From Wood to Waste and Waste to Wood

Aspects on Recycling Waste Products from the Pulp Mill to the Forest Soil

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Photo front: Spruce seedlings surrounded by ash pellets (Sven Magnusson, 2007)

Abstract

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In this thesis the flow of elements from the forest to the pulp-mill and the possibility to recycle nutrients in solid pulp-mill waste back to the forest have been studied. To get improved estimations of element removal at whole tree harvesting (WTH), the changing element concentrations with changing diameter of *Picea abies* stems were investigated. The results showed that element concentration for Ba, Cd and Pb in wood and Ba, Ca, Cd, Co, Mn, Sr and Zn for bark were significantly positively correlated with diameter whereas Cu, Fe, K, Mg and P in wood and Cr, Cu, Fe, K, Na, Ni and P in bark were negatively correlated. In order to test the recycling potential of different solid waste products a mass-balance study was made for three pulp mills in Sweden. Bark-ash had the best composition of plant nutrients but high concentrations of some heavy metals. Green liquor dregs (GLD) and lime mud contain less nutrients, except Ca and Mg. Mixing of bark-ash and GLD can be a way to improve nutrient composition and achieve a high degree of recycling. Pelleting and heat treatment of ash and GLD was evaluated as a way to get stable pellets with long-lasting effect in the field. Pelleting decreased the reactivity of the pellets, resulting in less effect on pH and low leaching rates of elements. The heating of ash pellets gave a decreased surface area and decreased reactivity in the soil. Mixing bark-ash with GLD resulted in an increased leaching of DOC and DON. Heating of GLD pellets increased pH significantly in the leachate due to formation and subsequent dissolution of MgO. The pre-treatments did not decrease the rapid leaching of K and Na from the pellets. There was no tendency for increased N or C mineralisation in the mor layer for any pellet type. Thus, when pure ash pellets are used, the risk of high N losses from mor layers in podsolised spruce stands after ash application is small, even under disturbed conditions. However, more caution should be taken with mixtures containing GLD, which show a greater interaction with the mor. Heating of GLD pellets should be avoided.

Key words: stem, bark, concentration, element, nutrient, *Picea abies*, DOC, DON, mass-balance, ash, green liquor dregs, leaching, pellet, heat treatment

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Contents

Introduction, 7
Element content in trees, 7
Origin and content of waste products, 8
  Stabilisation and heat treatment, 11
  Mineralogy of inorganic waste products, 11
Effects of waste products on soil properties & processes, 12
  Metal accumulation, 12
  pH & salt effect, 12
  Carbon & nitrogen, 12
Aim, 14

Materials and methods, 15
Element contents in trees – Paper I, 15
Mass balance of pulp mill – Paper II, 16
Element leaching from bark ash in field – Paper III, 16
Effects of waste products on soil properties & processes – Paper IV, 17
Mineralogy & surface properties of the pellets, 18
Statistics, 19

Results, 19
Element contents in trees – Paper I, 19
Mass balance of pulp mill – Paper II, 21
  Element composition of waste products, 21
  Mass balance budgets for nutrients, 21
Element leaching from ash pellets in field – Paper III, 26
  Weight changes of pellets, 27
  Element losses, 27
Effect of waste products on soil properties and processes – Paper IV, 28
  Carbon & nitrogen efflux, 28
  Effects of pelleting on leachate, 28
  Effects of heat treatment on leachate, 29
  Effect of green liquor dregs on leachate, 29

Discussion, 32
Element export from the forest, 32
Element flow through the pulp mill, 34
Recycling of waste products to the forest, 35

Conclusions, 38

References, 39

Acknowledgements, 43

Appendix

Papers I-IV

The present thesis is based in the following papers, which will be referred to by their Roman numerals:

I. Rothpfeffer, C. & Karltun, E. 2007. Inorganic elements in tree compartments of *Picea abies* – concentrations versus stem diameter in wood and bark and concentrations in needles and branches. *Biomass and bioenergy, doi: 10.1016/j.biombioe. 2007.06.017.* (In press)

II. Karltun, E. & Rothpfeffer, C. Nutrient and heavy metal content and recovery in waste products – a case study of three Swedish sulphate paper-pulp mills. (Manuscript)

III. Rothpfeffer, C., Pommer, L, Boström, D., Nordin, A. & Karltun, E. Element release from pellets of bark ash – a field study. (Manuscript)

IV. Rothpfeffer, C., Pommer, L, Boström, D., Nordin, A. & Karltun, E. Element release in a mor layer fertilised with pelleted ash and green liquor dregs – a column experiment. (Manuscript)

Paper I is reproduced with the kind permission of Biomass & Bioenergy.

Contribution of Caroline Rothpfeffer to the papers in this thesis:

> As first author of Paper I, III and IV, I was mainly responsible for the field sampling, laboratory experiments, analyses of samples, data analysing and writing. The experimental designs were planned together with co-workers and co-authors. The co-authors also reviewed and commented the manuscripts before the theses were printed. The input from the co-authors was about 20% in each paper. In Paper II, I was mainly responsible for the field sampling and analyses of samples. I contributed to about 30% of the work of the paper.

Introduction

The increased interest of CO_2-neutral and renewable energy has led to intensified use of forest residues (tops, branches, needles) as fuel (Bäcke, 2004). Whole-tree harvesting can lead to depletion and acidification of the soil unless the nutrients are replenished from mineral weathering and atmospheric deposition (Akselsson, 2005; Olsson, Rosén & Melkerud, 1993). One way to counteract both the acidification and depletion is to return ash and other waste-products generated in the paper-pulp industry to the forest sites where whole-tree harvest has been practiced. In theory, optimal would be to return the same amounts of nutrients that are removed from the site, but this is not achievable in practice. However, in order to develop a recycling practice that is acceptable, both from an environmental as well as an economic point of view; we need to understand the pathways of nutrients and potentially toxic elements. This thesis deals with element cycling along the pathway from the forest to the pulp-mill and the return to the forest in recycled waste-products. It considers aspects on element export from the forest site, the recovery potential within the pulp-mill and the suitability of the waste-products to be returned to the forest.

Element content in trees

The element content of the tree primarily depends on the physiological need of the tree for building and maintaining its biological tissues. It may also be influenced by the chemistry and moisture conditions of the soil and the deposition of elements from the air at the forest site (Halliday *et al.*, 1991). Also pathogens affects the content in the trees (Nilsson, Karltun & Rothpfeffer, 2002; Rennerfelt & Tamm, 1962). Trees take up most nutrients with the water flow through roots or ion exchange between the soil and the roots. Element mobility in the tree is based on a number of factors such as essential nature, ion solubility, ion charge, sap pH, cell wall quality and concentration gradients within cells (Cutter & Guyette, 1993). It is these factors that influence the distribution of elements at different locations and tissues in the tree. There are few studies done on how the elements are allocated in tree stems but it has been shown that the concentration of Fe K, Mg and P increases closer to the top whereas no differences was found for Al, B, Ca, Cl, Mn, N, Na, S, Si and Zn (Helmisaari & Siltala, 1989; Werkelin, 2002). Helmisaari & Siltala (1989) concluded that the younger the tree the smaller vertical increase in nutrient concentrations. Studies have been done on the nutrient status versus age of branches and needles (Finér, 1992; Ingerslev, 1999) which implies that all macronutrients, except Ca, are allocated to the most vital and fastest growing parts of the trees due to the importance of those elements in the photosynthesis, cell and membrane production, and enzyme activity.

In an undisturbed forest all elements taken up by the tree are re-circulated to the forest ecosystem when the tree falls to the ground but this re-circulation is interrupted if the tree is harvested and removed from the forest. Thus, harvest and subsequent removal can lead to depletion of the soil unless the nutrients are replenished from some other sources than decomposed organic matter. Calculations of the removal of nutrients and other elements upon harvest are usually done on the basis of biomass functions, for example the biomass equations developed by Marklund (1988). These functions predict the biomass in different tree compartments on single tree basis. The amount of biomass is then multiplied by the concentration of the nutrient in different tree parts to get the amount removed with each tree compartment. However, most often it is assumed that the concentration of the nutrient is constant throughout the tree compartment; however, if this is not the case, an error will be introduced in the mass balance calculations leading to misleading recommendations to the foresters.

The knowledge of element concentrations and distribution within the tree are also of importance for the industry because some elements are favourable for the characteristics of the final products whereas others disturb the processes or decreases the quality of the final products. Especially the pulp-industries are vulnerable to non process elements which disturb the processes or cause corrosion, plugging and up-scaling of deposits (Anon., 2003).

Origin and content of waste products

In Sweden, clear-cutting in combination with planting and/or natural re-generation is the most common method for renewal of forest stands, which means that all trees at a site are harvested at the same time. This gives a period of 2-3 years before the new generation trees are established. During the last decades rising prices of energy and the interest for CO_2-neutral and renewable energy sources have increased the use of forest biomass in the energy sector. This has led to a situation where whole-tree harvest has become more common (Bäcke, 2004) which means that not only commercial round-wood but also smaller dimensions and logging residues (i.e. tree tops and branches with or without needles) are removed from the site. These parts are then used as fuel for heat and in some cases electricity production.

Whole-tree harvesting has increased the nutrient export considerably since concentrations of nutrients are highest in biologically active parts of the tree e.g. needles and branches (Alriksson & Eriksson, 1998; Eriksson & Rosén, 1994; Helmisaari & Siltala, 1989; Ingerslev, 1999; Ingerslev & Hallbäcken, 1999). Nutrient balances for managed soils in Sweden show that weathering can sustain the losses of magnesium (Mg) and potassium (K) but not calcium (Ca) on most sites when practicing stem harvest only. If biomass removal increases, as at whole-tree harvest, weathering does not compensate for the export of Mg, K and Ca and the plant available pools of those nutrients are depleted (Akselsson, 2005; Sverdrup & Rosén, 1998). One way to counteract both the acidification and depletion of the soil is to return ash and other waste-products from the forest industries to the forest sites where whole-tree harvest has been practiced.

The clear-cut method gives a period of 1-3 years after harvest before the new generation trees has established on the clear-cut area. From a practical point of view, spreading of ash would be easiest to carry out in this phase. However, at that time there is an increased risk of nutrient losses by leaching due to an increased pH in the soil, high nutrient availability due to degradation of litter and not enough vegetation to take care of the added nutrients (Lundell, Johannisson & Högberg, 2001). The effects of whole-tree harvest combined with re-circulation of ash might, in a situation like that, lead to elevated nutrient losses due to nitrification and leaching.

The sulphate pulp-mill is a complex industrial plant and each pulp-mill is unique in its way of processing and bleaching the paper pulp, utilizing energy and re-circulating chemicals. A simplified scheme of the processes in a sulphate pulp-mill is presented in Figure 1. The major input sources to a pulp-mill are the wood and water. Before the wood goes into the boiler, the bark is removed from the wood and used as fuel in the integrated energy plant. The cellulose fibres are separated from the lignin in the boiler by heating together cooking chemicals (Na_2S and NaOH). The cellulose fibres are then washed and bleached in several steps before the paper-pulp is ready. Apart from the production of pulp, the pulp industries also produce commercial by-products such as tall oil, soft soap and turpentine. Pulp-mills are also large producers of bio-energy.

The residual liquid from the boiler is called black liquor and contains the transformed chemicals, lignin and residual fibres together with water. Before the black liquor goes into the chemical recovery system, the water content is reduced in several evaporation steps and the black liquor is transformed into thick liquor. The organic compounds in the thick liquor is used as fuel in the recovery boiler where the transformed boiling chemicals are re-circulated in high temperatures to Na_2S, which is a boiling chemical ready to use, and to $NaCO_3$, which has to go through the causticising process before NaOH is re-created. In the bottom of the recovery boiler is Na_2S, $NaCO_3$ and other rest components collected as a melt. This melt is dissolved into weak liquor from the causticising process and this mixture is called green liquor. The solid parts are thereafter separated from the liquid on a filter drum and leave the paper-mill as a waste-product; green liquor dregs (GLD). The filtered liquid goes into the causticising process where CaO from the lime cycle is added and several chemical reactions occur: the water reacts with CaO and $Ca(OH)_2$ is produced. This $Ca(OH)_2$ reacts with $NaCO_3$ in the green liquor and NaOH, and $CaCO_3$ is formed. The lime is separated from the liquor, now called white liquor, and the NaOH and Na_2S is ready to be used in the boiler. The separated lime (lime mud) is returned to the lime cycle and converted back to CaO by heating and thereafter again re-used in the causticising process. However, some lime-mud must be used at the filter drum to make the separation of GLD more effective. The exhausts from the recovery boiler are containing particles and vaporised elements and must be cleaned before exiting the chimney. The particles are usually collected on an electrostatic filter and the solid material collected on the filter is referred to as recovery boiler dust (RBD).

Substantial quantities of water are used in the boiling, washing and bleaching processes. This water has to be purified before it is returned to a recipient. The water passes through basins for sedimentation of cellulose fibres and other solid remains before it is biologically purified. The biological sludge, consisting mostly of wood fibres and dead microorganisms from the water purification, are sometimes used as bio-fuel in the recovery boiler or in a separate combustion plant.

The increased interest of environmental tasks and work toward no or minimized pollution have put a pressure on the pulp industries and the re-circulation of chemicals. Increased closure has led to problems with inorganic non-process elements (NPE) which disturb the processes and leading to *e.g.* decomposition of bleaching chemicals, incrustation, clogging and corrosion. Before, these elements were removed from the pulp-mill together with the waste-products but the higher re-circulation within the industry has lead to an enrichment of the NPEs.

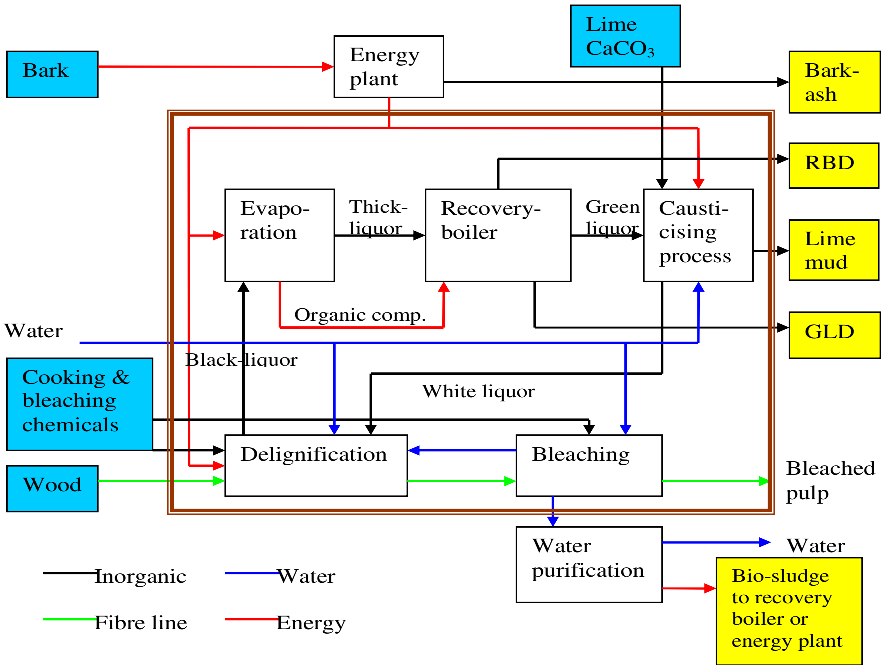

Figure 1. *The main entering and exiting streams of a pulp-milll (Anon., 2003). The solid waste-products are marked with yellow and their source is marked with blue. GLD = green liquor dregs. RBD = Recovery boiler dust.*

Despite the efforts towards increased re-circulation within the pulp-mills, there are substantial quantities of solid waste-products produced in the pulp-mills in Sweden (Table 1). Some of those (bark-ash, GLD and lime mud) may be suitable for re-circulation to the forest. These waste-products are highly alkaline and contain some of the mineral elements originating from the forest ecosystem. Recycling of the waste-products has been suggested as a possible way to counteract acidification and nutrient deficiencies (Eriksson, 1998a; Greger *et al.*, 1998; Olsson, Bengtsson & Lundkvist, 1996). Ashes usually differ in their composition and the properties are mainly determined by the fuel and combustion method used (Hower, Trimble & Eble, 2001; Steenari & Lindqvist, 1997). GLD contains higher levels of Mg and Na compounds than the ash because of addition of those elements in the industry processes.

Table 1. Amounts of waste-products produced in Swedish pulp-mills in 2005 (Arm, Lindeberg & Helgesson, 2007)

Waste-product	Mton^{-1}
Fly ash	222
Green liquor dregs	125
Lime mud	162
Lime grids	11

Stabilization and heat treatment

Recycling of nutrients is not just a question of putting the waste-products back in the forest. Their leaching properties and the way they influence chemical and biological soil processes are important to understand in order to be able to minimize possible negative impacts. Raw ash has a high reactivity and stabilization is needed before re-circulation to the forest to avoid a drastic increase of pH (Steenari & Lindqvist, 1997; Zimmermann & Frey, 2002), high salt concentrations in the soil solution (Steenari & Lindqvist, 1997) and to avoid scorch damage on ground vegetation (Arvidsson & Lundkvist, 2003; Jacobson & Gustafsson, 2001; Kellner & Weibull, 1998). The cheapest method of stabilizing ash is to self-harden the ash by adding water to the ash and let it react spontaneously with the atmosphere. Series of transformations of the Ca species occur and more stable secondary minerals are formed. According to Steenari *et al.*, (1999), the most important reactions are:

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (1)$$
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (2)$$

The hydration of CaO, reaction (1), is fast and exothermic and the second reaction (2) requires the presence of a water phase in which the reactants can dissolve and be transported. Once the calcite ($CaCO_3$) is formed, it precipitates from the solution and creates a layer on surfaces and in the pores of the ash aggregates. After the stabilization the ash can be crushed and sieved to a suitable particle size. A more expensive option is to make pellets or granules of the ash, which gives a more homogenous product. This method gives a better opportunity to control the size, hardness and leaching characteristics of the product. Another method for further refinement is to treat the pellets or granules in a controlled high temperature and atmosphere (Byström, 2001; Sundqvist, 1999). The method is possible to adapt to different waste-products. The controlled temperature and atmosphere during the heat treatment control the volatilization and transformation between the species of a certain element. A positive effect with heat treatment is that heavy metals (As, Cd, Pb) and radioactive isotopes such as ^{137}Cs can be volatilized and separated from the ash pellets and the contents of persistent organic pollutants can be reduced considerably (Byström, 2001; Ljung & Nordin, 1997; Sundqvist, 1999).

Mineralogy of inorganic waste products

The mineral composition of the waste-products is of importance for their leaching properties. Calcite ($CaCO_3$), Mg-silicates and apatite ($Ca_3(PO_4)_3(OH)$) are the major forms of Ca, Mg and P in stabilized ash and those compounds are stable or relative stable in the actual pH ranges (Eriksson, 1998b; Ljung & Nordin, 1997; Steenari *et al*., 1998). Other common forms of Mg in ash are periclase (MgO), and brucite ($Mg(OH)_2$) which is more soluble than the Mg-silicates. The speciation of K and Na is dominated by salts with a high solubility such as sulphates and carbonates. Potassium (K) and Na are therefore quickly leached from the ash (Holmberg, Lind & Claesson, 2000; Ljung & Nordin, 1997; Rumpf, Ludwig & Mindrup, 2001; Steenari *et al*., 1998). Ash application increases the concentrations of exchangeable Ca and Mg in the soil (Arvidsson & Lundkvist, 2003; Bramryd & Fransman, 1995; Jacobson *et al*., 2004; Rumpf, Ludwig & Mindrup, 2001; Saarsalmi, Mälkönen & Piirainen, 2001). In a field experiment with loose ash did Bramryd & Fransman (1995) also find increased concentrations of exchangeable K in the mineral soil. Some studies have also reported enhanced concentration of P (Jacobson *et al*., 2004; Saarsalmi, Mälkonen & Kukkola, 2004) although it is in a species with a low solubility.

Effects of waste products on soil properties and processes

Metal accumulation

Many studies have been done on how wood ashes affect the forest ecosystem but little is known about the other waste-products. A possible negative effect of recirculation of wood ash is that, depending on the ash quality, it may lead to an increased total amount of heavy metals in the soil (Eriksson, 1998b; Rumpf, Ludwig & Mindrup, 2001). Elevated concentrations of Cd, Mn and Zn in the humus layer have been found 10 years after ash application (Saarsalmi, Mälkonen & Kukkola, 2004). This increase caused by the addition of metals with the ash is counteracted by the increase in pH which lowers the solubility of the heavy metals in the soil (Eriksson, 1998b; Rosén *et al*., 1993). With time, the liming effect of the ash may decline and if the pH decreases, the solubility of the metals increases (Steenari & Lindqvist, 1997).

pH & salt effect

Re-circulation of ash to the forest affects the soil chemistry in various ways and pH must be considered to be the most important factor. When the ash dissolves, it releases hydroxide and (bi)carbonate ions which effectively neutralizes H^+ and the pH might rise up to 13 close to the ash pellets and in the pores of the pellets (Steenari *et al*., 1998). In the humus layer, exchanges between the ash cations and cations attached to the soil particles, mainly H^+ and K^+, take place and leads to an increased pH and buffering capacity in the upper layers of the soil. Reportedly, the released H^+ and acidifying Al^{3+} can percolate with the water and contribute to a decreased pH in the soil solution deeper in the soil (Bramryd & Fransman, 1995; Eriksson & Rosén, 1994; Eriksson, 1998b). This effect is referred to as the salt effect.

Carbon & nitrogen

The biomass of the soil fauna, *e.g.* microorganisms, worms, collembolans and nematodes, in the soil are affected by changing pH (Bååth & Arnebrant, 1994; Jokinen, Kiikkila & Fritze, 2006; Persson *et al*., 1989) and thus by ash application.

One way of measuring the soil microbiological activity is to measure the soil respiration rate which is the production of CO_2 in the soil. A high respiration rate indicates that there is available dead organic material that is decomposed by the microorganisms releasing nutrients for the vegetation whereas a low respiration rate indicates that either (i) there is no available substrate to be decomposed or (ii) the microorganisms are negatively affected by some soil property. The soil respiration rate is stimulated by liming (Andersson, Nilsson & Saetre, 2000; Andersson, Valeur & Nilsson, 1994; Persson *et al.*, 1989) and ash treatments (Bååth & Arnebrant, 1994; Fritze *et al.*, 2000; Fritze, Kapanen & Vanhala, 1995; Jokinen, Kiikkila & Fritze, 2006; Zimmermann & Frey, 2002) due to the increase of pH in the humus layer. No effect on soil respiration after ash application has been reported from a nutrient-rich forest in Finland (Maljanen *et al.*, 2006) but a positive correlation between temperature and soil respiration was found. How long the liming or ash application increases the respiration rate is unknown. One column study (Persson *et al.*, 1989) showed a quick increase of CO_2 evolution already the first day after liming whereas in another study (Andersson, Nilsson & Saetre, 2000) the increase did not occur until day 63. In the latter study the increase remained throughout the study time (160 days). Maljanen *et al.* (2006) found in a field study that ash treatment increased the CO_2 production in mineral and peat soils in the long term (15-50 years) but not in the short term ($\leq$1 year). It has also been shown that the C:N ratio in the organic material is important for the outcome of the result (Persson *et al.*, 1989). The C:N ratio is an indicator of the nitrogen proportion in organic matter and a low C:N ratio indicates a potential supply of mineralised nitrogen that can be made available to the plants. The C:N ratio is usually between 25 and 50 in the O-horizon (mor-layer) of Swedish podsols whereas it is between 20-30 in the B-horizon due to a higher degree of humification of the organic matter (Eriksson, Nilsson & Simonsson, 2007). Liming gave a greater increase of the respiration in soils with higher C:N ratio (c. 44) than in soils with lower (c. 31) despite a lower pH for the first mentioned material (Persson *et al.*, 1989). This implies that carbon availability (higher C:N ratio) is of greater importance for the microbial activity than acidity.

The knowledge about how ash application affects the solubility of dissolved organic carbon (DOC) is scarce and inconsistent. However, it is known that an increased pH dissociates the H^+ from the organic substances which become more water soluble. In a catchment study, where a 20-ha watershed was treated with ash, the DOC in the runoff water was not affected (Parkman & Munthe, 1998). On the other hand, column studies with ash-treated mor-layers have shown increased levels of DOC in the percolated water (Eriksson, 1998b; Jokinen, Kiikkila & Fritze, 2006). The DOC is probably translocated to deeper horizons but it is still effectively retained in the soil, which not might be the case in the disturbed soils in column experiments. This can explain the different results of the studies. It has been shown that application of a mixture of ash and GLD to the forest might increase the solubility of DOC further. Greger *et al.* (1998) compared the leakage water from ash and ash mixed with GLD and found that the leachate from the treatments with GLD released more DOC than the ash treatment. The conductivity was higher in the GLD treatment, but the pH was the same in both treatments. They concluded that the differences were caused by higher levels of released SO_4^-, K^+

and Na^+ in the GLD treatment causing an ion exchange effect, which in turn led to greater release of humic acids and DOC.

The main purpose of adding ash to a mineral soil is to counteract long-term depletion and acidification of the soil after harvest, rather than to enhance the tree growth in the short term. Nitrogen is the growth limiting nutrient for the majority of Swedish forests (Binkley & Högberg, 1997) and addition of wood ash probably affects the availability of the inorganic N for the vegetation. Results from liming experiments show increased mineralization in soils with a C:N ratio below 30, whereas the mineralization decreases in soils with higher C:N (Nömmik, 1968; Persson & Andersson, 1988). Results of wood ash addition on N-limited soils have resulted in unchanged or reduced tree growth in up to 15 years in very poor sites (Jacobson, 2003; Saarsalmi, Mälkonen & Kukkola, 2004; Sikström, 1992). Ash application on N-rich soils and organic soils has increased the growth (Jacobson, 2003; Moilanen, Silfverberg & Hokkanen, 2002; Silfverberg & Issakainen, 1996). The ground vegetation is an important sink for NO_3^- after clear cut and decreases the losses of nitrogen from the forest site (Örlander, Egnell & Albrektson, 1996). Lundell *et al.* (2001) showed that NO_3^- leaching increased after wood ash application in N-rich soils without vegetation and active root uptake, whereas no effects were found in soils with vegetation and in N-poor soils. Further, liming and ash application on N-limited sites can cause a decreased mineralization and mobility of N leading to a decreased growth rate of trees (Örlander, Egnell & Albrektson, 1996; Persson & Whirén, 1996).

Aim

It is important to understand element flows between the forest ecosystem and forest industries to be able to minimize the environmental impact, to make the industry more effective and to treat the waste in the most appropriate way. In this thesis different aspects of the element flow from the standing trees, through the paper pulp-mill, to different waste-products are described. The properties of some of the recyclable inorganic waste-products (bio-fuel ash and green liquor dregs) is also studied with focus on different pre-treatments, weathering characteristics and how they affect the humus material when they are returned to the forest soil. The aim of this thesis is to evaluate the potential for a more efficient cycling of nutrients between the forest and the pulp-mill.

Specific objectives are to:

- Investigate whether the element concentrations in wood and bark vary with tree trunk diameter and to develop empirical functions for the relation between concentration and trunk diameter for those elements where a significant variation is found.
- Evaluate the possible recycling efficiency for different nutrients in the pulp-mill waste-products and the potential accumulation of heavy metals.
- Determine the release of element from biomass ash pellets in field conditions to evaluate the effects of heat treatment, in (i) a normal

combustion atmosphere and (ii) an atmosphere elevated in CO_2 to enhance carbonatisation and decrease the release rates of elements.

- Investigate how pellets of ash and bark-ash/green liquor dregs affect the chemical and biological processes in a mor-layer. Three treatments of the pellets were used in addition to loose ash: spontaneous stabilization, heat treatment in a 6% oxygen atmosphere and heat treatment in an atmosphere elevated in CO_2.

Materials & methods

This thesis consists of four separate studies. In Paper I, the element contents of Norway spruce and the element distribution of different compartments of the tree were studied. A mass balance study of the pulp-mill is made in Paper II where the entering sources and exiting sinks of many elements are investigated. Paper III describes a field experiment where the effects of heat treatment of ash on element leaching are studied. In Paper IV, the leaching from a mor-layer is studied after it is treated with different waste-products.

In all the studies wet digestion of different materials (wood, bark, branches, needles, ash, GLD, lime mud, RBD, pulp and biological sludge) were made. The collected samples were dried and well mixed before 0.5 ± 0.005 g (for ash 0.25 ± 0.005 g) of each sample was diluted in 1M HNO_3 and digested in an open-vessel sample preparation with an auto step temperature controller (Tecator, Höganäs, Sweden) in 135° C for 4 hours. Concentrations of the elements were determined with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Perkin Elmer Elan 2000). Al, As, B, Ba, Ca, Cd, Co, Cu, K, Mg, Mn, Mo, Na, Ni, P, Pb Sr, Ti, Zn, and Zr were analyzed with argon (Ar) gas whereas Cr, Fe and V were analyzed in DRC-mode with hydrogen gas to eliminate disturbance of Ar.

Element content in trees – Paper I

We used Norwegian spruce (*Picea abies* (L.) Karst.) and sampled trees from 9 stands in central and south of Sweden (Paper I, Table 1). This study was based on data from two earlier studies, one which investigated the content of chloride (Cl) in different tree compartments as an affect by sea-salt deposition (Munther, 2002) and one which investigated possible effects of soil moisture conditions on element composition in trees (Isberg, 2002). In the south of Sweden, 3 trees were sampled on each site and in central Sweden, 12 trees were chosen along a slope. All trees were of average size and age (40-83 years old) for the specific stand. The trees were felled and divided with a chain saw. Disc samples were taken from the trunks of each tree at 10%, 30%, 50%, 70% and 90% of the total tree height. Three living branches from different heights (low, middle and top) of the green crown were collected and treated as a bulk sample. The bark of the stem was separated from the wood and the needles from the branches. The discs, bark, branches and needles were ground before digestion. Regression analysis was carried out to find any correlations between the diameter of the trunk and the element concentrations. The element content in the branches and needles were also analyzed.

Mass balance of pulp mill – Paper II

We studied three sulphate pulp-mills located on the east coast of Sweden: one in the south, one in the middle and one in the north. Eight different fractions were sampled at every pulp-mill. From the input line, the wood chips (mainly Norway spruce) on its way into the boiler and the bark going into the energy plant were sampled. From the output line, pulp, biological sludge from the water purifying system, fly ash from the energy plant and GLD, lime mud and RBD from the recovery process of cooking chemicals were sampled. Element content in air emissions and in raw water and discharge water were taken or estimated from other sources (Paper II). Fractions were sampled at two occasions, one winter day and one summer day for each of the three investigated pulp-mills. On each sampling day each stream was sampled at three separate times and on each time, three sub-samples were taken. All samples were analyzed separately. Different streams were quantitatively estimated using plant statistics, reports to environmental authorities and frequent consultations of the staff at the respective plants. The recovery potential of different elements was also estimated.

Element leaching from bark ash in field – Paper III

We used fly ash from an energy plant in a sulphate pulp-mill in Sweden. The major part of the fuel consisted of bark from Norway spruce but some organic sludge from the biological water purification system and fibres washed out from rinsing of the paper pulp were also used. The fly ash was collected directly from the flue gas cleaning device with a glass beaker in which the ash was also stored until it had cooled down.

The ash was pelletitized and dried in +40°C. One set of pellets were heat treated in a CO_2-dominant atmosphere at +860°C to facilitate carbonatisation, and one set of granules were heated in a more normal combustion with 6% O_2 in +1000°C. The bench-scale, high temperature treatment furnace is thoroughly described by Sundqvist (1999). The following treatments were included:

1. Ash pellets (PA)
2. Ash pellets –heat treated in 6% O_2 (PAO)
3. Ash pellets –heat treated in 100% CO_2 (PACO)

The field site was located in Garpenberg in central Sweden (Paper III, Table 1). Carefully weighed amounts of pellets (±0.01g), c. 8 g bag^{-1} were sawn into nylon bags of the size 10*10 cm with a mesh size of 0.1*0.1 cm. Thereafter, the bags were placed directly in the mor-layer (F and H layer) in a randomised grid with 5 rows and 6 columns, resulting in 30 crosses where one bag of each treatment was placed. The bags were collected after different time intervals in the field and at each occasion 5 bags of every treatment were collected. The first bags were collected after 45 days in field and subsequently after 175, 210, 330, 700 and 1300 days (ca 1, 6, 7, 11, 24 and 43 months).

The content of the ash was analyzed before and after the time in the field as described above. The mineralogy and morphology of the pellets were analyzed before (0 PA, 0 PAO, 0 PACO), after 330 days in the field (330 PA, 330 PAO, 330 PACO) and after 1300 days (1300 PA, 1300 PAO, 1300 PACO) for identification of crystalline phases.

Effects of waste products on soil properties and processes – Paper IV

We used fly ash and GLD from the same pulp-mill as in the study described in Paper III. The GLD was collected directly from the filter drum and put in plastic bags and stored in room temperature until the pellets were made. The GLD contains some lime mud used on the filter drum to simplify the separation of the GLD from the green liquor. This lime mud is included in the analyses of GLD.

The different pellets were made in a small scale pellet press at the laboratory. The use of the press made it possible to produce a homogeneous pellet with a well defined size and form. Half of the pellets were then high temperature treated in 1000°C in normal atmosphere.

A column experiment was built up with a homogenized mor-layer material from a Norway spruce (*Picea abies* (L.) Karst.) stand close to Garpenberg in central Sweden. The mor-layer was placed above a layer of sand in columns with a drainpipe in the bottom connected to a tube where the leachate water could be drained (Figure 2). The following treatments were included:

1. Control (C)
2. Raw ash mixed in with the entire mor layer (LMA)
3. Raw ash in one layer (LA)
4. Ash pellets (PA)
5. Ash pellets – heat treated at 1000°C (PAH)
6. Ash and green liquor dregs pellets (PAG)
7. Ash and green liquor dregs pellets heat treated at 1000°C (PAGH)

The amount pellets added to each bucket corresponded to a dose of 3 Mg ha^{-1}. The loose ash (LA) and the pellets were applied just under the surface of the mor-layer to create contact between the pellet and the mor whereas LMA was mixed in with the entire mor-layer. To simulate the seasons, the columns were incubated in alternating temperatures; a 20°C period of three weeks followed by a -20°C period of about 1 week and the cycle was repeated 6 times. During the warm period the columns were irrigated daily with an amount that during the three weeks period represented an annual rainfall (c. 800 mm). The six temperature and irrigation periods mimicked six years in the field. The irrigation water chemistry was adjusted to have the similar pH and ionic strength to normal throughfall; pH = 4.5, ionic strength = 52 mM (16 mM H_2SO_4 and 4 mM NaCl).

Figure 2.

Figure 3.

After each irrigation, leachates were collected and analyzed for pH, DOC, NH_4^+, NO_3^- and 20 elements. The rate of change in element concentrations was highest during the first leaching periods. Within each period it was also highest at the beginning of the period. During the first two leaching periods a more intensive sampling was made and in the following four periods a less intensive sampling schedule was followed. To calculate complete mass balances concentrations in samples, non measured samples were interpolated through linear interpolation between the measured values. Carbon mineralization was measured in an open container containing 2 M KOH placed on top of the mor in which the CO_2 was trapped (Figure 3). The container was left to equilibrate for 12 hours in the closed column and the CO_2 was quantitatively dissolved in the KOH solution. Barium chloride (BaCl) was added and the CO_2 precipitated as $BaCO_3$ and could then be determined by titration HCl. The content of the mor and waste-products were analyzed before and after the experiment.

Mineralogy and surface properties of the pellets

The mineralogy of the pellets were analysed for identification of crystalline phases using powder X-ray diffraction (XRD). In the field study the analysis was made before (0 PA, 0 PAO, 0 PACO), after 330 days in the field (330 PA, 330 PAO, 330 PACO) and after 1300 days in the field (1300 PA, 1300 PAO, 1300 PACO) and in the laboratory study before (0 PA, 0 PAH, 0 PAG, 0 PAGH) and after the 6 irrigation periods (6 PA, 6 PAH, 0 PAG, 6 PAGH). A Bruker d8 Advance instrument in θ-θ mode was used with an optical configuration that involved primary Göbel mirror and Våntec PSP detector. Analyses of the diffraction patterns were performed using the PDF-2 databank. Identified minerals were semi-quantified by Rietveld refinements.

Morphology and element composition of the pellets were determined using an environmental scanning electron microscope (SEM) equipped with an energy dispersive spectroscopy detector (Philips XL-30). The pellets were mounted in epoxy, cut and polished with SiC-sand paper (dry) and the cross sections were then analyzed. For each pellet 13-spots analyzes were performed. An accelerating voltage of 20 kV was used during the analysis.

The specific surface area (BET surface area) of the samples was determined from nitrogen adsorption studies conducted at -196°C using Tristar 3000. Prior to adsorption measurements, the sample was degassed at 40°C overnight.

Statistics

We used the statistical program SAS (SAS Institute, 2004) to carry out all the statistical analyses in the thesis. Analyses of variance tests (ANOVA) were performed of the element content in all studies, except the mass balance study. In the by-product studies were also the Tukey´s Studentized Range tests used to detect significant differences between the treatment means. The significant level used was $p<0.05$. For further information, see Paper I, III and IV.

Results

Element content in trees – Paper I

The needles and branches had the highest concentrations of most elements, followed by bark and wood (Figure 4). Significant positive correlations between element concentrations in stem wood and stem diameter were found for Ba, Cd and Pb whereas significant negative correlations were found for Cu, Fe, K, Mg and P (Paper I, Figure 1). In bark, significant positive correlations between element concentrations in stem bark and stem diameter were found for Ba, Ca, Cd, Co, Mn, Sr and Zn whereas significant negative correlations were found for Cr, Cu, Fe, K Na, Ni and P (Paper I, Figure 2). The equations for variation in element concentrations with tree diameter are shown in Table 2 and 3. No correlations were found between bark thickness and element concentrations in the bark.

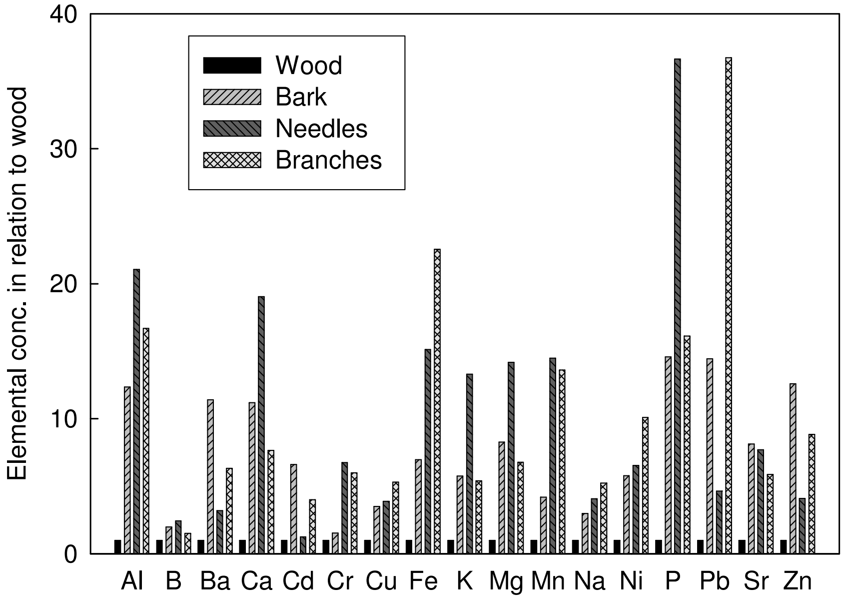

Figure 4. *Element content in different tree compartments of* Picea abies *in relation to content in stem wood. Stem wood is set to 1.*

Calculations of the element removal based on the functions with changing element concentrations with stem diameter were compared to calculations using the mean value for concentrations in stem and bark for the whole tree trunk. The calculations were done on the element content of the tree top only because the tops make the difference in stem part removal between whole-tree harvest and conventional harvest. The largest differences between the two methods of calculation were found for K and P which showed an increase with 30% and 51% respectively when using the changing element concentration with diameter, and for Ba and Pb which both showed a decrease of 29%. The estimated removal of Cd decreased by 24% whereas the estimated removal of Cu, Fe and Mg increased by 26%, 17% and 22% respectively.

Table 2: Variables for linear (A) and logarithmic (B) correlations between tree diameter (cm) and concentrations (mg kg^{-1}) of elements in spruce wood. Independent variable (x): diameter (cm). The equation used is: (A) y=a+bx and (B) y=exp(a+bx)

	Type of equation	Intercept (a)	Diameter (b)	n	R^2
Ba	A	6.77	0.163	180	0.894
Cd	A	0.0805	0.00128	180	0.726
K	A	577	-8.96	180	0.578
Cu	B	0.538	-0.0289	178	0.534
Fe	B	2.35	-0.0240	173	0.436
Mg	B	5.31	-0.0241	180	0.855
P	B	4.80	-0.101	171	0.664
Pb	B	-2.52	0.0432	176	0.564

Table 3: Variables for linear (A) and logarithmic (B) correlations between tree diameter (cm) and concentrations (mg kg^{-1}) of elements in spruce bark. Independent variable (x): diameter (cm). The equation used is (A) y=a+bx and (B) y=exp(a+bx)

	Type of equation	Intercept (a)	Diameter (b)	n	R^2
Ba	A	40.6	4.62	179	0.853
Ca	A	3880	222	179	0.785
Cd	A	0.263	0.0219	179	0.703
Co	A	0.233	0.00493	179	0.892
Cr	A	0.588	-0.00890	179	0.351
Cu	A	5.05	-0.0743	179	0.677
K	A	3480	-34.4	179	0.800
Mn	A	755	9.15	171	0.946
Sr	A	18.0	0.950	179	0.871
Fe	B	4.48	-0.0285	179	0.656
Na	B	5.21	-0.0397	177	0.881
Ni	B	1.40	-0.0228	179	0.816
P	B	6.85	-0.0242	179	0.795
Zn	B	4.76	0.0289	179	0.835

Mass balance of pulp mill – Paper II

Element composition of waste-products

The element composition of the different waste-products is found in Table 4. Bark-ash has, from a re-cycling perspective, the most complete nutrient composition with a balanced composition of Ca, K, Mg, Mn, P and Zn. GLD and lime mud contains somewhat lower amounts of all mentioned elements, except Mg which is in concentrations comparable with those in bark-ash. RBD contains mainly K and Na and the content of other nutrients is very low. The highest concentrations of Cd and Pb are found in the bark-ash and GLD, but some Cd is also found in the RBD and some Pb in the lime mud.

Mass balance budgets for nutrients

A summary of the results of the budget calculations for the paper-pulp production are presented in Table 5 and 6. Calcium (Ca) and Mg differ from most other elements by not having the incoming wood as the dominant source of input. For Ca the major input is added $CaCO_3$ and for Mg it is $MgSO_4$. The dominant output streams for Ca are GLD and lime mud, but c. 20% leaves with the discharge water. Most of the Mg exits the pulp-mill with the discharge water or the GLD. The estimated quantities of Ca leaving the pulp-mill agrees relatively well with the input. The output of Mg fluctuated widely between the pulp-mills with 20-180% of outgoing Mg compared to input. The one plant that has reported data on Mg concentrations in discharge water is the one showing the best balance between output and input.

For both K and P, the dominant input stream is the wood chips. Over 90% of the K and more than 70% of the P originate from the wood. The $CaCO_3$ used for renewing the lime contains some P. The output of K from the plant occurs predominantly through the RBD and the discharge water. Poor quality of K concentration data in discharge water negatively affects the input/output balance and the output lies between 67-148% of the input. For P, GLD is a major output stream and contained c. 40% of the incoming P. Bio-sludge contents of P varies considerably between the plants and was for one plant the dominant output for P. This plant also has a higher amount of P left in the paper-pulp due to unbleached pulp. The estimated quantities of P leaving the pulp-mill agrees relatively well with the input.

Table 4. Element composition of different solid waste-products produced in a sulphate pulp-mill. Averages from the three investigated pulp-mills. GLD = Green liquor dregs. RBD = Recovery boiler dust.

		Fly ash			GLD			Lime mud			RBD		
	Unit	Mean	±CI	n	Mean	±CI	n	Mean	±CI	n	Mean	±CI	n
Al	g kg^{-1}	62.2	22.4	27	5.25	1.58	47	0.595	0.06	46	0.02	0.002	56
As	mg kg^{-1}	7.56	2.8	29	0.31	0.06	48	0.16	0.044	31	0.9	0.14	62
B	mg kg^{-1}	341	63.1	29	634	7.88	35	<3					
Ba	mg kg^{-1}	2420	288	29	523	95.9	48	319	57.3	48	2.5	0.33	62
Ca	g kg^{-1}	262	34.7	29	253	28.1	43	347	16.6	48	0.083	0.02	62
Cd	mg kg^{-1}	23.5	3.27	29	9.36	2.09	48	1	0.36	43	4	0.66	62
Co	mg kg^{-1}	20	5.26	29	73.6	12.7	48	0.4	0.07	29	<0.2		62
Cr	mg kg^{-1}	86	13.6	29	118	19.6	48	11.7	1.55	48	<1.0		62
Cu	mg kg^{-1}	131	16.9	29	102	19.6	48	5.01	5.77	23	4	1.04	62
K	g kg^{-1}	65	12.6	29	3.07	0.92	48	0.61	0.25	45	51.6	6.13	62
Mg	g kg^{-1}	29.3	4.47	29	29.8	5.7	47	3.4	0.37	48	0.071	0.01	62
Mn	g kg^{-1}	16.7	3.58	29	11.6	2.33	48	0.18	0.04	48	0.063	0.009	62
Mo	mg kg^{-1}	13.8	2.49	29	1.74	0.62	37	1.13	0.47	16	5.3	0.74	62
Na	g kg^{-1}	47.4	21.6	29	35.4	10	48	6.79	0.34	48	299	21.5	62
Ni	mg kg^{-1}	82.8	11.6	29	83.7	12.1	48	5.06	0.69	48	1	0.15	62
P	g kg^{-1}	19.4	3.2	29	3.79	0.91	48	6.03	0.35	48	0.038	0.005	62
Pb	mg kg^{-1}	83.8	26.4	29	12.8	2.54	48	8.25	2.8	48	1.5	0.24	62
V	mg kg^{-1}	37.7	5.38	29	1.93	0.38	48	1.11	0.19	48			
Zn	g kg^{-1}	4.59	0.88	29	1.03	0.16	48	0.053	0.015	46	0.081	0.008	62

[*] One pulp-mill had considerable higher concentrations of Na in the fly ash resulting in a wide CI

[**] One pulp-mill had considerable higher concentrations of Al in the fly ash resulting in a wide CI

Zn and Cu are both heavy metals and micronutrients. Thus, their content in biomass is relatively high. The incoming wood dominates the input streams of both Cu and Zn but they are also present in the input lime and raw water. For Zn, GLD contained between 15-111% of input amounts. Both air emissions and discharge water also contain considerable amounts of Zn. For Cu, the discharge water and the GLD are the dominant output streams. Both Zn and Cu have higher outputs compared to inputs for all plants. This indicates that there are internal sources of these metals. It is likely that corrosion contributes to the concentration of these elements in the waste-products.

For Ni and Cr, wood chips are the dominant input stream. The lime contributes also to the input of Cr. The dominant output stream for both these metals is the

GLD. Between 20-30% of the Cr is lost through air emissions. The discharge water contains fair amounts of Ni but little Cr. The bio-sludge concentrations are very variable for Ni but are generally low for Cr. The output of Cr is generally higher than the input indicating internal sources. The Ni budget is more balanced. It should be noted that no data on air emissions of Ni were available.

The wood chips are the largest incoming source of Cd and Pb except for one plant where the amount of Pb in the lime is larger than the amount in the wood chips. The pulp-mill situated in the most southern part of Sweden has higher amounts of Cd and Pb in the incoming wood chips compared to the other plants. Discharge water is a significant output stream for both Cd and Pb whereas comparatively more Pb than Cd is lost through air emissions. The RBD contains more Cd than Pb. The bio-sludge is as with other elements a large source of variation in the budget. Between 2 and 75% of the incoming Cd and <1 to 49% of the incoming Pb is found in the bio-sludge. Although the budgets for both Cd and Pb show higher output than input, the differences are not so large and not consistently higher so that any conclusions about internal sources can be made.

Results of the recovery calculations for the energy plant showed no systematic increases or decreases between the input and output of Ca, Cu, K, P, and Zn (Table 7). The concentrations of Cd increased and Cr and Ni decreased in the ash compared to the incoming bark. The Pb content increased in one of the pulp-mills but decreased in the other two.

Table 5. Input-output budget of the pulp-mills for nutrients expressed as percentage of total input

	Ca			K			Mg			P		
	% of total input			% of total input			% of total input			% of total input		
Pulp-mill	A	B	C	A	B	C	A	B	C	A	B	C
Input												
Wood chips	32	28	18	93	96	94	7	51	19	88	83	74
Process chemicals	n.d	n.d	n.d	n.d	n.d	n.d	90	33	75	n.d	n.d	n.d
Lime	62	67	73	3	<1	2	1	5	3	11	16	25
Raw water[a]	6	6	9	4	4	4	2	11	2	<1	1	1
Total input	100	100	100	100	100	100	100	100	100	100	100	100
Output												
Paper-pulp	3	19	1	5	48	4	3	26	12	<1	28	6
GLD	84	88	43	5	1	7	12	40	52	54	32	36
RBD	<1	<1	<1	34	33	15	<1	<1	<1	<1	<1	<1
Lime mud	1	n.f.	44	<1	n.f	1	<1	n.f.	4	1	n.f	45
Lime grit	7	10	n.f	<1	<1	n.f	<1	1	n.f	3	6	n.f
Bio-sludge?	4	3	<1	1	2	<1	1	3	<1	95	23	1
Discharge water	11	25	25	22	64	78	5	109	55	5	6	6
Air emissions	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Total output	109	146	113	67	148	106	20	180	123	159	96	94

n.d – no data
GLD – green liquor dregs
RBD – recovery boiler dust
[a] All data from the Swedish Environmental Monitoring Program (Department of Environmental Assessment - Databank, 2007)

Table 6. Input-output budget for the pulp-mills for heavy metals expressed as percentage of total input

	Cd			Cr			Cu			Ni			Pb			Zn		
	% of total input			% of total input			% of total input			% of total input			% of total input			% of total input		
Pulp-mill	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C	A	B	C
Input																		
Wood chips	95	97	97	89	95	86	96	92	75	94	97	92	93	73	39	92	89	88
Process chemicals	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Lime	4	3	16	10	4	13	2	1	21	3	1	6	5	15	60	7	<1	10
Raw water[a]	1	<1	<1	1	2	1	2	7	4	3	1	3	1	12	1	1	11	2
Total input	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Output																		
Paper-pulp	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
GLD	54	118	36	144	89	105	87	76	85	98	38	77	30	67	25	111	15	20
RBD	10	11	3	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	2	<1	3	4	4
Lime mud	1	n.f	10	<1	n.f	8	<1	n.d	13	<1	n.f	4	<1	n.f	37	<1	n.d	7
Lime grit	<1	<1	n.f	1	1	n.f	<1	<1	n.d	<1	n.f	12	1	3	n.f	<1	<1	n.d
Bio-sludge	75	7	2	26	18	1	36	49	3	44	12	1	28	49	<1	7	9	1
Discharge water	18	25	37	3	2	2	10	113	101	10	16	53	18	24	12	52	53	61
Air emissions	8	10	12	45	39	34	2	2	1	n.d	n.d	n.d	21	70	32	71	80	76
Total output	167	171	100	219	150	149	135	240	203	156	61	98	111	215	107	245	161	169

[a] All data from the Swedish Environmental Monitoring Program (Department of Environmental Assessment - Databank, 2007)

Table 7. Quantities (mg of elements in input and output streams in the bark combustion in the 3 investigated pulp-mills

	Input Bark			Output Ash		
	A	B	C	A	B	C
Ca	784	694	802	749	958	905
Cd	0.04	0.04	0.05	0.10	0.07	0.07
Cr	1.0	0.45	1.5	0.19	0.33	0.33
Cu	0.38	0.38	0.38	0.42	0.52	0.38
K	169	139	223	117	309	216
Mg	63	62	76	127	75	96
Ni	0.50	3.3	4.8	0.30	0.24	0.29
P	43	38	52	88	46	64
Pb	0.40	0.14	0.48	0.18	0.53	0.13
Zn	11	8.1	14	8.3	22	15

Element leaching from ash pellets in field – Paper III.

In the studies presented in Paper III and IV bark-ash and GLD pellets were used. The properties and mineralogy of the bark-ash and GLD are affected by the pelletization and heat treatment. The heat treatment decreased the concentrations of Cd, Hg, Pb and Ti in relation to non-heated pellets. The Cd concentration was decreased to levels between 2-83% of the amount in the non-heated pellets and Hg decreased to levels below detection limit (<0.1 mg kg^{-1}). Pb decreased to 20-31% of the original amount and Ti to 35-82%. For all other elements, the heat treatment increased the concentrations in the pellets due to release of crystal bound water and oxidation of element carbon from the pellets. Elevated levels of Cr and Ni after the heat treatment of the pellets used in the field study indicated contamination from the furnace surface.

The mineralogy of the pellets is presented in Table 8 & 9. The non-heated pellets consist mainly of quartz (SiO_2), albite ($NaAlSi_3O_8$), microcline ($KAlSi_3O_8$) that originate from soil contamination of the fuel and calcite ($CaCO_3$), aphthitalite ($K_3Na(SO_4)_2$) and apatite ($Ca_5(PO_4)_3(OH)$) which are formed during combustion and spontaneous stabilisation processes in ash. Magnesium (Mg) is bound into periclase (MgO), but some Mg is probably also bound into brucite ($Mg(OH)_2$). Brucite is not completely crystallized and hence not totally detectable using XRD.

During the heat treatment, the pellets were sintered and the surface area of the pellets decreased markedly. The heat treatment in the oxygen atmosphere led to reduction of the original soil minerals to levels below 5% and is, hence, not visible in the XRD analyse. The calcite was re-formed to high temperature silicate minerals such as bredigite ($Ca_7Mg(SiO_4)_4$), merwinite ($Ca_3Mg(Si_2O_4)_2$), åkermanite ($Ca_2MgSi_2O_7$), wollastonite ($CaSiO_3$) and calcium silicate (Ca_2SiO_4). Calcium (Ca) from the calcite was also included in the formation of portlandite ($Ca(OH)_2$). Magnesium (Mg) in the ash was oxidized to periclase and this was particularly apparent in the pellets containing GLD. After the heating in the CO_2 atmosphere, some calcite still remained in the pellets but the high temperature minerals, wollastonite and calcium silicate, were also formed. Mg was oxidized to periclase in the same way as in the PAO pellets. Phosphorous (P) was found as apatite ($Ca_5(PO4)_3(OH)$) in all pellets.

Weight changes of the pellets

The weight of the non-heated pellets (PA) decreased with time in the field with 24% and the decrease took place mainly during the first 45 days (Figure 5). Initially, the heated pellets increased in weight and the increase was significant from the original weight for the pellets treated in the oxygen atmosphere. After about six months in the field the pellets heated in a CO_2 atmosphere started to decrease in weight whereas the increase lasted for 12 month for pellets heated in oxygen atmosphere.

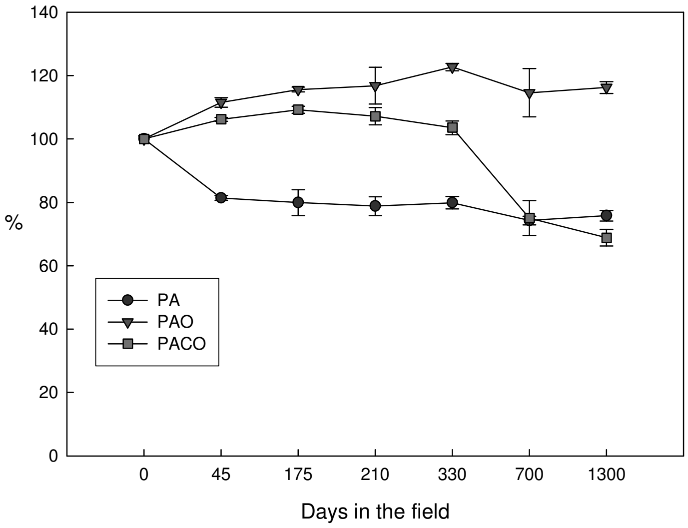

Figure 5. *Weight changes (%) of the pellets after different time in the field. Original weight is set to 100. PA = not heated ash pellets. PAO = ash pellets heated in an atmosphere with 6% oxygen. PACO = ash pellets heated in a* CO_2*-dominated atmosphere.*

Element losses

The content of Ca and P in the PA and PAO pellets decreased significantly compared to the original content and at the end of the field time 76% and 80% of Ca remained and 71% and 73% of P remained in the pellets from respective treatment (Paper III, Figure 3). A non-significant decrease to 92% for Ca and 87% for P was found from the PACO pellets. The K and Na content decreased significantly to levels below 50% of the original content already after the first 45 days in the field, independent of treatment. At the end of the field time the K contents decreased to 4.5% of the original amount in the PA pellets, 26% in the PAO pellets and 9.4% in the PACO pellets and the Na content decreased to 18%, 25% and 16% in respective treatment. No significant changes were found for Mg which declined to 78% of the original amount in the PA pellets, 81% in the PAO pellets and 71% in the PACO pellets after the field trial.

The content of Pb stayed intact until day 210 in the field, independent of treatment, and decreased thereafter to 69% of the original content in the PA pellets, 56% in PAO and 77% in PACO at the end of the experiment (Paper III, Figure 3). Significant losses of Sr were found for pellets of all treatments; 66%, 70% and 77% of the original content remained at the end of the experiment in PA, PAO and PACO respectively. The heat treatment resulted in Cd levels below detection limits in the heated pellets. The levels in the non-heated pellets stayed intact the first 210 days in the field. Then, a decrease took place to a new level at c. 80% of the original content, remaining constant throughout the field period. The content did not change significantly during the field period in any of the treatments for Al, As, Ba, Co, Cu, Fe, Mn, Ti and Zn.

Effects of waste-products on soil properties and processes – Paper IV

Carbon and nitrogen efflux

No treatment effects on carbon mineralization rates, measured as CO_2 evolution, could be detected. The loose ash treatments (LMA and LA) had the highest CO_2-respiration rate and the heated ash pellets (PAH) tended to have a lower CO_2 respiration rate throughout the measurement period but did not differ significantly from the control. The respiration rate varied between 2.36 and 23.1 $\mu g\ C\ g^{-1}\ h^{-1}$ and there was no trend over time.

Leaching of inorganic N (NO_3^- and NH_4^+) was highest at the initial stage of the experiment but fell rapidly to low levels. No significant treatment effects were observed, but PAGH leached more NH_4^+ than LMA from irrigation period 3 onwards. The concentrations of NO_3^- and NH_4^+ were during the first irrigation period 0.326 ± 0.0307 and 3.76 ± 0.215 mg L^{-1} respectively. Thereafter, the concentrations levelled out to in average 0.018 mg L^{-1} for NO_3^- and 1.5 mg L^{-1} for NH_4^+. The C:N ratio in the mor layer increased slightly during the experimental period from 26.6 to 28.9±1.05 and the control had a C:N ratio of 28.5 at the end of the experiment. No treatment effects were found.

Effects of pelleting on leachate

After an initial rapid decrease in pH during the first three leaching days, pH in the leachate water became similar to the pH of the irrigation water (pH=4.5) for all treatments except the treatment with loose ash mixed into the mor-layer (LMA) (Figure 6). The LMA treatment showed a significantly higher pH in the leachate from start throughout the whole experiment than the other treatments. With time, pH increased slowly in all treatments, including the control, and the differences between the treatments tended to increase. The pelletization significantly affected pH in the leachate water and pH remained low from all pelleted treatments, except for PAGH which increased and was similar the LA treatment from period 3 onwards (Figure 6, Period 6).

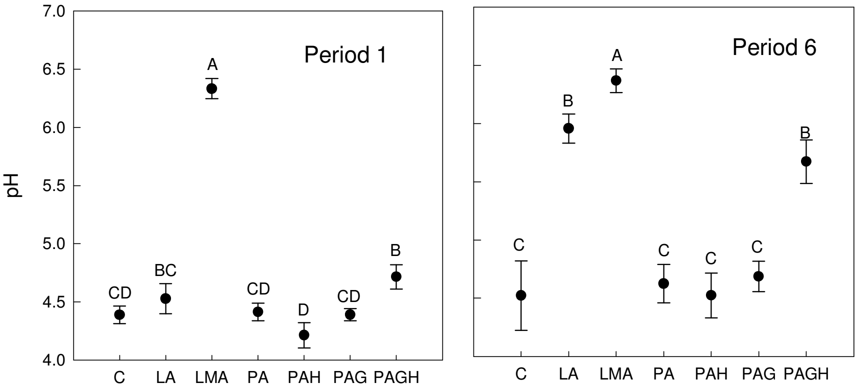

Figure 6. *pH in leachate water from all treatments, control (C), loose ash (LA), loose ash mixed into the mor (LMA), ash pellets (PA), heat treated ash pellets (PAH), ash and green liquor dregs pellets (PAG) and heat treated ash and green liquor dregs pellets (PAGH), from the 3 last days of the first and last irrigation period of the experiment. Plots indicated with the same letter do not differ significantly at p=0.05. Error bars show 95% confidence intervals.*

The pelletization strongly affected the leaching of many elements. At the end of the study, significantly higher amounts of As, Ca, Mg, P and Sr had leached from the columns with loose ash (LA, LMA) than from columns with pelleted ash (PA). In addition, LMA also leached more Ba than PA.

Effects of heat treatment on leachate

The heat treatment affected pH in the leachate differently depending on the composition of the pellets (Figure 6). The heating of pellets containing GLD (PAGH) resulted in a higher pH than in the non-heated (PAG), whereas heating of pure ash pellets (PAH) resulted in the lowest pH in the leachate from the first to the last irrigation period. Heated ash pelleted (PAH) leached smaller amounts of DOC and DON than non-heated ash pelleted (PA) and this difference was significant for DOC. This effect could only be seen the first irrigation period. The heat treatment did not affect the leachate rates of the elements to a great extent. Most affected was Cr with a significantly lower leaching from PAH than from PA and from PAGH compared to PAG. The opposite behaviour was found for Zn.

Effects of green liquor dregs on leachate

The two GLD treatments (PAG and PAGH) resulted in significantly higher leaching of DOC than the control and the heated pellets with GLD (PAGH) leached more DOC than the heated ash pellets (PAH). PAGH led also to a significant higher release of DON in the first irrigation period than control and PAH. Element leaching was not affected by the presence of GLD in the pellets, except for Ti which had higher leaching rates from heated GLD pellets (PAGH) than heated ash pellets (PAH) and for Zn where the opposite was found with lower leaching from the GLD pellets.

Table 8. Distribution between the minerals in the pellets of different treatments. PA = pelleted bark-ash. PAO = PA heat treated in 6% oxygen. PACO = PA heat treated in an CO_2-atmosphere. 0 = Distribution before the experiment, 330 = after 330 days in the field, 1300 = after 1300 days in the field

		Field study								
Mineral	Chem. formula	0	0	0	330	330	330	1300	1300	1300
		PA	PAO	PACO	PA	PAO	PACO	PA	PAO	PACO
Quartz	SiO_2	14		10	13		12	13	7	7
Albite	$NaAlSi_3O_8$	4		3	3		1	3	4	
Microline	$KAlSi_3O_8$	4			2		1	2	3	4
Calcite	$CaCO_3$	67		9	78	72	75	77	79	86
Portlandite	$Ca(OH)_2$		11							
Periclase	MgO		7	8						
Aphtitalite	$K_3Na(SO_4)_2$									
Apatite	$Ca_5(PO_4)_3(OH)$	4	17	8	4	4	11	5	7	3
Kalsilite	$KAlSiO_4$					6				
Bredigite	$Ca_7Mg(SiO_4)_4$		22							
Merwinite	$Ca_3Mg(Si_2O_4)_2$		43			18				
Åkermanite	$Ca_2MgSi_2O_7$	3								
Wollastonite	$CaSiO_3$	4		24						
Calcium silicate	Ca_2SiO_4			38						
		100	100	100	100	100	100	100	100	100

Table 9. Distribution between the minerals in the pellets of different treatments. PA = pelleted bark-ash. PAH = heat treated PA in 6% oxygen, PAG = pelleted mixture of green liquor dregs and bark-ash, PAGH = heat treated PAG in 6% oxygen. 0 = Distribution before the experiment. 6 = Distribution after 6 irrigation periods

		Column experiment							
Mineral	Chem. formula	0 PA	0 PAH	0 PAG	0 PAGH	6 PA	6 PAH	6 PAG	6 PAGH
Quartz	SiO_2	19		17		29		18	
Albite	$NaAlSi_3O_8$	3		7		4		3	
Microline	$KAlSi_3O_8$	4		3		5		4	
Calcite	$CaCO_3$	49		56	2	50	12	71	87
Portlandite	$Ca(OH)_2$	3	2	2	2		7		8
Periclase	MgO		5	3	25				
Aphtitalite	$K_3Na(SO_4)_2$	10	9	5	8				
Apatite	$Ca_5(PO_4)_3(OH)$	7	9	7	2	12	7	4	
Merwinite	$Ca_3Mg(Si_2O_4)_2$	5	24				15		
Åkermanite	$Ca_2MgSi_2O_7$		25				42		
Wollastonite	$CaSiO_3$		13				17		
Calcium silicate	Ca_2SiO_4		13		61				5
		100	100	100	100	100	100	100	100

Discussion

Element export from the forest

The removal of elements from the forest is increasing with increasing harvest rates. This affects the soil chemistry with a decreased pH and depletion of exchangeable base cations (Olsson, 1995). The discussion on the increased export of nutrients and potential re-cycling has to a large extent been focused on the fractions that are used as bio-fuel, i.e. branches, tops and needles, and re-cycling of the resulting ash since these fractions have higher concentrations of nutrients (Alriksson & Eriksson, 1998; Eriksson & Rosén, 1994; Helmisaari & Siltala, 1989; Ingerslev, 1999; Ingerslev & Hallbäcken, 1999) than the stemwood harvested as paper-pulp wood and timber. However, the fraction of nutrients that leaves the forest as paper-pulp wood is not neglible due to the large quantities processed. The total amount of wood fuel used for district heat production in Sweden constitutes less than one third of the amount of wood used for paper-pulp production (Bäcke, 2004). The paper-pulp is also processed in large-scale industrial plants where investments facilitating re-cycling might be more cost-effective than similar investments in small-scale biomass combustion plants.

The functions for variation in element concentrations with tree diameter were developed to improve calculations of element removal and partition into different products in connection to thinning and harvesting operations. If the concentration of elements is negatively correlated with diameter, like for P and Mg, the estimated removal of nutrients as a result of harvesting the upper part of the tree (pulp-wood and tops) will be higher than previously anticipated. On the other hand, if the concentration of an element is positively correlated with diameter, the removal will be lower like for e.g. Pb. Consequently, the effects of timber removal will be the opposite, e.g. an overestimation of the removal of P and Mg and an underestimation of the removal of Pb if the average concentrations used are based on representative sampling of the whole stem. The differences for elements with small concentration changes with diameter, e.g. Fe, are of less importance. The functions are based on diameter, not on tree height, due to the fact that the diameter is one of the parameters for quality classification of the stem. The diameter is also easy to measure, both on standing and already harvested trees, which makes the functions more user friendly. The removals of nutrients and other elements upon harvest are usually calculated on the basis of constant concentrations in wood and bark throughout the whole stem but my results shows that this gives misleading results for many elements, especially for K, Mg and P.

Among the macronutrients, all concentrations, except Ca, did increase significantly with decreasing diameter, which is in agreement with other studies (Almberg, 1999; Helmisaari & Siltala, 1989; Werkelin, 2002). Phosphorous (P), K and Mg are essential elements for cell and membrane production and enzyme activity, which makes it natural that higher concentrations of the nutrients are found in the most biological active parts of the trees such as tops, shoots and needles (Alriksson & Eriksson, 1998; Basham & Cowling, 1976; Eriksson &

Rosén, 1994; Ingerslev, 1999; Ingerslev & Hallbäcken, 1999). Ca shows no correlation between concentration and diameter in the wood but a decreasing trend with decreasing diameters in the bark. The same results are described by others (Helmisaari & Siltala, 1989; Werkelin, 2002) and horizontal studies of tree stems (Basham & Cowling, 1976; Momoshima & Bondietti, 1990; Nilsson, 2000; Prohaska *et al.*, 1998; Watmough, 1999; Watmough & Hutchinson, 1996) show a decrease of Ca from the pith of the stem out to the splint wood. This indicates a higher concentration of Ca in older tissues than in younger trees (Helmisaari & Siltala, 1989; Meerts, 2002). The role of Ca in the tree is primarily related to structural linkages, predominantly in the cell walls and the plasma membranes, which can be the reason for high amounts in older tissues (Cutter & Guyette, 1993).

The micronutrients Fe and Cu showed the same pattern in wood as the macronutrients and increased significantly with decreasing diameters. Cu and Fe are necessary for some enzyme activities, which can be the explanation for finding those elements in biologically more active parts of the tree. However, Basham and Cowling (1976) found that Cu and Fe had low concentrations in tree rings and did not show any trends from older to younger wood. The concentration of Zn in wood in this study did not vary with trunk diameter reported by others (Helmisaari & Siltala, 1989; Werkelin, 2002). Horizontal studies of the stem have found a decreasing trend of the Zn concentration from the pith towards the bark indicating that the tree can reallocate Zn (Basham & Cowling, 1976; Nilsson, 2000; Prohaska *et al.*, 1998). We found a decreasing trend in bark with diameter, contradictory to the results presented by Helmisaari and Siltala (1989) who found an increase and Werkelin (2002) who did not find any trend at all.

Although an element is non-essential for the tree, e.g. Cr, it can behave like a nutrient with increasing concentrations in the upper parts of the tree. This might depend on the greater amount of sapwood in the smaller diameters (Holmbom & Ekman, 1996). Sapwood contains more water including salts and sucrose while heartwood is more or less impregnated with organic compounds harts, oils and tannins. The chemical characteristics of those compounds bind different elements to the molecules and might therefore influence the concentration of the tree tissue.

Toxic elements such as Pb and Cd enter the tree with the water flow. The concentrations of those elements decrease towards the top of the tree indicating that the tree can store those toxic elements in biologically inactive or dead tissues such as heartwood and bark. It has been shown that the tree can reallocate Cd and Pb vertically in the stem to avoid harmful effects on the living tissue (Baes & Ragsdale, 1981; Brackhage *et al.*, 1996; Hagemeyer & Schafer, 1995).

There are few studies done on the distribution of elements vertically in spruce stems and more studies must be done at different locations, tree species and tree ages to get more reliable equations for the element distributions within a stand. Comparisons between a vertical study and a horizontal study (where tree rings have been studied) can be done to a certain degree but the relation between heartwood and sapwood must be well known since the treetop contains a higher proportion of sapwood than the lower part of the tree where the heartwood dominates. These differences in proportions can affect the element contents due to different sap pH, cell wall quality and concentration gradients within the cells between the two wood types (Welsh, 1995).

Element flow through the pulp mill

Making a mass balance of elements for a complex and large industry such as a paper-pulp plant presents many difficulties (Meister & Sixta, 1997). The production varies over time due to changes in the process e.g. changing of wood species, re-construction/repair of the plant, unplanned stops and other events that all contribute to uncertainty. Each plant is also unique, often specialized in a certain pulp quality, and has its own solutions for treatment and handling of waste-products, which sometimes makes comparisons between plants difficult (Gleadow *et al.*, 1996). Some data needed for a complete budget will also be unknown and have to be estimated, which increases uncertainty in the mass balance. Further, the contents of the by-products, *e.g.* tall oil and turpentine, are not included in this budget, which also contributes to the uncertainty of the mass balance. However, if we are aware of the uncertainties, the mass balance studies give us an insight in the efficiency in a potential nutrient recovery for different elements and whether it is associated with accumulation of eco-toxic elements in some waste-products.

The composition of the waste-products is influenced by process conditions, element composition of the wood, raw water quality, chemicals added in the process and contaminants from corrosion processes within the pulp-mill. Here the solid waste-products are evaluated from a recycling perspective looking at their content of different plant nutrients and contents of heavy metals. Looking at the chemical composition of the investigated waste-products, one can see that the bark-ash has the most complete composition of plant nutrients and metals. When compared to the recommended content of ashes intended to be re-circulated to the forest from the National Board of Forestry (2002), the mean properties of the ash falls within recommended values with one exception. The content of Ni is 82.8 mg kg^{-1} compared to the recommended limit of 70 mg kg^{-1}. The mass balance budget for the bark combustion showed a good correlation between input and output for Ca, Cu, K, Mg, P and Zn with small fluctuations between the pulp-mills. The analyses of element content are made on fly ash only, whereas the data of total amount produced ash per ton_{90}^{-1} is for mixed fly ash and bottom ash. The concentrations of most elements are higher in the fly ash than in the bottom ash, and the density of bottom ash is much higher than that of fly ash. This can result in overestimated amounts of the output data. Additionally, other fuels are often burnt together with bark, such as bio-sludge and fibres from the water purification, saw dust and waste wood from adjacent saw mills or used construction materials, and this input was not included in the calculations. This can be the explanation for the elevated contents of Cd and for Pb in pulp-mill B.

The elemental compositions of GLD and lime mud are not well balanced from a plant-nutrition perspective compared to the bark-ash, but they have a good liming potential. Due to the mixing with lime mud (mainly $CaCO_3$), the major element in

GLD is Ca. It has slightly higher levels of Mg compared to the bark-ash. If GLD is recycled Ca and Mg can be effectively recycled due to their high concentrations in GLD, which in turn is explained by the input of make-up chemicals. The large imbalances between input and output of Mg (20-180%) in the pulp-mill, is probably due to bad precision in the estimations of Mg lost in the effluent which we have had to estimate from data from other plants. This is indicated by the fact that the only plant that has data on Mg concentrations in discharge water shows the best balance between output and input. The GLD is low in K and P with contents well below the recommended minimum values (Swedish National Board of Forestry, 2002). A major part of K is lost through water and RBD and only a minor part (<10%) of the K coming into the plant with the wood is found in recyclable waste fractions. For P the recycling efficiency is 30-60% of the incoming P. GLD is low in most metals compared to the bark-ash except for Co, Cr and Ni which are higher. The content of Cr and Ni exceed the recommended values. Mixing of bark-ash with GLD and/or lime mud is a possible way to improve recycling efficiency and field experiments with mixed ash and GLD fractions has been tested (Österas, Sunnerdahl & Greger, 2005). If recommended application rates are followed, a mixed product could become suitable recycling product with an acceptable plant nutrient composition and lower metal concentrations compared to the fly ash.

The RBD from the soda boiler consists of easily soluble salts of which the dominant part is Na salts. RBD contains fair amounts of K but hardly any other important plant nutrient. The high solubility is negative from a recycling perspective since the nutrient may be easily leached before taken up by plants. The high content of soluble salts may also cause a ‘salt-effect’ in the soil releasing exchangeable acidity to the soil solution if it is recycled (Eriksson & Rosén, 1994; Eriksson, 1998b).

Recycling of waste-products to the forest

An ash product aimed for re-circulation to the forest has to be stabilised before application to reduce the reactivity of the ash, but the ash cannot be too stable because then the release of nutrient is too slow. The most optimal would be if the elements leach linearly from the ash during a period of 10-15 years to moderately affect the soil and give a long-lasting effect.

No significant treatment effect on carbon respiration rates was found in the study presented in Paper IV although the respiration from the mor-layer treated with heated ash pellets was the lowest through the whole measuring period. The respiration rates fluctuated widely from day to day.

The high concentrations of DOC, DON, NO_3^- and NH_4^+ in the leachate during the first irrigation period can be an effect of disturbance of the mor material when preparing and storing it before the experiment. A build-up of soluble C and N is the result of decomposition of organic material to carbohydrates and ammonium and this soluble pool is rapidly leached out (Andersson, Nilsson & Valeur, 1999) during the first irrigation period. None of the treatments investigated in Paper IV had any significant effects on N mineralization compared to control. After the first irrigation period, the N leaching was low and this, together with the observed low respiration rates, suggests that the mineralization rates were low. The fact that the C:N ratio remained virtually constant throughout the experiment in all treatments supports this observation. The N losses from a forest site are dependent on the N status of the soil before ash application (Ring, Jacobson & Nohrstedt, 2006). Persson *et al.* (1989) showed that N release from N-poor sites (C:N > 32) was not affected by liming, whereas liming increased the losses from humus in N-rich sites (C:N <28). The C:N ratio in this study lies on the borderline of N-rich and N-poor soils. The leaching of DOC and DON in the first irrigation period was significantly higher compared with control in the mor-layers treated with pellets containing GLD. This may be explained by the high content of SO_4^{2-} and Na^+ in the green liquor dregs causing an ion exchange effect in the mor, leading to an increased solubility of DOC (Greger *et al.*, 1998; Norman, Kurtz & Stevenson, 1987). The concentrations of Na^+ and SO_4^{2-} were not measured in the present study because these ions were added in the irrigation water. In summary, the results from my study with low leaching rates of C and N after the first irrigation period, and the stable C:N ratio, indicate that pelleted ash and GLD can be returned to forest soils (haplic podsol) without negative effects on C and N turnover. However, more studies need to be done, particularly on mor-layers with a considerably lower C:N ratio.

The pelletization and heat treatment of the pellets resulted in more stable species of most of the elements and, hence, smaller leachate rates. The significantly higher pH and higher concentration of Ca in the leachate from the loose ash treatments in the column experiment supports this. The absence of calcium oxide (CaO) and portlandite in the pelleted ash (not heated) indicates a successful carbonatisation process, in which CaO reacts with H_2O and CO_2 in several steps to calcite ($CaCO_3$) (Steenari & Lindqvist, 1997). Calcite has considerably lower solubility than CaO and, hence, initial harmful effects in the soil after ash application will be avoided (Ohlsson, 2000) and the liming effect will be extended over a longer period. The fact that almost no Ca is lost from the CO_2-treated pellets and that the calcite content increases considerably after 330 days in the soil environment, supports the assumption that the dissolved Ca from the high temperature minerals gradually form calcite. This small loss of Ca from pelleted ash (not heated) was also found by Nieminen *et al.* (2005) after a 5-year field study. The higher solubility of Ca in not heated and oxygen-heated pellets are similar to results from ash studies with self-hardened ash (Eriksson, 1998a; Larsson & Westling, 1998; Sundqvist, 1999) and originates from the content of portlandite and more soluble high temperature minerals than in the CO_2-treated pellets. When those minerals dissolve, some Ca reacts with CO_2 forming calcite, and some leaches out from the pellets giving the initial losses of Ca. The release rates decrease after 330 days in the field when calcite becomes the dominant species (Steenari *et al.*, 1998).

In this study, the losses of P during the field period are similar to results from ash studies with self-hardened ash (Holmberg, Lind & Claesson, 2000; Steenari *et al.*, 1998). No treatment effects were found on the leaching rates from the pellets in the field, but pelletization decreased the leaching of P from the mor-layer in the column experiment compared to the loose ash. Phosphorous (P) is present in the pellets as apatite, regardless of treatment, and has low solubility (Steenari *et al.*, 1998).

The quick release of K and Na the first month in the field and the first leaching period in the column experiment agrees well with other field studies (Alriksson & Eriksson, 1998; Nieminen, Piirainen & Moilanen, 2005; Steenari, Karlsson & Lindqvist, 1999) and laboratory studies (Eriksson, 1998b; Ljung & Nordin, 1997; Steenari *et al.*, 1998). Besides, in the feldspars, K and Na in ash are usually bound into different oxides and salts with SO_4^{2-} (Steenari & Lindqvist, 1997). The leaching of K and Na is not affected by hardening (Steenari & Lindqvist, 1997) or heat treatment, and no method have been found to prevent the high losses of K and Na. On the other hand, in this study the oxygen-treated pellets leached significantly less K and Na than the other treatments but I have not found any explanation for this in our mineralogical analyses. Nieminen *et al.* (2005) found that the solubility of K in peat ash is considerably lower than that from wood ash and a mixture of these ash types might give better leaching characteristics of K. Potassium (K) and Na in forest litter (leafs and needles) have similar release rates (Eriksson, 1998b; Palviainen *et al.*, 2004) as Na and K in ash materials which suggests that the fast leaching from the ash does not differ much from that of K and Na from forest litter.

The release rate of Mg in the field study is greater than that is reported from other studies who found almost no leaching of Mg from self-hardened or granulated wood ash after up to 5 years in the field (Holmberg, Lind & Claesson, 2000; Nieminen, Piirainen & Moilanen, 2005; Steenari *et al.*, 1998). In ash, Mg is present as periclase and magnesium silicates. Some Mg is probably also bound into brucite ($Mg(OH)_2$) but brucite is not totally crystallized and hence not totally detectable by XRD-diffraction. Periclase has relative high solubility and was completely dissolved after 330 days in the field. In the column experiment the leaching of Mg decreased significantly from the mor-layer treated with heated GLD pellets compared to mor-treated with non-heated GLD although the content of soluble periclase (MgO) is much higher in the heated pellets. The pH in the leachate from the mor-layer with heated GLD pellets is significantly higher than pH in the leachate from the other pelleted treatments. This could be explained by the dissolution of periclase leading to an increase of pH. The whole amount of Mg^{2+} released when periclase reacts with water is considered to be found as exchangeable ions due to the increased cation exchange capacity (CEC) (Greger *et al.*, 1998) which allows for increased retention in the mor-layer.

Apart from the macronutrients, only Pb showed significant changes in content after four years in the field. Initially, the leaching rates were slow from all treatments but they increased after approximately one year in the field. The high losses observed in this study correlate poorly with other field trials (Holmberg, Lind & Claesson, 2000; Steenari *et al.*, 1998). Heavy metals are seen as insoluble in the high pH that occurs in and around the ash particles (Larsson & Westling, 1998; Steenari *et al.*, 1998; Westling & Larsson, 2006). The oxygen-treated pellets lost most Pb compared to the original amount during the time in the field but the actual losses were the same from all treatments (c. 6 mg kg^{-1}) due to the lower original concentration in the heated pellets.

Conclusions

The aim of this thesis was to investigate the flow of elements between the forest and the paper pulp industry. The suitability of solid waste-products for recycling to the forest was studied with focus on element composition and the effect on soil properties and processes. Possible improvements of the recycling properties of the waste-products were also investigated.

Results from Paper I show that the concentrations of several elements in bark and stemwood have either positive or negative correlation with stem diameter, and it should be considered when export of different fractions of the stem is evaluated. The largest changes in concentration with changing diameter were found for K and P in wood, which increased with decreasing diameter and Ba and Pb, which decreased with decreasing diameter. The variation in concentration between individual trees was high for all the elements and the presented empirical relationships should therefore only be used when a larger population of trees is considered.

The outcome from the mass balance study of the pulp-mill (Paper II) is that the recovery potential of many elements is good from the energy cycle whereas the element recovery in solid wastes from the pulp-making process is more defective. Bark-ash has the most complete composition of plant nutrients and metals of the investigated waste-products. Green liquor dregs and lime mud contain less of most of the elements making them less suitable for re-circulation to the forest. On the other hand, they are rich in Ca and Mg and have a good liming effect in the soil. Mixing of bark-ash with green liquor dregs and/or lime mud is a way to improve recycling efficiency and if recommended application rates are followed, a mixed product could become a suitable recycling product with better nutrient composition than green liquor dregs and lower metal concentrations compared to the fly ash. However, green liquor dregs is a more reactive product than ash and mixing ash with green liquor dregs led to higher leaching rates of DOC and DON directly after ash application than the pure ash (Paper IV). Heat treatment of green liquor dregs pellets should be avoided due to formation of the reactive mineral periclase leading to an increased pH in the soil solution with a significant increase in pH and increased DOC leaching compared to ash pellets as a consequence (Paper IV).

Pelleting proved to be an effective stabilisation method, resulting in small effects on pH in the leachate and low leaching rates of most elements. Heat treatment resulted in a sintered structure of the pellets, with a smaller surface area affected by the soil solution (Paper III and IV). The mineralogy of the pellets changed, with changed leaching characteristics depending on the mixture of the waste-products. The heating of pure ash pellets in an atmosphere dominated by CO_2 resulted in the most stable pellet with no effect on pH and low leaching rates of the elements. Heating in a normal atmosphere also gave good characteristics of the pellets. The stabilisation and heat treatment did not decrease the rapid loss of K from the pellets, and further studies are needed to explore other methods to prevent these losses. Heat treatment decreased the content of Cd, Hg and Pb in the pellets compared with non-heated pellets, showing that the heat treatment is an effective way of cleansing contaminated ash of these heavy metals. The risk of causing high nutrient or carbon losses through increased pH and mineralisation is small when using pure ash pellets, even under disturbed conditions.

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