|------|-----|-----|------|-----|-----|-----|------------------|
| Loose | 21.1 | 2.0 | 3.2 | 1.1 | 1.2 | 1.2 | 0.1 | 11.8 |
| Crushed | 18.2 | 2.0 | 1.4 | 11.6 | 0.5 | 2.1 | 0.1 | 26.2 |
| Granulated | 16.4 | 1.6 | 4.0 | 0.9 | 2.2 | 2.2 | 0.1 | 22.0 |

 Table 8.
 Chemical content of hardened and granulated ash - % dry wt

Advantages of granulated wood ash

The hydration of wood ash has several beneficial chemical effects. Newly burnt ash, with Ca oxidised into the form of $Ca(OH)_2$ (Portlandite), on exposure to air and moisture results in carbonate formation $CaCO_3$ (calcite). The consequence of this is:

i) Lowered solubility of Ca, through the formation of ettringite $(Ca_6Al_2(SO4)_3(OH)_{12}$. $26H_2O)$ with reduced calcium leaching rate and thus

ii) reduced alkalinity and more moderate pH.

iii) reduced rates of mobility of heavy metals

In a series of papers in the Scandinavian Journal of Forest Research (Suppl. No.2) in 1998 major work on laboratory and field tests of granulated wood ash were published. These are summarised below.

Laboratory Studies.

J.Eriksson's (1998) tests used a CFB ash (from Perstop) and a bottom ash (from Ljungby), hardened through water addition and used as fine and coarse fractions (><5 mm) for the experiment. Prepared ash of both sizes was bagged and incorporated into two columns: one with mor type humus, and one with quartz sand. Water was poured through the column to simulate five years of rainfall .The results showed that CFB fine ash lost nutrients more rapidly (K, Na, Cl and SO₄), whereas the loss rate from the sintered bottom ash were slower. The finer fractions dissolved faster than the coarser particles, and immediate liming effect was achieved with Ca and K being the most mobile elements. Mg and P were released more slowly, and heavy metals hardly at all. In the mor column they appeared to be bound in a non-exchangeable form. Eriksson states that the amount of heavy metal release in this experiment is comparable to that released in the field from pine needle litter decay on the forest floor (Laskowski & Berg, 1993).

Steenari, *et al.* (1998) completed a practical study using a CFB and a grate fired (GF) ash for experiments on nutrient loss during alternate wetting and drying cycles. Ash particles previously spread through the forest were also tested for their remaining nutrient content. Fragile GF ash lost Ca and K content faster than the hardened CFB ash which retained its structure and 90% of its weight after 2 years simulation. At this point, most of the GF ash had dissolved. The rates of leaching are shown in Fig 2.

Field Studies

Steenari *et al.* (1998) undertook an analysis of granules from the field (cover crop and soil type unknown). The results are also shown in Fig 2. This illustrates the loss of elements over a one year period and particularly demonstrates the speed at which elements (e.g. Ca) are lost continuously from the GF ash. Although the Ca loss from the CFB ash was initially very fast, indicating the presence of a very soluble form of calcium in the ash (possibly from Portlandite), the level stabilised out within a few weeks. In the GF ash some 50-60% of the original amounts of K and Na had been lost, and only 0-10% of the alkali metals over the period of a year remained leachable. In the CFB ash calcite had been formed, along with gypsum and Ettringite. P fractions dissolved amounted to 0-20% only, but no loss of Al had occurred and only minimal amounts of Mg, Fe, Mn and Zn through weathering.

H.Eriksson (1998) investigated ash granules after two years on two clear felled forest sites, previously under pine and spruce, on acidic podzolic soils in NE and SW Sweden. The granulated wood ash used was from a CFB boiler and had been applied at between 1-6t/ha. After two years, CEC, pH and base saturation in the soils was still positively correlated with the ash dose, and exchangeable acidity was negatively correlated. Results

compared to the effects of applying loose ash (citing Bramryd & Fransman ,1995) at southern Swedish sites indicate that there was no increased N mineralisation from the granulated ash in similar locations.

(See Section C for further ecological effects of loose vs granulated ash)

Section B: Wood ash as a soil amendment

1. Alkalinity and toxicity

Generalised comparisons with commercial fertilisers such as ground limestone, hydrated lime (CaO) and potash have been made by American authors (Naylor & Schmidt, 1986; Campbell, 1999; and Someshwar, 1996) to support the case for the use of wood ash in soil amelioration in agriculture as opposed to discarding in land fill. Under the Resource Conservation and Recovery Act in the US, ash is not classified as a hazardous waste, because there are no pH criteria for solids. However, the state of Washington classifies wood ash as dangerous waste when the pH exceeds 12.5 and ash use is under licence in New York State. In Maine and New Hampshire ash use in agriculture is regulated by requiring the land owner to prepare an application for land spreading which includes soil and topographic maps, and subsequent soil analyses result in recommendations by a soil scientist of loading rates on the desired crops. The process takes six months, as the company generating the ash sends these reports to the State, and the Department of Environmental Protection circulates copies for review to other agencies for comment before approval can be given.

The resultant use of ash on land rather than in landfill cuts the costs of disposal for the producing companies by 33-66 % in Maine and New Hampshire. (In Europe, the disposal of mixed and pure fly ash in Denmark to landfill (at a current production rate of 2,500 t/pa) totals over 1 million kroner each year- (Pers. Comm)).

Equivalent Neutralising Values (ENVs)

The neutralising capacity of wood ash is defined in America by its calcium carbonate equivalent expressed as percentage (where a standard limestone equates to 100%). ENV's of hogged fuel ash have been summarised by Vance (1996) at a median value of 48.1%, but the range over 18 samples was from 13.2 - 92.4 %. Hakkila (1989) quotes ENVs from various fuels over a range from pure wood ash at 115%(compared to standard lime) to bark ash mixes at 64%. The liming effect of ash addition on the soil pH is a function of both calcium and magnesium carbonates (i.e. the Total Neutralising Value) and the fineness of the material (expressed as the percentages passing a 20 µm and 100 µm mesh screen). Wood ash may also include a proportion of charcoal dependent on burn efficiency, which reduces its final TNC value. Where recommended liming rates are quoted, using a limestone standard at 100%, the equivalent application rate for wood ash to achieve a similar liming effect is:

Recommended limestone addition(kg/ha) x (100ENV limestone/ENV value of ash) (Naylor & Schmidt, 1986)

The change in soil pH which may occur also relates to the original soil chemical and physical properties such as exchangeable Al, CEC, base saturation and organic matter content. All of these may act to buffer the effects of carbonates.

Dose rates and Loading factors

Experimental work using incubation studies (Naylor & Schmidt, 1986) tested the equivalence of ground limestone and wood ash on two soils common in the NE USA. The ash came from hardwoods only, burnt in a domestic stove (i.e. at relatively low temperature). Six dosage rates were drum mixed to homogenised pots of soil at the equivalent rate of 0, 2.2, 4.5, 9.0, 17.9 and 35.9 metric tons/ha with three replicates of each. After 60 days at 25 °C, with periodic watering to simulate wetting and drying cycles, the resultant samples were measured for water pH and extractable nutrients. Mardin and Burdett silt loams used in the study have pH typically of 5.7 and 4.8 respectively. The amount of change under the dose rates for both wood ash and limestone are summarised in the following diagram, which demonstrates the consistent change of pH with rising application rate for both substances, at an equivalence of 47-50%. To raise Burdett soils to pH 6.2 would thus take 9.7 tons/ha limestone and 17 tons/ha of wood ash.

In a similar short term experiment by Etiégni *et al.*, (1991) the rise in pH after 45 days with increasing ash loading onto a similar silty loam soils is also shown in Figure 3.

Persistence of effects

Data given in Section A on granulation includes references to studies run over two to five years. The delivery rate of calcium is very dependant on the initial form of the ash, being slowly released over several years (Steenari *et al.*, 1998) from granulated ash, but released very swiftly from loose ash.

This causes a transient fast rise in pH in the soil. However, data given in Section C on long term studies indicate that pH rise has been sustained for up to 16 years after ash application (Saarsalmi, 2001) at an elevated value of 0.6-1.0 pH units higher than control forest soils in Finland. The study was completed on two contrasting dry and moist sites under pine and spruce, where effects were greater with the increased water regime. The mineral soil layers (below 10 cm depth) showed very little change at seven years after ash application, but pH values had increased in the period up to 16 years later. Thus there was slow downward transfer of activity from the top soil over a very long time period.

2. Nutrient additions by wood ash and availability from soils

Cation Exchange Capacity

Grim (1968) quoted in Etiégni *et al.* (1991) gives a value of CEC in the literature for wood ash of 2.7meq/100g. This ranks alongside inactive clay minerals like kaolinite which are essentially inert, and will not hold extra nutrients once mixed with other substrates.

N-P-K

Naylor & Schmidt (1986) have equated wood ash fertilisation effects to commercial fertilisers on the basis of the N, P (P_2O_5) and K(K_2O) concentrations. For a commercial wood boiler this would be similar to a 0-1-3 fertiliser, but for a domestic wood stove (lower temperature burn) the ash has a higher proportion of K and would be equivalent to a 0-3-14 fertiliser. Following the experiment outlined in Sect. B1, Naylor & Schmidt showed that the availability of K was a linear function of the amount added to the soil. Only approximately 18-35% of that added in boiler ash, but 51% from the wood stove would be available to plant uptake. This was probably due to K compounds forming with Si at higher temperatures. This compares to 65-70% availability from commercial potash fertiliser. Between the two experimental soils tested, the release rate was higher from the less acid soil (Mardin pH 5.7) and lower in the Burdett (pH 4.8).

The relationship between K applied and K available was as follows:

| Mardin: | y = 165 + 0.35x |
|----------|-----------------|
| Burdett: | y=113+0.18x |

Other studies have suggested that availability of K might be more similar to that from commercial fertiliser (Ohno,1992; Erich, 1991), but these authors both stress the importance of dissolution rate in the soils with pH dependance. The range of agricultural soil types tested by Ohno ranged from pH 4.0 - 6.2. In an extraction of major elements from his commercial wood ash (60%hardwood/40% softwood) using a pH 3 solution of 1 *M* NH₄ OAc the percentage elements recorded were as shown in Figure 4.

However, all the above authors report reduced rates of P availability in wood ash, due to its low solubility, and uptake of P by maize plants in eight different soils ranged from 28-70% of that in commercial fertilizer (Erich & Ohno,1992). The variability here was due to pH buffering capacity of the soils, with P availability at a maximum for soil pH of 6.0-7.0, decreasing at pH over 8.0 (Etiégni *et al.*,1991). Ohno (1992) reported an initial fast release of P into solution in his soil mix experiments, followed by a decrease by absorption. This effect was greatest in the lower pH soils, which he attributed to the possible formation of Fe and Al phosphates. There is therefore some conflict between reported possible mobilities of P in soils after wood ash application.



Figure 4. Fractions of elements soluble in wood ash (source: Ohno, 1992)

3. Heavy Metals reactions with soils

It is difficult to assess whether heavy metals in ash pose a direct or indirect threat to either plants or humans.

In the UK the ICRCL (Interdepartmental Committee on the Redevelopment of Contaminate Land, 1987) trigger concentrations (mg/kg) of metal in contaminated *soils* are a guide to the potential redevelopment of brown field sites. The list is split into contaminants posing a hazard to human health, such as As, Cd, Cr, Pb, Hg, and Se, and those that may still be phytotoxic, but are not normally hazardous to humans, such as B, Cu, Ni and Zn.(DoE, 1987).

European regulations limiting maximum metal concentrations allowed in soils treated with sewage sludge are generally more stringent than those in the US, and a selection appear in Table 9 below. The variability of the trace elements *Zn*, *Cr*, *Ni* and *Cu* in bottom ash means these might potentially exceed the current limits if applied in large quantities, but Cd, As, Hg and Pb should be less problem, as long as no fly ash is used.

| | ICRCL 'trigger' conc (open space) | Maximum soil limits for sludge treatment | | | | | Bottom ash metal conc. (Hakkila 1989) |
|------------|---|--|-----|---------------------------------|--------------------|---------|---|
| | | EU | UK | Denmark All data in n | Sweden | Germany | · · · · · |
| As | 40 | _ | _ | | <u>18/ Ng</u> - | _ | 0.2-3.0 |
| Cd | 15 | 1-3 | 3 | 0.5 | 0.5 | 1.5 | 0.4-0.7 |
| Cr (total) | 1000 | 100-150 | 400 | 30 | 30 | 100 | 40-250 |
| Cu | 50 | 50-140 | 135 | 40 | 40 | 60 | 15-300 |
| Hg | 20 | 1-1.5 | 1 | 0.5 | 0.5 | 1 | 0-1 |
| Ni (total) | 70 | 30-75 | 75 | 15 | 15 | 50 | 40-250 |
| Pb | 2000 | 50-300 | 300 | 40 | 40 | 100 | 15-60 |
| Zn | 300 | 150-300 | 300 | 100 | 100 | 200 | 15-1000 |

Table 9. Soil limits for heavy metals from UK and European regulations

(Data from Alloway, 1995)

The occurrence of many heavy and trace elements in **agricultural fertilisers** frequently exceeds the concentrations in bottom wood boiler ash. The following data from various specialist authors in Alloway (1995) summarises such data. It has been calculated that the addition of phosphatic fertilisers accounts for 54-58% of all Cd deposition to soils in western countries. Note the high Cd concentration in farmyard manure compared to Wood ash.

| Element | Cr | Ni | Cd | Zn | Hg |
|-------------------|--------|--------|-------------|---------|-----------|
| Fertilizer type | | | | | |
| N type | 50 | 80 | - | - | - |
| Phosphate | 1000 | 300 | EU 9-30 | 5-1450 | <50 ng/kg |
| Potassium | 1000 | 80 | (USA 7-156) | - | - |
| Farmyard | 12 | 17 | 0.3-1.8 | 15-250 | 100 ng/g |
| Wood ash (Bottom) | 40-250 | 40-250 | 0.4-0.7 | 15-1000 | 0-1 |

 Table 10.
 Summary data for common fertiliser constituents (mg/kg)

American authors such as Vance (1996) and Campbell (1990) compare the loading limits for heavy metals set in the USA by USEPA (1993) for sewage sludge application, with those for potential wood and fossil fuel ash additions. They conclude that applications of wood ash at up to10 Mg/ha from ordinary hog fuel boilers would result in soil heavy metal levels being two orders of magnitude below the loading limits suggested by the advisory body. USEPA National limits are set for both annual and cumulative effects on the soils (see Table 11), but individual States particularly in the East (e.g. New Hampshire, Vermont, Washington and Maine) also have their own limits where programmes of wood ash use have now been in action for over ten years .

 Table 11. A comparison of selected heavy metal standards in US with average wood ash composition (Data from Campbell, 1990 and Vance, 1996)

| | Metal addition (kg/ha from ash spread @ 10 Mg/ha | | limits (sewage adings (kg/ha) | USEPA max conc.(clean sludge) mg/kg | Maine State limits for soil amendment | Mean wood boiler ash conc. N= 22 |
|----|---|--------|----------------------------------|--|--|--|
| | | annual | cumulative | | ррт | |
| As | 0.06 | 2.0 | 41 | 41 | - | - |
| Cd | 0.02 | 1.9 | 39 | 39 | 10 | 3.5 |
| Cr | 0.36 | 150 | 3000 | 1200 | 1000 | 26.1 |
| Cu | 0.70 | 0.7 | 15 | 1500 | 1000 | 123 |
| Pb | 0.70 | 15 | 300 | 300 | 700 | 28 |
| Мо | 0.13 | 0.9 | 18 | 18 | - | - |
| Ni | 0.21 | 21 | 420 | 420 | 200 | 75.5 |
| Se | 0.05 | 5.0 | 100 | 36 | - | - |
| Zn | 3.2 | 140 | 2800 | 2800 | 2000 | 522 |

In the Maine data, comparison is with hogged fuel wood ash, but the concentrations are still below recommended limits by a factor of three. American researchers suggest that, in general, changes brought about by added K and carbonate effects on soil pH are likely to be more limiting to ash use on soils, than heavy metal additions (Vance, 1996).

The various **adsorption and consequent mobilities** of individual heavy metals in soils is obviously critical to understanding potential dangers to human health through agricultural crops (Alloway, 1995). MAFF have published data for regulation limits based on soil pH range 5-7.0 units over which some heavy metals adsorption into soils changes dramatically, with adsorption decreasing with falls in pH.

 Table 12. Metal concentrations limits in agricultural soils after sewage sludge application

 (MAFF 1993) (mg/kg)

| Soil pH | Zn | Cu | Ni | Cd | Pb | Hg | Cr |
|----------|-----|-----|-----|----|-----|----|-----|
| 5.0-5.5 | 200 | 80 | 50 | | | | |
| 5.5-6.0 | 250 | 100 | 60 | | | | |
| 6.0-7.0 | 300 | 135 | 75 | | | | |
| >7.0 | 450 | 200 | 110 | | | | |
| All soil | | | | 3 | 300 | 1 | 400 |
| pH > 5.0 | | | | | | | |

Cadmium adsorption into sandy and loamy soils *increases* by a factor of 3 for every pH unit increase between pH 4 and 7.7. Alloway *et al.* (1985), through multiple regression techniques, have shown that pH, organic matter and hydrous oxide content are the key factors controlling Cd adsorption to 22 different soils. Cd is much more mobile in soils than either Pb or Cu. His research on over 50 different soil types into the movement of Cd into parts of food crops, such as potato and carrot tubers, and above ground green parts of edible plants, e.g. spinach and cereals, has shown statistical relationships between total soil Cd and bioaccumulation.

However Cd may be absorbed on to CaCo₃ in the soil with consequent reduced bioavailability. Increased calcium concentration of the soil has been shown to increase the adsorption capacity of a sandy loam by 67%. One of most widely used amelioration processes to reduce Cd in contaminated soils is to lime to pH 7 - thus adding Cd in ash with high proportions of calcium compounds, might automatically lock up that Cd in the soil (Cd frequently replaces Ca in these compounds). Cd also bonds with hydrous Mn oxides, through a wide range of soil pH's, and Mn is plentiful in both bottom and fly ash. Cd also binds with chloride ligands, such as might be found in saline soil/water conditions, and to hydrous iron oxides. The latter are likely to be associated with more acid podsolic soils where there might also be humic and fulvic acids (organic ligands), but Alloway considers the resulting compounds to be unstable, especially at low pH. Between 10 and 50% of the adsorbed quantities of Cd, Zn and Cu are exchangeable, compared to only 1-5% of Pb.

Skogforsk reports (1999) indicated that at a soil pH of 4.2 Cd (as delivered in nitrogenous fertilizers) becomes dissolved in soil water, and may be traced to depths of 50 cm.

Zinc is a vital plant trace element. Its mobility in the soil is also sensitive to substrate pH but in reverse to that of Cd, with increasing adsorption at decreasing pH values. Thus Zn levels are normally least in podzols and luvisols (28-35 mg/kg) and highest in fluvisols and histosols (58-60 mg/kg). Zn is absorbed reversibly by cation exchange at low pH, but irreversibly by lattice penetration into clay particles. Zn hydroxide captured on clay surfaces may produce strongly pH dependant retention of Zn with retention greatest at alkaline pHs – the formation of Zn carbonates is common according to Misra and Tiwari (1966). For soils low in organic matter, Zn availability relates directly to chelating ligands, originating in decaying organic matter or root exudates. There is widespread knowledge of Zn with P and Fe–antagonism. i.e high P values result in lowered Zn values largely related to activity in the root rhizosphere. However Kiekens (in Alloway 1995) considers that the biologically active fraction of Zn is most soluble at low pH values. Thus additions to low pH soils would result in the maximum soil adsorption of this mineral.

The concentrations of Zn recorded particularly in bottom ash (Hakkila's mean is 15-1000mg/kg) are high compared to other metals. The source of this is not entirely clear (Zn oxides or carbonates?), since from available wood analyses, conifers contain 5-10 mg/kg and broadleaves slightly more at up to 30 mg/kg. (see Kennedy, Soil Sustainability Output 8, 2002), in very similar concentrations to Fe, S and Al. The range of Zn contents in the ash is almost on a par with concentrations measured in commercial fertilisers and about half those of sewage sludge, which in the EU must not be used at limits above 2500-4000 mg/kg Zn. The maximum allowable loading (EU) of this material to soils is given as 550 kg/ha, so that with an assumed average soil background content of 80 mg/kg soil, a 1mg/kg increase in concentration results from an application of 2.5 kg/ha of sludge.

Chromium and Nickel The natural incidence of Nickel and Chromium in soils is highly correlated with geology. Surveys of Scottish soils produced mean concentrations of 62 and 27 mg/kg of Cr and Ni respectively, whereas England and Wales produced concentrations of 34 and 20 mg/kg, as measured by McGrath & Loveland (1992). The highest levels are found in coarse loamy, sandy and peaty soils, and not clay-rich types. Those authors conclude that added amounts of Cr or Ni in fertilisers (phosphatic types), sewage sludge or other soil amendments are unlikely to cause a build up of these metals in the soil above the naturally occurring levels. Note that guidelines for the permitted soil concentrations in the EU for Cr and Ni in sewage sludge are one tenth of those in US (Tables 9 and 11), and wood ash levels are well below those levels permitted in commercial fertilisers.

By contrast Pulverised Fuel Ash (PVA from bituminous burning) spread onto soils is often high in chromium and nickel, but very little of it seems to be taken up by crop growth. Both metals become increasingly soluble at lower pH values. Nickel then has greatly increased mobility as pH and cation exchange decrease. Cr activity in soils is a function of its oxidation state, but Cr(III) is the final state often produced by reduction, and this is then

less mobile, with complete precipitation above pH 5.5. There has been some recorded oxidation of Cr(III) above pH 5 in the presence of high amounts of oxidised Mn.

Manganese The need for Mn among the trace elements for plant growth is particularly acute in cool temperate agricultural systems, on soils of high pH, with high organic matter and high carbonate content (particularly in those systems growing cereals and soya bean). Wood ash has great quantities of Mn in it, being higher from conifers than broadleaves (Hakkila., 1989). Smith & Patterson (in Alloway, 1995) state that oxidation states from Mn(II) to Mn(VII) occurs in combination with carbonates, silica and oxygen. These oxides have variable solubility, but the Mn(II) form in solution is most readily available to plants. This is largely governed by the supply of H+ ions in the soil, so that plots of extractable Mn against pH (H₂0) yield a straight line relationship with maximum values at pH 5.5 and minima at pH 7.0. However, they point out that reactions taking place in the rhizosphere may have an even greater effect on the availability of Mn to the roots, which can differ by as much as two units from the rest of the soil. A sharp increase in extractable Mn is detectable at pH 5.5 which has been attributed to MnO₂ solubilisation by root exudates – some plants such as lupin have been shown to be able to lower the pH in the immediate root zone, which then develops more chelating agents than the bulk soil. These exudates may be low molecular weight organic carbon compounds including mucilage, sloughed off cells and tissue containing malic acid, which is very effective in this solubilisation process. Microbial populations in the rhizosphere may be up to 50 times higher than in the bulk soil. The exact amounts of increase are however limited by oxidising bacteria, which are most effective between pH 6 and 7.5, but may well be adapted to more acid conditions (Smith & Patterson in Alloway, 1995). It is not clear whether either reaction is maintained at pH below 5.0. Mn toxicity is often associated with warm climates and acid soils, with soil levels of available Mn at 80-5000 mg/kg reported from rice and other food crops. From the literature it seems unlikely that addition of wood ash to temperate soils would result in toxicity, but might be a positive benefit to agriculture systems. Mn does not appear as a hazardous metal in either the ICCRL tables, or those for EU or USA limits on hazardous limits

4. Water holding capacity

Etiégni *et al.* (1991) studied wood ash structure and its change during wetting. They suggest that ash is essentially hydrophilic, with particle swelling through absorption of water into the pores by capillary action simultaneous with chemical changes through hydration of oxides to form new compounds. SEM of wood ash revealed many irregularly shaped inorganic particles with thin layers of crystalline structures which swelled to clusters of rosette crystals after wetting. After four weeks of wetting, expansion had increased the volume by 12.5% on the original. The probable compounds responsible for this, determined by X-ray patterns, were calcite, portlandite and calcium silicate.

This effect could be both beneficial and detrimental in soils where ash might be used as an amendment – in clay soils small pores might easily be clogged by wetted ash, causing decreased aeration but in sandy, free draining soils this water holding capacity could be very beneficial to plant growth.

In studies by Lumme & Laiho (1988) soil water tensions were measured on a site growing *Salix sp* over two contrasting years, but ash treated plots were not significantly different to the controls.

N.B. Ash and Pesticide/Herbicide use

Magdoff *et al.* (1984) as reported in Campbell (1990), have shown that, due to the alkaline conditions caused by the ash and its liquid retention properties, both types of chemicals will be readily adsorbed by ash on the ground. Ash application and other spraying should be staggered to avoid this synergistic effect.

Soil water leachate

Studies on water chemistry from forest soils treated with wood ash in the USA and Sweden have been completed using a variety of surface water sampling (Piirainen, 2001), soil suction methods (Högbom *et al.*, 2001), lysimeters (Kahl *et al.*,1996, Staples et al, 2001) and shallow wells (Williams *et al.*, 1996). Summaries of the ash application rates and results in these studies are given in Table 13. This is then followed by a more detailed discussion of their findings.

| Area | Soil type | Ash loading | Effects n | nonitored |
|--|-------------------------------------|-------------|---|---|
| | •• | U | Soil | Water |
| Maine, USA (Williams et al., 1996) | loamy sands (unknown pH) | 11-44 Mg/ha | High surface K and Ca, no change at 45 cm. Conc. equalled control at 60 weeks | Small increase in Ca, K and SO ₄ . Heavy metals were below detection limits |
| Maine, USA (Kahl et al., 1996) | sandy Spodosol, acidic pH4 | 6-20 Mg/ha | pH increased from 4-5, exchangeable Ca, K and Mg increased, Mn and Al decreased. Treatments declined to equal the control after 25 months. | Transient increase in base cations, minimal response at low loads, raised conc. of H, K & SO ₄ for 20 months, <i>loss</i> of N in solution at high loadings |
| Finland (Piirainen, 2001) | drained bogs Carex & Sphagnum | 3-6 Mg/ha | | All ashed sites increased in Ca, Mg, K and SO4. Some sites increased in P, NH4 and Cr |
| Finland (Högbom <i>et al.</i> , 2001) | Acidic till, high N deposition | 4.2 Mg/ha | Increase in Ca and Mg. pH rise of 0.2 units | Increase in NO ₃ |

Table 13. A comparison of wood ash effects on soil leachate water

Figure 5 displays the data from Kahl *et al.*, (1996) which summarises the nutrient change over time in the soil solution chemistry sampled by lysimeters beneath White birch and American beech woodland. The soil solution shows minimal effects at low ash dose rate, but heavier additions overload the soil's buffer capacity. Swift increases in Ca, Mg, Cl, NO₃ and SO₄ were sustained to the end of the experiment in the case of the maximum load. There was, however, no effect of leaching of trace metals. The work of Williams *et al.* (1996) showed, in particular, increased concentrations of both Ca and K in the soils and ground waters, with some movement of Mg and Al at all ash loading rates. Of the anions, the highest rates of movement were found for sulphates at the lowest application rate. There was also some increase in phosphate at the lower rate. Nitrates were also consistently higher on treated plots than on controls peaking at twelve weeks after the ash application. This was coincident with the highest recorded soil pH (6.25) in the experiment, under the heaviest ash loading. The occurrence of heavy metals showed no clear trends, but the low levels of Cd suggest that the Fe and Al oxides in the acid forest soils absorbed Cd, Zn and Mn.

The loss of N from the soil detected by Kahl *et al.* (1996) at high ash applications, was also recorded by Högbom *et al.* (2001) at a site on the Swedish west coast, where Norway spruce grows on acidic till soils. Ash was applied at a rate of 4.2 Mg/ha and the soil solution sampled over the next two seasons. Soil solutions not only showed significant rises in Ca and Mg , but also some tendency (authors words) for increases of NO₃ at 50 cm depth. However, these were not statistically proven in 2 of the 6 samplings over two years and incubation of soils did not show mineralisation of N in the top soils. Atmospheric N deposition at this site is known to be high, and thus the formation of NO₃ and its leaching is accelerated when ash addition increases soil pH. Note also that increased amounts of Al leached out of the top soil and then detected at depth makes the lower horizons also more acidic.

In Finland powdered ash has traditionally been applied to forests in winter, onto the snow pack. This treatment has been shown to increase the loss of base cations and SO₄ through leaching through the soil (Piirainen, 2001). Summer applications were found to create less leachate loss. Work by Piirainen between 1996-1999 as part of the 'Biomass Ash Utilisation Project ' also monitored leaching of nutrients and heavy metals from two drained former peatlands (one a *Carex* peat, one a *Sphagnum* peat). Tree cover consisted of *Pinus sylvestris* natural regeneration, over *Deschampsia* grass and *Vaccinium myrtillus* shrubs. Both fly ash and granulated bottom ash were tested, and drainage waters sampled from drainage ditches and ground water sources. As in other studies, all ash treatments resulted in high values of Ca, Mg and K base cations in the soil and ground water, along with increased SO₄ concentration. In the *Carex* site with higher N content in the peat, increases in the NH₄ concentration was linked to possible N mineralisation . Some rise in Cr was also detected at this site, but no increase of groundwater concentrations of Zn, Cd, Cu and Ni were found after any ash treatment at any site.

The possible effects of nitrogen mobilisation have been discussed in the SkogForsk Report No.2 (2001) where some ecologists have proposed that increased tree growth resulting from peat breakdown by N mineralisation would take up the available nutrients – other researchers are not certain that this would happen. However, the above papers show that the initial N status of the soil to which ash is applied is obviously critical to potential increased leaching rates

Section C: Plant and animal responses to wood ash additions

1. Agricultural crops

Both field and greenhouse experiments have shown increases in yield after the application of wood ash – its historical use by generations of gardeners for soft fruits and leafy vegetables is well known, but the American authors have completed the most thorough organised research at large scales. According to Vance (1996) crops favouring soils with a relatively high pH do best from ash fertilisation – grass species including the cereals such as wheat and maize, alfafa and vegetables.

From the summary below it is clear that the best crop response is frequently at relatively low application of ash, with a consequent reduction of yield or nutrient content above threshold of approximately 10 Mg/ha.

| Peak production | Ash application rate | Time elapsed | Increase over control | Author |
|-------------------------------------|----------------------|-----------------|--|----------------------------|
| Alfafa (nutrients in harvest) | 11 Mg/ha | 1 year | Sustained | Naylor & Schmidt 1989 |
| Wheat (yield) | 40 Mg/ha | 45 days | 25-69% | Etiégni et al. 1991 |
| Snap beans (yield) | 2.4-9.7 Mg/ha | 90 days | None | Lerner & Utzinger 1986 |
| Oats & Beans (biomass) | 30-50 Mg/ha | 6 weeks | Beans 49-64% (rise) Oats 45-0% (fall) | Krejsl & Scanlon (1996) |
| Poplar cuttings (ht & DBH) (rooted) | 40 Mg/ha | 8 weeks | 9% ht 15% DBH | Étiégni et al. 1991 |

Table 14. A summary of the effects of wood ash application on yield for various agricultural crops

Graphs from Etiégni *et al.* (1991) and Naylor & Schmidt (1989) follow (Figure 6b), showing the decrease in yield at higher application rates (also seen by Krejsl & Scanlon (1996) for oats at the highest dosage rate). This they attributed to reduced phosphorus availability at the higher pH (>7.5) and the possible inhibitory effects of B and K at high ash dosage levels.

2. Tree crops

Positive tree growth response has been recorded by many authors cited in Vance (1996) including, Silfverberg and Hotanen (1989), Etiégni *et al.* (1991), Ferm *et al.*(1992) and Steponkus (1992).

There are four major components to the wood ash effect on tree growth which need to be considered and which Vance has tried to summarise in his 1996 paper:

- The nature of the **ash**
- the soil type
- the tree crop species
- time elapsed since treatment

Short term experiments with tree seeds and seedlings

There is some very old evidence on the growth of seedlings in ashed soils in Finland to show that excesses of wood ash inhibits both the **germination** and initial growth of tree seedlings (Heikinheimo, 1915 cited in Rikala & Jozefek, 1990). In Finland seedling trees have traditionally been grown on low humified Sphagnum peat, with additions of dolomite. Persson (1994) has investigated the growth of Norway Spruce fine roots into separate root-free cores composed of dolomite, limestone, wood and peat ash over a five year period. Crushed dolomite cores had the greatest recorded root weight increase, with wood ash second. High doses of lime had an inhibitory effect on root growth. Work by Clemenson et al. (1995) has shown better root response to wood ash addition than ammonium sulphate fertilizers, with increases in fine root length/dry weight ratio over the control plots.

In the reported experiments of Rikala & Josezefek, wood ash from bark and other wood residues was used as a limestone substitute test, mixed with peat over the treatment range of 0-16.0 kg/m³. Other pots were given similar amounts of dolomitic limestone to make comparison with traditional nursery techniques. Scots pine, Norway spruce and silver birch seeds were sown into the pots, thinned out after four weeks and allowed to grow forward for two successive years with the addition of top dressings of 0.1% nutrient solution twice a week. As expected the pH of the peat increased from 3.8 to between 7.0 to 8.0 according to the range of wood ash dose rate, with linear increases in P, K and Ca in the peat. The germination response was best for the conifers in the lowest pH treatment (< pH 5), whilst birch seeds had a wider tolerance. However, the onward growth of all seedlings was best in dose rates of 0.5-2.0 kg/m³, with the peat pH between 4 and 5. Dolomite and ash treatments generally had the same effect with the exception of a slight improvement of the nutrient balance in pines.

This study could have field implications for the success of natural regeneration at sites where wood ash has been applied, as a raised pH in the soil, maintained over several years might favour broad leaf germination and growth over that of conifers.

The seedling growth of spruce under soil ammendment with paper mill sludge and ash mixtures have been trialled in America (Shepard, 1995) and Canada (Staples et al, 2001), for Black spruce (*Picea mariana*) and White spruce (*P. glauca*) respectively. Both studies varied application rates between 0 - 5 t/ha. At the Canadian site, soil pH was raised from 4.8 - 6.9 units and a decrease in spruce growth recorded at higher dosage rates was attributed to salt phytotoxity effects of the ash. At the Maine site, onward growth of second and third year seedlings was inhibited by vigorous weeds!

Four further short term experiments with *cuttings/established seedlings* from fast growing trees on different soil types are summarised here as an illustration of the variability of tree crop temporal response to ash application.

In Table 14 above the experimental work of Etiégni et al was completed in the nursery with three different soils, with varying additions of ash, up to 6 % of the pot substrate. The poplar growth monitored was most marked in pots with low dosage rates (see Fig. 5a), and the noted lag time in response of the cuttings to ash addition (compared to control plants), they attributed to P in the ash being unavailable until the high initial calcium induced pH became reduced by leaching.

Unger & Fernandez (1989) experimented with *Acer rubra* seedlings in a trial that only ran for 18 weeks. No significant increase in growth rate over the controls was achieved through a range of ash additions from 4-20 Mg/ha and N amended treatments. The soil used was a Hermon sandy loam of low pH (3.12-3.98) with a CEC of 18 meq/100g. However, raised foliar levels of K and Na were recorded, and the soil pH and exchangeable base cations were increased. This experiment however, did record decreased levels of exractable Al and Fe which it was proposed had come from displacement of Al from exchange sites by other base cations in the ash, and not a pH effect on Al and Fe solubility – CEC remained unchanged during the process. Soil pH in the A horizon was raised 0.59 units(i.e relatively little within the context of wood ash experiments).

In the experiments of Lumme & Laiho (1988) *Salix* cuttings were also established on an abandoned mire, with pH 5.1 and a known deficiency of K, Ca and Mg. The ash used was from conifer bark (spuce/pine) and applied at two doses, 5 and 20 t/ha. The soil pH rose within the first month to 6.8 and 8.2 units for the treatments respectively and remained high into year two of the experiment. Soil K levels rose in the heavier application in the first season, and both treatments were raised over the control in the second year. Cellulose decomposition activity remained close to the control plot levels and there was little increase in soil microbiological activity.

Organic N mineralisation was low throughout the two years (2%) and the recorded growth of the willows did not exceed that in the controls, even at higher dose rates. The foliar levels of K and P increased in year two of the experiment, but the authors conclude that without extra added N nutrients might dissolve from the ash too slowly to deliver sufficient to increase growth to these pioneer species. It is proposed that the higher dose rate of ash may have inhibited growth through either the death of soil microflora, the inhibition of Mg uptake by Mn at higher pH, or by the development of increased osmotic pressure in the root zone. Lumme & Laiho (1988) have cited other Finnish authors who have recorded increases for sapling growth such as those in Weber's study from wood ash application to mire sites (Paavilainen, 1980), reported increased nitrification of heath sites (Martikainen, 1986) and increases in microbiological activity (Karsisto, 1979) from wood ash use.

In the early experiments of Weber et al.(1985), an N rich drained and previously cultivated spruce mire site with a current vegetation of *Deschampsia* and *Poa* species, *Ranunculus* and *Urtica*, was planted with *Salix* species and *Alnus incana* in 1979. Commercially produced wood ash was applied at 10 t/ha and compared with NPK fertiliser treatments in the form of urea, superphosphate and potash (dosage rate of 150 kgN, 92.4 kgP, 382 kgK per ha). Over 4 months the pH of ash treated soils rose to 5.5 compared to the control at 4.6, and soil microbe numbers rose and remained at the same level as in the fertilised plots. Cellulose decomposition also increased. The ash addition increased the willow harvest at the end of year 1 over the control by 65-70%. Significant soil N mineralisation had occurred over this time due to the raised pH stimulating microbial activity, and C:N ratios rose from 16.2 to 17.4. Compared to the NPK fertilizer effects where there was increased soil denitrification, the ash treatments had a more balance effect on soil N with less depletion of water soluble organic matter.

Long Term Experiments with mature trees

Due to the 'swailing' tradition in Finland (cropping on burnt forest clearings), formal Finnish research work on wood ash addition to soils has been undertaken since 1935 (Silfverberg and Moilanen, 2001). This initially used all available ash types in a dry powdered form in the experiments, traditionally spreading it on at the end of the winter snow cover. Now the raw material is sorted (ASH project) and investigations are underway into granulation. Swedish research work has already investigated the effects of slower delivery of granulated ash (Steenari *et al.*, 1998) and produced specialist papers on the effects to forest components such as ground flora, bryophytes and microbial soil changes (see parts 3-6 of this Section), as well as the tree growth.

The longest running experiments reported by Korpilahti *et al.*(1998) in Finland have shown consistently sustained increases of 3-4 cubic metres additional timber yield per year (Silfverberg, 1996) over 55 years. This followed a loose ash addition of 5000 kg/ha in 1937 to drained peat land in Finland. Tree response to the ash addition was initially slower than growth responses to commercial NPK fertilisers, but reached equal performance at ten years. No ash use showed any disturbance to levels of trace or heavy metals. Other long running experiments reported by Bramryd & Fransman (1995) over 35 years under pines in S. Sweden have shown the same effect.

In detailed nutritional studies of forest trees in NW Finland following birch ash application in 1933 to a drained mesotrophic Sphagnum bog, analyses of the chemical concentrations in the needles were made to assess the status of the tree crop (Silfverberg & Hotanen, 1989). Increases in the pH and nutrition of treated plots was still evident after 40 years in plots treated with both low (8 t/ha) and higher doses (16 t/ha) of wood ash. Needle levels of P and K in the controls show a severe deficiency. The ash had increased the amount of litter fall, and the raised nutrient content of needles contributed to higher rates of decomposition at the ashed sites. K appears to be the lowest available nutrient in the wood ash – the levels of K in the top soil at all sites was still over 90 kgK/ha in the surface peat which is well above the levels in the controls. The current growth rates of 8.1 and 9.9 m³/ha (for low and high ash treatments) is still good. Similar nutritional changes have been recorded very recently by Ardvisson & Lundkvist (2002). They reported an increase in nutrient concentration after 5 years in the needles, having applied hardened wood ash at 3000 kg/ha to sites of differing fertilities across four climatic zones in Sweden.

However, overall Korpilahti (1998) points out that growth response to ash addition is definitely more successful where there is already high N in the soil profile (1.5-2.5% dry weight). On nitrogen poor soils (under 1% content) growth remained low. Confirmation of the successful use of ash on peatlands comes from Ferm *et al.* (1992) monitoring the growth of *P. sylvestris* over 13 years after ash fertilisation. They reported decreased symptoms of tree disorders and decreased levels of die-back, even at high doses of ash. The volume of growing stock exceeded 70 m³/ha under the ash treatments, whereas the control produced only 15 m³/ha. Higher rates of

decomposition of the peat was reported from the heavier ash deposition sites (5 and 10 Mg/ha), along with the high N content suggested N mineralisation of the peat was feeding into the tree growth very successfully.

A further confirming result comes from the work by Jacobson (2001), who monitored stem growth of Scots pine and Norway spruce at four locations across Sweden on podsolic mineral soils. The ash used was granulated and applied in a range of 3 doses at a maximum of 6 Mg/ha in 1988/89. In all three southern experiments the tree growth was increased in ash treated soils over the eleven years, most significantly for Norway spruce. The production volume averaged 1.2 m³ha/yr for each addition of 1Mg/ha wood ash. However, at the northern site (lat.64⁰N) the opposite effect occurred, with reduced growth on ashed soils correspoding to a reduction compared to controls of 0.8 m³/ha/yr. It is suggested that the mobilisation of N is therefore critical to increased tree growth, where the poorer soils and worse climatic conditions of north Sweden create immobisation of N in ashed mor top soils. The C:N ratio would therefore seem to be a good indicator of the likely effect that increased pH would have on the N status of a particular soil .Other Swedish authors have suggested an increase in mineralised N after liming if the C:N ratio in the humic layer rises above 30 after ash application (Persson, 1988).

2. Effects on ground vegetation

Higher Plants

A handful of Scandinavian studies consider the effect of wood ash additions to forest areas specifically with regard to the ground flora. Within the overwhelming needs of forestry tree production, the conservation of ground vegetation has only recently been seen as worthy of separate research. It has also come second to the health and safety aspects of wood ash use – for instance earlier papers on vegetation have been prepared in order to investigate the heavy metal concentrations of berries that are collected as food sources - particularly from *Vaccinium* species (Silfverberg & Issakainen, 1987). More recently Levula *et al.*(2000) have looked more closely at *V.vitis-idaea* berries for both heavy metals, S and ¹³⁷Cs concentrations after the application of wood ash. In the earlier study by Silfverberg and Issakinen the effects of both peat and wood chip (*Betula*) derived ash was investigated on a mineral and a peat soil in the NW coastal area. On the peat soil, now a *V.myrtillus* and spruce swamp, the wood ash increased surface pH by 1.0 units. K concentrations increased at the soil surface and in soil water – and in the berries produced by both *V. myrtillus* and *V. vitis-idaea*, but Ca, Mg and Mn values decreased. On the mineral soil a large berry harvest increased for both species in the 2-3 months of the experiment following ash application, but no berries contained Cd or Pb concentrations above normal (usually <1 mg/kg). This was despite the known high Cd content of the wood ash applied. Higher concentrations of Cd have reported for edible fungi such as ceps (*Boletus edulis*), reaching up to 12 mg/kg (Ruhling,1996).

Levula *et al.* (2000) worked in central Finland on a dry site under *P.sylvestris* on an iron podsol with only a 3 cm humus layer. Ash fertilisation was made at rates from 1000-5000 kg/ha, with material from conifer bark. Surface samples were taken one season later, and berry samples in the following year and five years later. Ash fertilisation had no effect on the heavy metal content of the berries- K was the only macronutrient showing an increase in concentration. The berry content of ¹³⁷Cs showed some decrease on ashed plots, particularly in the samples seven years after ash spread. The authors attributed this change to the rise in pH of the humus layer and possible increases in exchangeable Mg. However, a mechanism is not obvious here and the authors did not propose one. Some small reduction in the dominance of *V.vitis-idaea* were also noted as a by product of the ashing, particularly at the highest dose rates. Earlier studies in Sweden by Gyllin & Kruuse (1996) had not noted any difference in *Vaccinium* stands after 2-9 years of the use of wood ash at their sites under the tree crop.

However, there is some emerging data to show that ground flora has made subtle changes after ash application in some sites. Silfverbegr & Hotanen (1989) recorded that changes in a *drained* herb-rich peatland treated with ash had resulted in the increase of N demanding species such as *Cirsium helenoides, Daphne mezereum, Paris quadrifolia, Prunus padus* and *Urtica dioica* – particularly in high ash dosed soils (Heightened by drainage?)

Recent Swedish monitoring of ground vegetation changes have come from pilot field experiments applying wood ash at between 1-8 t/ha (Lundkvist *et al.*,1998). Although a relatively small 0.5 pH rise was detectable in the runoff from the sites, no increase in nitrate leaching was detected and no increase in berry heavy metal content. More detailed studies by Arvidsson *et al.* (2001 and 2002) have looked at ash effects on 7-9 year old Norway spruce plots, with a *Vaccinium myrtillus* shrub understorey. In a spread of plots across Sweden four different climatic areas were represented: the north coastal, the SE (with summer droughts), the S uplands and the SW area, where both S and N deposition are high. In the SE study site, the dry conditions created a

noticeable gradient of vegetation, with *Vaccinium* dominance giving way to more grasses and herbs. Crushed, hardened wood ash of two kinds were used: Perstorp (a 90% wood ash from a Fluidised bed boiler), and Nymolla (a bark fired cyclone furnace), which were applied to the sites at 3 Mg/ha. Sampling began five years later. Neither ash seemed to have affected the *V.myrtillus* sites, even in the south east, but the grass dominated plots under Nymolla ash developed a herb flora more like that under the *Vaccinium* type with an increased species list - this would be an indication of a site fertility increase. The cover of *Deschampsia flexuosa* also increased in the S East on ashed plots compared to controls, and cover values for heather decreased in plots treated with Perstop wood ash. *Calluna vulgaris* is well known for its requirement for very nutrient poor substrates.

This study indicates the subtle ways in which different ash types may affect species composition in the ground vegetation, even at low ash dosage rates.

Bryophytes and Lichens

In a very comprehensive paper Kellner and Weibel(1998) review the data from Scandinavian ecologists and foresters concerning the effects of ash use on lower plants, and report experimental data from work with the moss, *Dicranum polysetum*. Citing the work of European authors such as Hofmann and Rodenkirchen in Germany, Mälkonen (Finland) and Jappinen and Hotanen (1990), Lundborg and Norsted in Sweden, they summarise the recorded effects that loose ash spreading in the past has had on moss carpets and lichens. In general there was good survival for most moss species at dosage rates of under 7 t/h, but some major declining cover changes have also been recorded, for instance for *Goodyera repens* (Kellner, 1993) and *Peltigera aphthosa* (Norsted et al., 1988), in which the latter subsequently was completely lost to the site. By contrast, work by Andersson(1995) has monitored increases in the growth of *Pleurozium schreberi* at the expense of other competing mosses after liming. In many other cases however, long term observation has shown complete recovery of the moss flora after five to ten years, though at a new equilibrium with respect to the species composition of the sward. As existing studies (e.g. Gyllin and Kruse,1996) have investigated only the effects of loose ash on the forest floor, Kellner and Weibel set out experimental plots under a *P. sylvestris* forest for ash addition in loose, crushed (self-hardening) and granulated forms.

At two sites north of Uppsala ($\sim 60^{\circ}$ N) on sandy or glaciofluvial deposits, random replicate quadrats were treated with prepared ash at doses from 0 - 8 t/ha, and monitored over the subsequent three years. At the moss site the ground flora was dominated by *Dicranum polysetum*, *Ptilium crista-castrensis*, *Pleurozium schreberi and Hylocomnium splendens* mosses - all of which are common Boreal species on acid substrates under a shrub layer of *Vaccinium myrtillus*. At the lichen site, a mixture of reindeer mosses with *Cladina arbucula*, *C. rangifera and C. stellaris* were intermixed with the mosses *D. polysetum and P. schreberi* under *Calluna vulgaris*, *V.myrtillus and V. vitis-ideae* shrub layer. The crushed ash was prepared from the commercial energy plant at Perstorp from 90%wood /10% peat, with particle sizes of under 5mm and both the loose ash and granulated ash (rolled into 4-20mm sizes) came from 100% wood, burnt at Ekilstuna. Treatment areas were monitored at 3,10,15 and 33 months after ashing, and scored on a damage scale of 1-3.

Plots covered with granulated ash had little or no noticeable damage throughout the length of the experiment, and the lichens were not at all affected in terms of visible damage or cover values. The greatest visible damage to the moss sites was noted at three months, when browned or dead foliage was scored for all species – three out of four Bryophytes decreased in cover values in the first year. Then regrowth repaired the ground layer or covered the old, so that damage scores declined to 15 months .The greenhouse experiments confirmed that the photosynthetic ability of the moss (*Dicranum polysetum*) decreased in line with the scored foliar damage - at treatments rates of 4t/ha, photosynthesis was reduced by half. This not only affects onward growth, but also potential reproductive capacity and the competitive ability of the species. The ceiling application rate creating no damage score from both loose and crushed ash was 4t/ha, but at this dose rate increases of *Pleurozium schreberi* cover were noted in the recovery period, at the expense of *Dicranum polysetum and D. crista-castrensis*.

The ash effects are obviously immediate on the mosses, and relate to the amount of surface area contact the particles have on the foliage. Granulated ash particles at over 5mm size have much less contact than finer ash, but the similar effects from both loose and crushed ash were difficult to explain except in terms of the combination of high pH with high ion concentrations. Granulated ash has the same or higher pH as crushed ash in this experiment, but a much lower ion concentration. The recommendations that could be made from this study by Kellner and Weibel is that the use of granulated ash should be preferred in sensitive Bryophyte areas, but where loose or crushed ash has to be used, application rates should be limited to under 2t/ha.

4. Soil Fauna

Very little published data exists on the effects specifically on soil fauna except for studies on enchytraeid and earthworm populations by Lundkvist (1998). This research monitored Cd levels in body tissues of these animals under forest fertilisation with wood ash at low levels(loadings of 3.2 t/ha of granulated ash). At this level Cd was found to increase in the body tissue in the second year after ash application, but there was no recorded adverse effects on the size of the population. In fact earthworm numbers increased in line with increases of ammonium nitrate.

5. Soil microbiology

In contrast to soil fauna, studies investigating the changes in soil microbial activity under ash application are well represented from 1985 to the present. Techniques have included measurements of cellulose decomposition; Agar plate colony counts; the recordings of N availability and mineralisation in a variety of substrates; the measurement of soil respiration rates and ATP for biomass estimates, and the thymidine incorporation rate (labelling technique at the level of macromolecules). Early studies in Finland were completed in the field on a cultivated and drained peat bog, planted with *Salix* and *Alnus* rooted cuttings. The soil amendment with wood ash from a commercial boiler was spread at 10 t/ha. Soil cores removed from the site indicated a pH rise attributable to the wood ash from 4.6 - 5.5 over a two year experiment, and consequent increases in the soil microbiota raised the mineralisation rate with the loss of 9% N in the first year. Cellulose decomposition increased by 53-86 % over the control plots. This site is known to be rich in N, due to past cultivation which would aid the mineralisation process, but levels of denitrification appeared in this study to be positively correlated with the presence of water soluble carbon, which was abundant in the wood ash.

In a similar study in Sweden on ash amended coniferous forest soils, for similar results of soil pH rise culturable bacterial numbers were calculated to have risen by 5.1 times over those in the control plots (Bååth & Arnebrant, 1994). The authors proposed that the bacterial colony would have to have altered in composition in order to accommodate the new pH level (rise from 4.0 - 6.1 units). Respiration measured from the soils was always higher in the ash amended treatments, but only sustained where the C:N ratio in the soil was lower, whereas respiration levels in poorer soils with high C:N ratio ceased or was soon reduced to those in the control plots. Denitrification is not recorded in this soil, neither is it in the experiments of Fritze *et al.* (1994) in Finland who worked under *P.sylvestris* on a podsolised sandy soil. In the latter research microbial respiration was much higher from the ash treated plots, though no increase in the fungal biomass C was detected against the control plots.

In a laboratory study of the effect of Cd levels on bacteria, Fritze (2001) has found that humus spiked with Cd and added wood ash greatly increased the activity of the bacterial population, changed fatty acid patterns and substrate use, but did not at any time indicate increased tolerance to Cd. Field studies under Scots pine on a dry *Empetrum-Vaccinium* heath with a thick humose podsol soil were completed with ash additions of 3 Mg/ha, and subplots of added Cd to the value of ca.400 mgCd/kg ash. Similar assessment techniques to those employed in the laboratory showed that within a three year period the bacterial population had changed, compared to the control – but the extra Cd in the spiked ash had not produced any additional effect despite soil levels still registering increased concentrations.

5. Soil fungi

Ectomycorrhizal (EM) communities have also been specifically studied very recently to determine species composition and groups present in forest soils. Up to 300 different types have been catalogued in Swedish forest soils (Erland, 2001). Species of *Telephora, Tylospora* and *Cenococcum* dominate under spruce forests in southern Sweden. In a similarity analysis of populations under wood ash applications limited small shifts around 20 types in the community could be identified, with some increase in the *Cortinarius sp.* identified. Ash granules were found to be heavily colonised by four particular mycorrhizal types, three of which were also found on the tree roots, and two matched types (one *Piloderma sp*) known to be abundant in ash at other sites. Mahmood (2002) in an extension to the study has calculated that these species together made up to 55% of the total EM community on the screened roots. The author suggested an active role for these ectomycorrhizal types in weathering ash on the forest floor and mobilisation of nutrients. Further laboratory tests showed that the ability of these EM fungi to colonise roots in the field is greatly enhanced by the addition of wood ash.

Concluding remarks on the application of wood ash to forest land

The potential effects of ash addition on forests are more complex than on agricultural crops. Agricultural soils are maintained as near as possible to neutral pH during cultivation, and fertiliser amendments are disked into the topsoil for immediate effect over short time periods. Forest soils by contrast, may be poorer and often more acidic, particularly under conifers due the release of organic acids and the subsequent release of base cations in litter. In Europe many forests only exist because the soils/topographic conditions have not been suitable for easy cultivation. Forest soils often have thinner A horizon top soil and very marked structural horizons which may be punctuated by macro pores, deep root channels, or animal burrows, altering water movement through its depth. The longer life of the crop complicates the treatment of the site, and the structure of the crop affects the physical delivery of soil amendments.

Vance (1996) has suggested that repeated **whole tree harvesting** in the Eastern USA over a period of 120 years might remove 20-60% of total site Ca, and 2-10% of K, P and Mg (citing Federer, 1989). From studies on nutrient losses from stem only harvesting Vance concludes that there is a 300% greater loss in nutrients from a whole tree harvested site. One single application of wood ash at 10 Mg/ha could replace leaching losses, and loadings of 20-30 Mg/ha would replace whole tree harvesting losses. Additional N amendments would also be needed to create balanced nutrient input. Similar research in Sweden has more recently investigated replacement values of nutrients from wood ash (Ardvisson & Lundkvist, 2002) and also concluded that applications of wood ash could be used to replace losses caused by whole tree harvesting.

Vance however, suggest there are several **specific cases** where ash amendment would have positive benefit to forest growth, for example: –

- a) K and Mg deficiencies in soils of NE USA and southern Canada (documented by Leaf *et al.*1975) (*Pinus resinosa, P.strobus, Picea glauca* and *P.abies* forests)
- b) In the South USA P-limited soils under pine forests could be treated with ash at 40 kgP ha

He considers it more likely that hardwoods would benefit more from ash application than soft woods due to their higher requirement of K, Ca and Mg which are often three times those of conifers. Hard wood nutrient ratios suggested for optimal growth are P:K:Ca:Mg @ 1:5:20:2.5 and ash delivers 1:7:45:2.5.

However, the complexity of the pathways of nutrient movement has been demonstrated in some more recent work by Clarholm (1994 and 1998) in Sweden. In these experiments wood ash was used to counteract phosphorous and potassium limitations monitored in the needles of a Norway spruce forest subject to air pollution. Phosphorous levels were monitored in the humus 18 months after the wood ash application at the rate of 4000 kg/ha , and later pathways were investigated using radioactive ³²P and ⁸⁶Rb assays in the humus and fine roots. No differences were found in the amounts of P between the control and treatments, and acid phosphotase activity in the humus appeared to be negatively correlated with the amounts found in the needles the previous year. It was suggested that as P in the ash is not in a water soluble form, more immediate remediation would be achieved by adding soluble P. The second experiment tracked the movement of ³²P, and showed that uptake was not related to tree demand, but was negatively related to the P/C ratio of the microbial mass around the roots. The author suggests that the levels of P at the same site after five years monitoring are now significantly greater in the biota and would be expected to allow an increased P uptake by the trees in the near future.

This study confirms the complex and time dependant effects that may accrue from applying wood ash to forest soils and ecosystems which need deeper research and long term experimentation.

This review shows that ash treatments at low levels have been successfully used in the past in both America and Europe for nutrient replacement into poor forest soils. The importance of the receiving soil type becomes evident from both short and long term experiments in the field, with regard to the effects of the added ash. Contrary to expectation, the real problems of ash use is not all in its heavy metal content, but is more likely to be in its heightened Ca content. This creates subsequent rises in pH of the soils and increases microbial populations and the potential mineralisation of N. Heavy metals can be largely removed or reduced at source during the ash burning and granulation phase but pH rises in soils, though potentially beneficial to tree growth, could make subtle changes to the ecology and the nature of forest sites over long time periods.

Wood ash use with minimal detrimental environmental impact – Reviewers recommendations

The following are general recommendations for the use of wood ash as a soil additive:

- 1. Hardwoods are better for ashing than softwoods allow only wood derived products in burn
- 2. Keep bark proportions to a minimum in the burn (particularly from conifers)
- 3. Burn at 500-900 °C not above for maximum nutrients and least heavy metals
- 4. Use only bottom ash do not mix with fly ash consider a reburn programme for fly ash before landfill i.e. quality assurance programme
- 5. Granulate ash to slow down the release rate of carbonates; this gives better health & safety conditions in field, and less direct effect on ground vegetation.
- 6. Spread at low rates e.g under 5-10 Mg/ha and at long intervals (or only once a rotation).
- 7. Do not treat with herbicides at the same time due to potential retention by ash layer (Magdoff et al.1984).
- 8. Use on broadleaf tree crops would have maximum fertilisation effect.
- 9. On balance, best used on soils of medium to low pH (approximately 5.5 down to 4) e.g. mineral soils, sandy or fine loams or shallow peat
- 10. Avoid very acid soils in case of extra Al and Fe immobilisation in the subsoil
- 11. Avoid soils enriched from N pollution to avoid triggering N leaching
- 12. Avoid conservation areas with special acid loving plants (particularly Bryophytes).

Other potential Uses of Wood ash

- Sewage sludge addition (used in Eastern USA) for bulking and odour eating. In an experiment ash removed BOD & COD (33%) and suspended solids(88%) in leachate columns
- Scrubber systems
- Concrete production
- Road base materials

Special Site ammendment

| Water holding capacity | Would granulated ash improve this? Could it's addition improve very free draining soils? |
|------------------------|---|
| Chemical effect | Liming effect on pyritic coalfield spoil |
| | Restoration of P values without added C or N. |
| Phytoremediation | Uptake of minerals by trees e.g. willows, ashed in smelter with removal of heavy metals in fly ash. (See papers by Riddel , Black , Ostman ad Goransson in Aronson and Pertu, (eds) 1994) |

APPENDIX 1

Danish Legislation relating to Wood ash Application (2001)

- 1. No recycling of wood ash with Cd content over 15 ppm. Specifically no fly ash. Three classes of content are designated of which content of 0.5-8.0 is the mid point.
- 2. Other heavy metal contents are restricted to Pb: 120 ppm, Hg:0.8 ppm, Ni:30-60 ppm,Cr:100 ppm
- 3. P content shall be limited to a maximum of 30 kg/ha or total of 90 kg/ha over three years.
- 4. No more than 7.5 Mg of wood ash may be applied to a stand over a single rotation, with a lower limit if the Cd content is relatively high (upper band).
- Analysis for polyaromatic hydrocarbons(PAH) must be made where residual carbon content is over 5%. PAH content must not exceed 3mg/kg (From SkogForsk Report No.2, 2001)

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