

**Associative properties of  $^{137}\text{Cs}$  in biofuel ashes.**

A. Ravila, E. Holm  
Department of Radiation Physics  
Lund University, Sweden

Slutrapport  
SSI P1021.97

## Associative properties of $^{137}\text{Cs}$ in biofuel ashes

Ravila, A., Holm, E.

Department of Radiation Physics, Lund University, Lund, Sweden.

### Abstract

The present study aims to reveal how radiocesium is associated to the ash particles derived from biofuel combustion. A sequential extraction procedure was carried out for the characterisation of radiocesium speciation in ash generated by different fuels and burner types. The ash types considered were fly ash and bottom ash collected from Swedish district heating plants using bark, wood or peat as fuel. A fraction of the radiocesium in biofuel ash can easily become solubilised and mobilised by water and also, a significant fraction of the radionuclides can be bound to the ash particles in cation-exchangeable forms. Therefore, at using the ash derived from biofuels to recycle mineral nutrients for forestry or short rotation coppicing, radiocesium solubilised and leached from the ash by rains has a potential to rather quickly enter the rooting zone of forest vegetation or energy crops. On the other hand, radiocesium strongly bound to the ash will migrate slowly into the soil column with the successive accumulation of litter and in the process act to maintain the external dose rate at an elevated level for a long time.

The results of the sequential extraction procedure and activity determination of the different extracted fractions implies that the bioavailable fraction of radiocesium in ash from bark, wood or peat is in the range between 20-85% of the total ash contents. Peat ash collected from a powder burner strongly retained a large fraction (70-90%) of its radiocesium content while the peat ash from a continuous fluidised bed type burner retained nearly 100% of the radiocesium in the bottom ash and only about 15% in the fly ash.

### Introduction

In order to counteract the negative effects on soil by the deposition of acidic air pollutants and to restore or improve the mineral nutrient balance in soils, particularly at whole-tree utilisation or intense short rotation coppicing, ash from biofuel burning can be returned to the forest or field. The trees or crop are at harvest containing large amounts of mineral nutrients valuable to sustain tree growth and vitality. At incineration for purposes of generating heat or electric power most of the nutrients are remaining in the ash and also, unwanted substances such as radiocesium and heavy metals will largely remain in the ash.

The incineration of biofuels results essentially in two types of ash: fly-ash and

At combustion in large scale incinerators volatilised Cs can condense on or be captured by ash particles as the temperature and available space for escape decreases at passing heat exchangers, smoke filters, cyclones or electrostatic precipitators before eventual release to the environment. The relatively larger surface area to weight ratio and faster cooling rate of smaller particles to that of larger particles favours the association of small particles and condensation of vapours to fly ash particles (Papastefano 1984, Jantunen 1988, Ravila 1994) and also, ash particles may become electrically charged by collisions and collect or repel oppositely charged particles or volatilised elements.

The resulting ash/fuel radiocesium concentration ratio is (in Sweden) for wood on average 40, ranging from 12 to 71 and about 14 for peat ash (Hedvall 1996). Manjón (1996) found a  $^{137}\text{Cs}$  enrichment factor of 108 resulting from burning the bark of eucalyptus trees and other woody wastes in a pulp mill power plant in S. Spain. Nilsson (1992) and Ravila (1992) found  $^{137}\text{Cs}$  enrichment factors of about 70 for bark burning in Sweden, while it was about 10 to 40 in a Norwegian bark burner (Krosshavn 1996). Due to the high temperatures during combustion the ash can melt, or usually partially melt, and in the process form alkali silicate glasses. Hallgren (1996) mentions that silica appears to easily form chemically bound silicates with alkali. Furthermore, after combustion and if the ash becomes wetted, hardening processes can occur whereas calcium silicate hydrates may form (NUTEK 1996:28).

Hardening of ash prior to further handling and distribution is desirable for purposes of avoiding dusting and controlling the release rate of nutrients and heavy metals from ash. Partial melting and a low carbon content in ash intended for the production of ash pellets are necessary characteristics for the ash particles ability to become solidified, i.e. agglomerate into a solid by means of the pozzolanic activity exhibited by melted or sintered ash particles upon hydration.

McCulloch et al (1984) studied the sorption of caesium by pyrogenic silica in cement and found that during calcium silicate hydrate formation, essentially all Cs sorbed to the reacting fraction of  $\text{SiO}_2$  was released to the solution. It is reasonable to believe that at ash hardening alkali silicate glasses or  $\text{SiO}_2$  can be consumed by  $\text{Ca(OH)}_2$  upon hydration of  $\text{CaO}$ , a major ash component, and in the process release radiocesium or convert vitrified alkaline compounds into water-soluble or exchangeable forms. In a study performed by NUTEK (1996:R28) it was concluded that about 25% of the potassium in an ash sample had become less soluble after hardening. An in situ study revealed that a solidified cement/wood ash mixture distributed in the form of small granulates in a coniferous forest in south-west Sweden lost on average 25-50% of its initial radiocesium content during a period of five years, i.e. a fractionate Cs leaching rate of 11-24%  $\text{a}^{-1}$ , while the potassium content in the granulates essentially remained unchanged (Ravila 1996).

In the light of the potential use of biofuel ash as a soil amendment it is important

to quantify the bioavailability of radiocesium in biofuel ash for the prediction of future activity concentrations in wood, energy crops and forest gifts. In this context it appears to be a worthwhile effort to depict the chemical association of radiocesium in the major ash types intended for recycling and use as fertilisers by using a sequential extraction technique.

#### Materials and methods

The sequential extraction procedure used in this study has been described by Andersson (1996) and Lujanienė (1997) and is essentially an extended and slightly modified extraction procedure based on the procedures used by Tessier (1979), Riise (1990), Hilton (1992), Oughton (1992, 1994) and described in an overview made by Van Loon (1992). The sequential extraction procedure was originally presented for the use in the analysis of sediment samples by Tessier in 1979 and later applied by Evans (1983), Holm (1987) and other authors and has also been used for soil samples (Cremers 1988, Riise 1990, Oughton 1992, 1994, Andersson 1994) and for airborne samples (Hilton 1992, Lujanienė 1997).

The basic idea of the sequential extraction methodology is to selectively remove metal species from the bulk of the sample by using progressively stronger extractants (Tessier 1979, Van Loon 1992). Reagent exhaustion and sample instability were commented and discussed in letters by Tessier (1988) and Kheboian (1988) as a response to the article by Kheboian and Bauer (1987). The reagent concentrations in this study have been essentially adopted from those used by Lujanienė (1997) with some small modifications. Since the ash samples in this study are different in both chemical composition and origin (burner type and fuel), no attempt was made to optimise neither shaking/heating times nor reagent concentrations. Instead, the extractability and possibility of reagent exhaustion were checked by repeating the extraction using fresh reagents.

The biofuel derived ashes cannot be considered as stable compounds and the addition of water to ash and exposure to air immediately changes the chemical form of many of the ash constituents and many salts, compounds and minerals are wholly or partially dissolved and other may result from chemical reactions after some time, e.g. different oxides, hydrates, carbonates, phosphates, sulphates such as CaO, Ca(OH)<sub>2</sub>, CaCO<sub>3</sub>, CaSO<sub>4</sub> and Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> to mention a few (NUTEK 1996:R28). In addition, some of the products will form after a long time in comparison with the extraction time. The changes in the ash composition of different compounds imposed by water addition will of course also happen upon distribution of ash to the forest or field environment due to exposure to air, air-humidity, irrigation and rains.

The liquid-solid ratios for the extracting agent and sample used by other workers are in the range 8-20 ml per g Tessier (1979), Evans (1983), Holm (1987), Riise (1990) and Andersson (1994). The extracting agent to dry ash weight was in this study set to 5:1 in the first four extracting steps (water soluble and ion-exchangeable species) and thereafter set to 10:1. The liquid

phases were separated from the solid phase by centrifugation once or twice at 1400 g for 10 min. The supernates were passed through a glass fibre filter (Whatman GF/A 0.7 - 1  $\mu\text{m}$ ). The filter was rinsed with the actual extracting agent and water and, when necessary, back-washed with water to transfer solids to the solid phase.

In brief the sequential procedure in this study consisted of the following steps:

| Fraction | Treatment   |
|----------|---|
| F1:      | Water, demineralised, water soluble species, 2 h shaking at 20 °C.  |
| F2:      | 1 M $\text{MgCl}_2$ , Non-specifically surface bound Cs, 2 h shaking at 20 °C.  |
| F3:      | 1 M $\text{NH}_4\text{Cl}$ , Specifically bound Cs, 2 h shaking at 20 °C.   |
| F4:      | 1 M $\text{NH}_4\text{Ac}$ , Displaceable Cs, 4 h shaking at 20 °C.   |
| F5:      | 0.04 M $\text{NH}_2\text{OH.HCl}$ in 25% $\text{HAc}$ , Cs bound to easily reducible (Fe, Mn) -oxyhydroxides, 6 h shaking at 20 °C.   |
| F6:      | $\text{H}_2\text{O}_2$ , 30% at pH = 2 (with $\text{HNO}_3$ ), organically bound species. The fierce reaction imposed by this extractant was allowed to calm down overnight before intermittent stirring at 90- 100 °C on hot plate for 4 h or until bubbles no longer evolved on addition of fresh $\text{H}_2\text{O}_2$ . In order to prevent absorption of released Cs 2 x 10 ml of 6 M $\text{NH}_4\text{Ac}$ was added 2 h prior to respectively just before recovery of the supernate by centrifugation. |
| F7:      | 8 M $\text{HNO}_3$ , acid soluble fraction. 4 h intermittent stirring at 80 - 100 °C on hot plate. 2 x 10 ml of 6 M $\text{NH}_4\text{Ac}$ was added half an hour prior to respectively just before recovery of the supernate by centrifugation.  |
| F8:      | The residual fraction was washed twice with 8M $\text{HNO}_3$ and 10 ml of 6 M $\text{NH}_4\text{Ac}$ , the washing solution was separated by centrifugation and combined with the acid leachable fraction (F7).  |

The extractants were transferred to 180 ml polyethylene tubs prior to activity determination using HPGe or Ge(Li) radiation detectors calibrated against standard activity solutions or untreated ash samples. The glassfibre filters were washed repeatedly using small portions of the fresh extracting agent and water in each step. Small portions of water was used for transferring back solids captured by the glassfibre filter to the solid phase of each extraction step. In the cases of visually detectable but from the glassfibre filter unseparable matter, usually in or after the fourth extraction step, the entire filter with its contents

was dried, ground and combined with the residual fraction. This procedure would to some degree exaggerate the radiocesium association to the residual fraction.

### Results

The radiocesium speciation in peat ash generated in a powder burner and peat bottom ash from the CFB type burner is distinguishably different from the radiocesium speciation properties of ashes of wood, bark and peat. Radiocesium in these peat ash types exhibits a low association to water-soluble and exchangeable forms (0-10%) and a strong affinity to the insoluble fraction (70-100%).

Radiocesium speciation in bark and wood ash is more complex: water-soluble forms: 35-55% in fly ash from bark burning and < 20% in other ash types of wood and bark; cation-exchangeable: 20-55 %; displaceable: < 20%; bound to reducible metal oxides: < 10%; organically bound: 5-30%; acid soluble: 5-30%; insoluble: < 10% of the radiocesium was left in the bark fly ash residues and 15-25% remained in the bottom ash from bark burning. The corresponding residual fractions in wood ash were 7-25% respectively 10-35%.

The total recovery of radiocesium, estimated from the summed activity in the different fractions by comparison with the untreated ash sample, was in the range 70- 80%. The figures 1, 2, 3 and 4 presents the radiocesium extractability from ash generated by combustion of wood or bark in grate fired burners. Figure 5 and 6 shows the radiocesium extractability from peat ash generated by two different burner types, powder burner respectively a CFB-type burner.

Figure 1, 2, 3, and figure 4, shows that a large fraction of the radiocesium is in the bioavailable fractions (here defined as the water-soluble and cation-exchangeable fractions). Figure 5 and figure 6 shows for comparison the different characteristics of radiocesium extractability from peat ashes generated by a powder burner (figure 5) respectively a continuous fluidised bed (CFB) burner (figure 6). The radiocesium in ash from the powder burner is largely in the insoluble and biologically unavailable fraction while the fly ash from the CFB-burner has the characteristics more similar to the ashes from wood and bark burning. The bottom ash from the CFB-burner has similar characteristics to the bottom ash from the powder burner. Table 2 shows the results from the sequential extraction procedure together with the estimated errors.

### Discussion

This study is to some degree biased to the presentation of rather homogenous and generally well behaving ash types regarding the use of the sequential extraction technique and the handling of samples. Some of the available bottom ashes from bark burners contains large fractions of unburned matter, sand, stones and slag were excluded from this study because it was too difficult to separate these samples into liquid and solid fractions without imposing large uncertainties. Anyhow, the excluded ash types are not subjected for recycling as

the rather high carbon content and low bioavailable nutrient content makes them less suitable for use as soil amendments.

Inevitably, and besides the presumed sample instability, the interpretation of the result of the sequential extraction procedure used is suffering from some losses of radiocesium during the recovery of the supernates formed in each extraction step and the residue. In order to check for reagent exhaustion and the completeness of radiocesium recovery by the extractants in each fraction, a second extraction was performed using the same but fresh extractant again. This second extraction showed that the first extraction contained more than 80 % of the combined radiocesium activity in the two extracts. This check was however not performed on the peat ashes, which in the case of the Uppsala powder burner ash clearly could have lead to reagent exhaustion due to its high iron content (10% of ash weight). Anyhow, the low contents of radiocesium in the two fractions (organically bound and acid leachable) following the fifth step (reducible metals) did not indicate any major effect from reagent exhaustion.

It was not established to which degree the radiocesium fraction in the second extract was a result of liquid retention by the pore volume of the ash or imposed by particle attrition or designed extraction mechanism, i.e. ion-exchange, reduction of oxides or dissolution or attack on the organically bound or mineral bound radiocesium. The total recovery of radiocesium, estimated from the summed activity in the different fractions by comparison with the untreated ash sample, was in the range 70- 80%. The losses (20-30%) are assumed to have an even distribution over the individual fractions as no single step in the extraction procedure could be accounted for the lion's share of the total loss. The losses are assumed to occur by sorption to the walls of the (glass or polyethylene) vessels and the glassfibre filters.

The results from the sequential extraction procedure must be cautiously interpreted as the radiocesium extracted into each fraction is to a significant part a result of the extraction method per se. However, it is quite clear that the observed behaviour of the different ashes when subjected to the sequential extraction method is reflecting true differences in radiocesium association to the ashes and that the reproducibility is good ( $\pm 20\%$ ). Our interpretation of the obtained results is that the ashes exhibit different characteristics in terms of association to the different extracted fractions as a result of the physical environments during combustion and ash collection and partly dependent on different chemical compositions of the fuels, combustion gas-products and resulting ashes.

The observed differences in the association of radiocesium to wood ash (figure 1 and figure 2) can not directly be attributed to differences in the fuel or ash metal content but possibly by the influence of the amount of unburned matter in ash which was accordingly to measurements by Holmroos (1991) comparable in the bottom ashes from the two burners (7-60% unburned) and the generally much higher fraction unburned in the fly ash from the Knivsta wood burner (42-78% unburned) than that from the Tranås wood burner (24-50%). This

would be consistent with the lower water solubility and higher organically bound radiocesium fraction of the Knivsta ash and that the ash from the Knivsta wood burner is a result of a rather low combustion temperature. Furthermore, the radiocesium concentration in fly ash samples from the Knivsta burner were usually lower than they were in bottom ashes.

The  $\text{NH}_4\text{Cl}$  step was omitted from the extraction scheme for the Skärblacka bark ash analysis, instead a new step with 6 M acetic acid (reflecting the carbonate bound fraction of radiocesium in ash) was included after the ammonium acetate extraction step partly because the authors temporarily ran out of the reagent ( $\text{NH}_4\text{Cl}$ ). The grate fired bark burner ashes from Karskär (figure 3) and Skärblacka (figure 4) shows very similar characteristics as reflected by the sequential extraction method. The water soluble and cation-exchangeable fractions are rather large which implies a high bioavailability of radiocesium from bark ashes. Lack of metal analysis data for the bark ash and fuel from the Skärblacka bark burner excludes a discussion of the influence of a presumed difference in fuel and ash composition due to the bark from different tree species used as fuel.

In contrast to the chemical composition of wood and bark ashes peat ashes generally contain little unburned matter and contain sometimes relatively large amounts of iron and silica (Holmroos 1991). Iron oxides may have acted as a catalyst for the alkali metal association to silica particles (Hallgren 1996) which could partly explain the characteristics of the rather iron-rich and strongly radiocesium retaining peat ash from the powder burner when subjected to the extraction method. The iron-poorer ash from the CFB-burner where sand, known to exhibit little sorption potential for Cs (McCulloch 1984), is used as fuel carrier/bed material is strongly retaining the entire fraction of radiocesium associated with the bottom ash while the radiocesium in fly ash exhibits an extractability more similar to that of wood and bark fly ash. The radiocesium in bottom ash from the CFB-burner is strongly bound but the fly ash to bottom ash partition ratio for radiocesium is 17 which is the highest partition ratio recorded for the ashes from 15 studied biofueled burners in an earlier study (Ravila 1992) implying that the major fraction of radiocesium is associated with the fly ash. The radiocesium partition (fly ash to bottom ash activity concentration ratio) may also change with time as the fuel/bed carrier material (sand) is recycled. Thus, the bottom ash from the CFB-burner has radiocesium retaining characteristics similar to the bottom ash from the powder burner and the radiocesium in the CFB fly ash exhibits a much greater extractability into the water soluble and ion-exchangeable fractions than that of the fly ash from the powder burner.

According to Oughton (1994) the fraction of radionuclides that can be extracted into 1 M  $\text{NH}_4\text{Ac}$  reflects the bioavailable fraction in both soil and vegetation. Depending on the actual ash characteristics, its ability to harden and the actual mixture with different binding agents, e.g. cement or lime sludge, the transfer of radiocesium from ash products to soil and vegetation will be extended over some period in time and hence, the radiocesium bioavailability from ash can



probably not be reflected by a given extracted fraction. It appears though that the bioavailable fraction of radiocesium in ash before hardening processes occurs can be reflected by the combined water-soluble and cation-exchangeable fraction.

In addition for radioecological assessments, it must be born in mind that there is also a possibility of remobilisation of the ubiquitous radiocesium inventory in soil through ion-exchange reactions induced by the salts leached from ash (Ravila 1996, NUTEK 1996:50). Other effects on the radiocesium distribution of liming or ash applications to forest soils can also be expected, such as changes in the biomass of earthworms (Schimmack 1997), fungi and bacteria (Jönsson 1994). Therefore, liming of forest soils can have an influence on the transfer of nutrients (and possibly radiocesium) between ectomycorrhizal fungi and tree roots (Read 1997, Simard et al 1997).

Liming forest soils with dolomite ( $4000 \text{ kg ha}^{-1}$ ) has been shown to decrease the migration rate of the radiocesium already present in soil (Schimmack et al 1997). The authors determined that the residence half-time had increased by a factor of about 3 in the Of2 and Oh soil layer. Liming can thus act to retard the decrease of the external dose rate in the forest by decreasing the migration rate of radiocesium in soil.

The abatement of the potential risk associated with the large bioavailable radiocesium fraction in ashes of wood and bark could involve mixing of ash with clays, radiocesium specific sorbents or radiocesium leaching with water or by ion-exchange. The potential radiological hazards from the use of biofuel derived ashes arises primarily from ingestion of forest gifts which constitutes a direct pathway to man and from external exposure in the forest and field or at the industries at the handling of ash. In the long term perspective and in the event of ingestion or inhalation of ash particles the carbonate and oxide bound fraction and even the acid leachable fraction may be important to consider for radioecological assessments in farming, forestry and industry and perhaps also for household wood burning for cooking and heating purposes.

### Conclusions

A large part of the radiocesium inventory in biofuel ashes from grate fired wood and bark burners can be regarded as having a high bioavailability upon distribution in forest or field environs. The bioavailable radiocesium fraction might naturally be of most concern at using the ash as a fertiliser but the retention of radiocesium in ash is also an important parameter to consider for estimating the external radiation in the forest or field. The sequential extraction technique used in this study of the associative properties of radiocesium to biofuel derived ashes clearly indicated some important characteristics of ash that may need to be considered for radioecological assessments or radioecological models aiming to determine or predict the flux of radiocesium in ecosystems subjected to fertilisation with biofuel derived ash.

### Acknowledgement

This study received financial support from the Swedish Radiation Protection Institute, and the European Community, contract F14P-Ct95-0021,

## References

- Amiro, B. D., Sheppard, S. C., Johnston, F. L., Evenden, W. G., Harris, D. R. (1996) Burning radionuclide question: What happens to iodine, cesium and chlorine in biomass fires ? *The Science of the Total Environment* 187, pp. 93-103.
- Andersson, K. G., Roed, J. (1994) The behaviour of Chernobyl  $^{137}\text{Cs}$ ,  $^{134}\text{Cs}$  and  $^{106}\text{Ru}$  in undisturbed soil: Implications for external radiation. *J. Environ. Radioactivity*, Vol. 22, pp. 183- 196.
- Cremers, A., Elsen, A., De Preter, P., Maes, A. (1988) Quantitative analysis of radiocesium retention in soils. *Nature*, Vol. 335, pp. 247-249, 15 September 1988.
- Evans, D. W., Alberts, J. J., Clark, R. A. (1983) Reversible ion-exchange fixation of cesium-137 leading to mobilisation from reservoir sediments. *Geochimica et Cosmochima Acta*. Vol. 47, pp. 1041-1049.
- Hallgren, A. (1996) Theoretical and engineering aspects of the gasification of biomass. Dissertation thesis, May 1996. Lund university, CODEN: ISRN LUTKD+I/TKKT--96/1037--SE.
- Hedvall, R., Erlandsson, B. and Mattsson, S. (1996) Cs-137 in fuels and ash products from biofuel power plants in Sweden. *J. Environ. Radioactivity*, Vol. 31, No. 1, pp. 103-117.
- Hilton, J., Cambray, R. S., Green, N. (1992) Chemical fractionation of radioactive caesium in airborne particles containing bomb fallout, Chernobyl fallout and atmospheric material from the Sellafield site. *J. Environ. Radioactivity*, 15, pp. 103-111.
- Holm, E., Gastaud, J., Oregioni, B., (1987) Chemical partitioning of plutonium and americium in sediments from the Thule region (Greenland). In proceedings: Radionuclides: A tool for oceanography. Eds. Guary, J.C., Guegueniat, P. and Pentreath, R.J. Elsevier Applied Science, London and New York.
- Holmroos, S., (1991) Karakterisering av vedaska, International report (in Swedish), VU-E93:64 . Vattenfall Utveckling, Vasteras, Sweden.
- Horril, A. D., Kennedy, V. H., Paterson, I. S., McGowan, G. M. (1995) The effect of heather burning on the transfer of radiocesium to smoke and the solubility of radiocesium associated with different types of heather ash. *J. Environ. Radioactivity*, Vol. 29 No. 1, pp.1-10.
- Jantunen, M.J., Reponen, A., Mustonen, R., Itkonen, A., Kauranen, P. (1988) Behaviour of the Chernobyl fallout radionuclides in peat combustion. In

proceedings: Fifth Nordic seminar on radioecology, 22-25 August 1988, Rättvik.

Jantunen, M.J., Reponen, A., Mustonen, R., Itkonen, A., Kauranen, P. (1992) Behaviour of the Chernobyl fallout radionuclides in peat combustion. Health Physics, Vol.62 No.3, pp. 245 - 249.

Jönsson, C. (1994) Modelling acidification and nutrient supply in forest soil. Licentiate Thesis, Reports in ecology and environmental engineering 1994:1. ISSN 1104-2877. ISRN LUTKDH/TKKT-3003-SE.

Lujanienė, G., Ogorodnikov, B. I., Budyka, A. K., Skitovich, V. I., Lujanas, V. (1997) An investigation of changes in radionuclide carrier properties. J. Environ. Radioactivity, Vol. 35, No. 1, pp. 71-90.

Kheboian, C., Bauer, F. (1987) Accuracy of selective extraction procedures for metal speciation in model aquatic sediments. Analytical Chemistry Vol. 59, pp. 1417-1423.

Kheboian, C., Bauer, C.F. (1988) Response to comments. Analytical Chemistry, Vol. 60, p.1477.

Krosshavn, M., Engh, L., Lien, H.N. and Salbu, B. (1995) Transfer, pathways, enrichment and discharge of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  in the pulp industry., In Fluxes and Technological Enhancement of Radionuclides In and Around Large-Scale Non-Nuclear Industries., Proceedings, Khoen Kaen, Thailand., 1995.

Krosshavn, M., Skipperud, L., Lien, H.N. and Salbu, B. (1997) Transfer, pathways, enrichment and discharge of  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  in the pulp industry. Health Physics, Vol. 71, No. 3, pp. 326 - 344.

Manjón, G., Vaca, F., García-León, M. (1996) Artificial long-lived radionuclides ( $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ) in an alkaline pulp mill in the south of Spain. Appl. Radiat. Isot. Vol. 47, No. 9/10, pp.1097-1102.

McCulloch, C. E., Crawford, R. W., Angus, M. J., Glasser, F. P., Rahman, A. A. (1984) Sorption of radiocesium by active silica. Health Physics. Vol. 46, No. 5 (May), pp. 1095-1100.

Nilsson, P. (1992) Cesium i en sulfatmassa fabrik. 1992:186e. Examensarbete, Inst. För Samhällsbyggnadsteknik Avd. För restproduktteknik. Tekniska högskolan i Luleå. ISSN 0349-6023 (In Swedish).

NUTEK (1996) Biobränsleaskors innehåll och härdningsegenskaper, Ramprogram för askåterföring. R 1996:28. Report to NUTEK (In Swedish).

NUTEK (1996) Härdade vedaskors upplösning i skogsjord, Ramprogram för askåterföring. R 1996:50 Report to NUTEK (In Swedish).

Oughton, D. B., Salbu, B., Riise, G., Lien, H., Ostby, G., Noren, A. (1992) Radionuclide mobility and bioavailability in Norwegian and Soviet soils. *Analyst*, March 1992, Vol. 117, pp. 481-486.

Oughton, D. B., Salbu, B. (1994) Influence of physico-chemical forms on transfer. In: *Studies in environmental science 62, Nordic Radioecology, The transfer of radionuclides through Nordic ecosystems to man*. Ed. H. Dahlgaard. Elsevier Science B.V. Amsterdam 1994, pp. 165-184.

Papastefano, C., Charalambous, S. (1984) On the escaping radioactivity from coal power plants (CPP). *Health Physics* Vol. 46, No. 2 (February), pp. 293-302.

Ravila, A. and Holm, E. (1992) Flux and concentration processes of radioactive elements in the forest industry; Dosimetry, Biofueled Heating Plants, The alkaline and the acidic pulp mill processes. Report SSI P 663.92

Ravila, A., Holm, E., (1994) Radioactive elements in the forest industry. *The Science of the Total Environment*, 157, pp.339-356.

Ravila, A., Holm, E., (1996) Assessment of the radiation field in a wood-ash-treated coniferous forest in south-west Sweden., *J. Environ. Radioactivity*, Vol. 32, Nos. 1-2, pp. 135-156.

Ravila, A., Hjerpe, T. and Holm, E.(1996) Shielding factors for gamma radiation in the forest environment. In: *Proceedings of International Symposium on Ionising radiation: "Protection of the natural environment"*, Stockholm, May 20-24.

Read, D. (1997) The ties that bind. News and views, *Nature* Vol. 388, 7 August, pp. 517 -518.

Riise, G., Bjornstadt, H. E., Lien, H. N., Oughton, D. B., Salbu, B. (1990) A study on radionuclide association with soil components using a sequential extraction procedure. *Journal of Radioanalytical and Nuclear Chemistry, Articles*, Vol. 142, No. 2, pp. 531-538.

Schimmack, W., Bunzl, K., Kreutzer, K. (1997) A long-term field study on the effect of acid irrigation and compensatory liming on the transport of Chernobyl-derived radiocesium in a forest soil. *The Science of the Total Environment*, 198, pp. 271 - 285.

Simard, S. W., Perry, D. A., Jones, M. D., Myrold, D. D., Durall, D. M., Molina R. (1997) Net transfer of carbon between ectomycorrhizal tree species in the field. *Nature* Vol. 388, 7 August, pp. 579 -582.

SNV (1992) Atmospheric emissions of sulphur and nitrogen oxides from the

Nordic chemical pulp industry. Swedish Environmental Protection Board (Statens Naturvårdsverk SNV) Report 4008.

Tessier, A., Campbell, P. G. C., Bisson, M. (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*, Vol. 51, No. 7, pp. 844-851.

Tessier, A., Campbell, P. G. C., (1988) Comments on the testing of the accuracy of an extraction procedure for determining the partitioning of trace metals in sediments. *Analytical Chemistry*, Vol. 60, pp. 1475-1476.

Van Loon, J.C., Barefoot, R.R. (1992) Overview of analytical methods for elemental speciation. *Analyst*, March 1992, Vol. 117, pp. 563-570.

Table 1, The major chemical elements in % of ash dry weight resulting from burning of bark, wood and peat. H, C, N and O are in the table bulked together as volatiles. The quoted errors refer to 1 SD. Compiled from original data by Holmroos in 1991, (Report VU-E93:64, table 3).

| Chemical element | Wood ash, Knivsta |        | Wood ash, Tranås |         | Peat ash, Uppsala |        | Peat ash, Nässjö |        | Bark ash, Karskär |        |
|------------------|-------------------|--------|------------------|---------|-------------------|--------|------------------|--------|-------------------|--------|
|                  | fly               | bottom | fly              | bottom  | fly               | bottom | fly              | bottom | fly               | bottom |
| Ca               | 6,7               | 13     | 10,86            | 11,66   | 14,6              | 8,84   | 7,8              | 5,4    | 24                | 11     |
| Si               | 4,9               | 8,7    | 11,66            | 5,78    | 15,6              | 23,2   | 27               | 38     | 3,4               | 23     |
| Al               | 0,9               | 1,9    | 0,55             | 1,038   | 2,28              | 3,62   | 4,6              | 2,8    | 1,3               | 4,4    |
| Fe               | 0,5               | 1      | 0,432            | 0,536   | 9,46              | 10,48  | 1,5              | 0,51   | 1                 | 2,9    |
| K                | 2,6               | 4,6    | 5,48             | 4,1     | 0,398             | 0,976  | 1,7              | 1,6    | 5,8               | 3,4    |
| Mn               | 0,3               | 0,5    | 1,1275           | 0,9375  | 0,1975            | 0,435  | 0,68             | 1,1    | 1,4               | 0,79   |
| Mg               | 0,7               | 1,6    | 1,168            | 1,232   | 4,9               | 1,538  | 2,2              | 5,4    | 2,3               | 1,6    |
| S                | 0,13              | 0,22   | 1,94             | 0,198   | 0,894             | 0,192  | 1,8              | 0,93   | 2,2               | 1      |
| P                | 0,4               | 0,8    | 0,912            | 0,878   | 0,572             | 0,48   | 0,57             | 0,16   | 0,89              | 0,56   |
| Na               | 0,3               | 0,6    | 0,568            | 0,758   | 0,194             | 0,46   | 0,1              | 0,82   | 0,6               | 1,5    |
| Volatiles        | 82,57             | 67,08  | 65,3025          | 72,8825 | 50,9045           | 49,779 | 52,05            | 43,28  | 57                | 52,5   |

Table 2, Extracted activity fractions from biofuel derived ashes. Fly ash and bottom ash results are presented the in upper respectively in the lower section with errors where 1 S.D. represents one standard deviation from the mean in counting statistics , n.e. should be read not extracted and b.d.l. as below detection limit.

| Extractant       | Karskär bark fly ash |        | Knivsta wood fly ash |        | Tranås wood fly ash |        | Uppsala peat fly ash |        | Örebro peat fly ash |        | Nässjö peat fly ash |        |
|------------------|----------------------|--------|----------------------|--------|---------------------|--------|----------------------|--------|---------------------|--------|---------------------|--------|
|                  | Fraction             | 1 S.D. | Fraction             | 1 S.D. | Fraction            | 1 S.D. | Fraction             | 1 S.D. | Fraction            | 1 S.D. | Fraction            | 1 S.D. |
| H2O              | 0.542                | 0.112  | 0.043                | 0.005  | 0.393               | 0.057  | b.d.l.               | b.d.l. | 0.064               | 0.008  | 0.163               | 0.036  |
| 1M MgCl2         | 0.190                | 0.039  | 0.129                | 0.016  | 0.209               | 0.030  | 0.027                | 0.011  | n.e.                | n.e.   | n.e.                | n.e.   |
| 1M NH4Cl         | 0.114                | 0.023  | 0.276                | 0.033  | 0.195               | 0.028  | 0.072                | 0.031  | n.e.                | n.e.   | n.e.                | n.e.   |
| 1M NH4Ac         | 0.006                | 0.001  | 0.139                | 0.017  | 0.038               | 0.006  | 0.030                | 0.013  | 0.186               | 0.024  | 0.412               | 0.124  |
| NH2OH.HCl/25%HAc | 0.037                | 0.008  | 0.054                | 0.007  | 0.028               | 0.004  | 0.021                | 0.009  | 0.107               | 0.014  | 0.113               | 0.034  |
| 30% H2O2 pH=2    | 0.031                | 0.006  | 0.093                | 0.011  | 0.034               | 0.005  | 0.008                | 0.003  | 0.023               | 0.003  | 0.019               | 0.006  |
| 8M HNO3          | 0.029                | 0.006  | 0.044                | 0.005  | 0.013               | 0.002  | 0.114                | 0.048  | n.e.                | n.e.   | 0.155               | 0.034  |
| RESIDUE          | 0.052                | 0.011  | 0.221                | 0.027  | 0.090               | 0.013  | 0.727                | 0.308  | 0.621               | 0.079  | 0.137               | 0.030  |

| Extractant       | Karskär bottom ash |        | Knivsta bottom ash |        | Tranås bottom ash |        | Uppsala bottom ash |        | Örebro bottom ash |        | Nässjö peat fly ash |        |
|------------------|--------------------|--------|--------------------|--------|-------------------|--------|--------------------|--------|-------------------|--------|---------------------|--------|
|                  | Fraction           | 1 S.D. | Fraction           | 1 S.D. | Fraction          | 1 S.D. | Fraction           | 1 S.D. | Fraction          | 1 S.D. | Fraction            | 1 S.D. |
| H2O              | 0.175              | 0.045  | 0.077              | 0.007  | 0.219             | 0.046  | b.d.l.             | b.d.l. | b.d.l.            | b.d.l. | b.d.l.              | b.d.l. |
| 1M MgCl2         | 0.075              | 0.019  | 0.072              | 0.007  | 0.214             | 0.045  | b.d.l.             | b.d.l. | n.e.              | n.e.   | n.e.                | n.e.   |
| 1M NH4Cl         | 0.130              | 0.034  | 0.089              | 0.008  | 0.248             | 0.052  | b.d.l.             | b.d.l. | n.e.              | n.e.   | n.e.                | n.e.   |
| 1M NH4Ac         | 0.031              | 0.008  | 0.042              | 0.004  | 0.076             | 0.016  | b.d.l.             | b.d.l. | b.d.l.            | b.d.l. | b.d.l.              | b.d.l. |
| NH2OH.HCl/25%HAc | 0.040              | 0.010  | 0.047              | 0.004  | 0.035             | 0.007  | b.d.l.             | b.d.l. | b.d.l.            | b.d.l. | b.d.l.              | b.d.l. |
| 30% H2O2 pH=2    | 0.073              | 0.019  | 0.132              | 0.012  | 0.070             | 0.015  | b.d.l.             | b.d.l. | b.d.l.            | b.d.l. | b.d.l.              | b.d.l. |
| 8M HNO3          | 0.295              | 0.076  | 0.174              | 0.016  | 0.032             | 0.007  | 0.079              | 0.011  | 0.170             | 0.017  | b.d.l.              | b.d.l. |
| RESIDUE          | 0.181              | 0.047  | 0.367              | 0.034  | 0.106             | 0.022  | 0.921              | 0.123  | 0.830             | 0.082  | 1.000               | 0.085  |



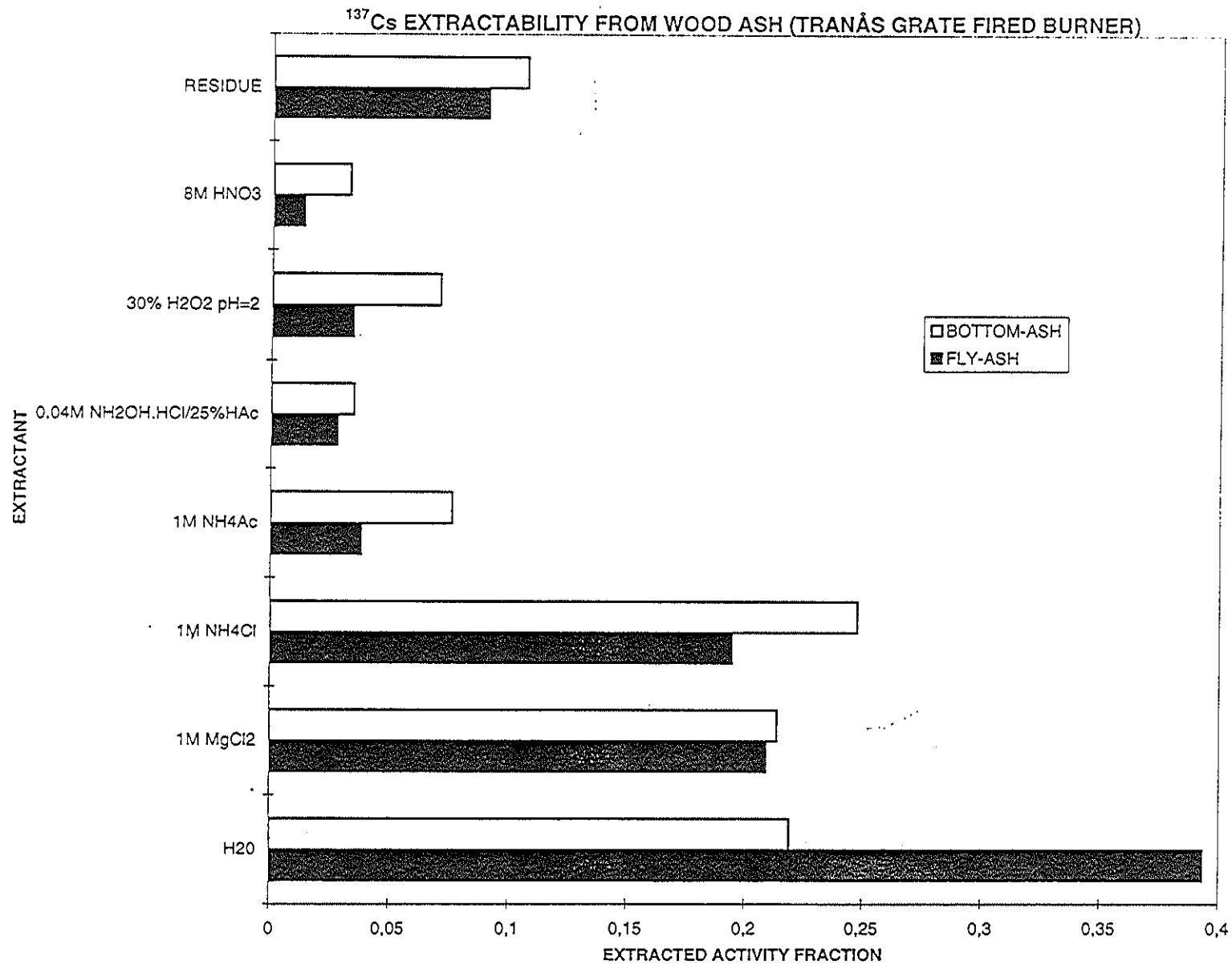


Figure 1, Radiocesium extractability from wood ash (fly-ash and bottom-ash) by sequential extraction. Ash from Tranás grate fired burner.

<sup>137</sup>Cs EXTRACTABILITY FROM WOOD ASH (KNIVSTA GRATE FIRED BURNER)

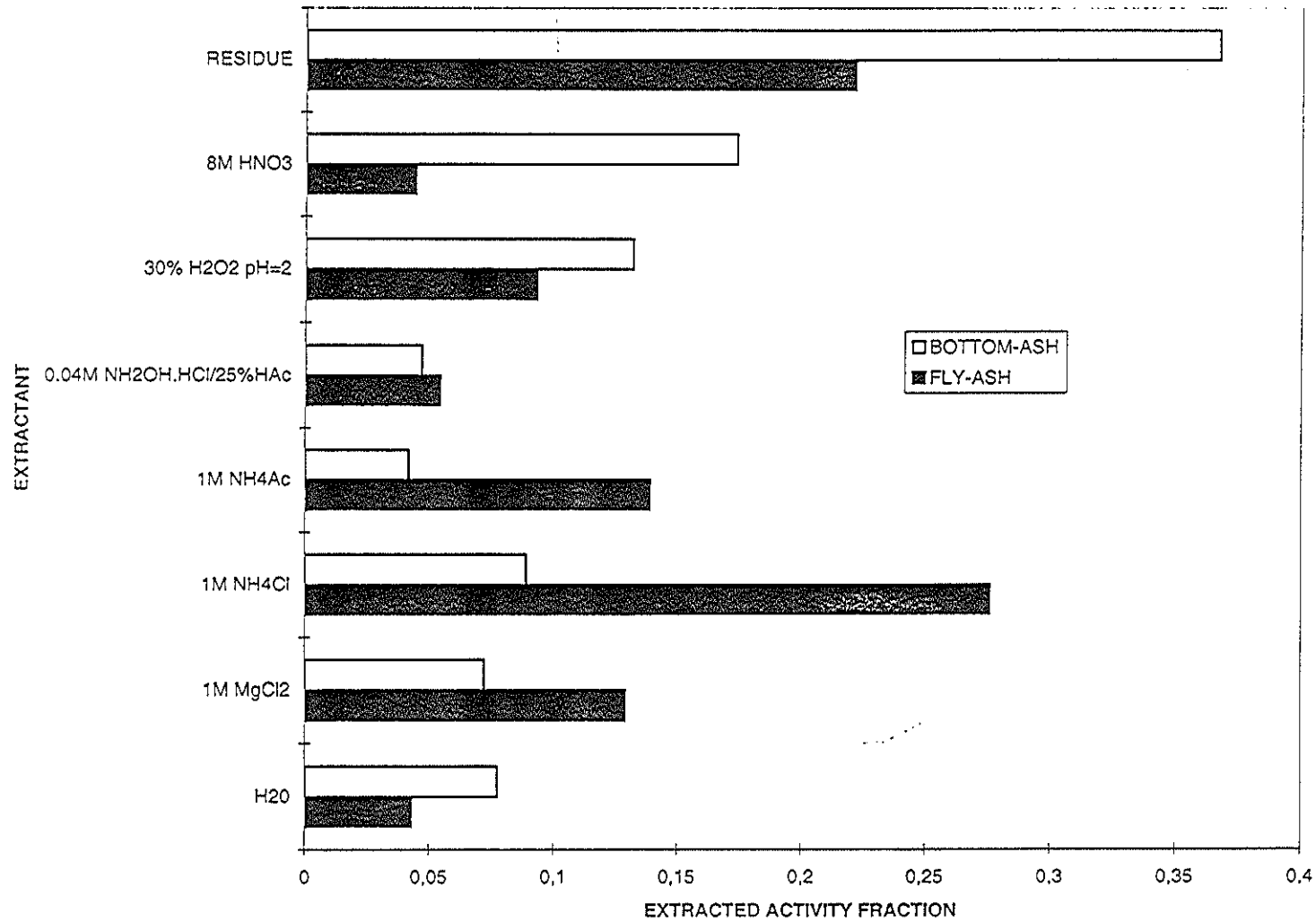


Figure 2, Radiocesium extractability from wood ash (fly-ash and bottom-ash) by sequential extraction. Ash from Knivsta grate fired burner.

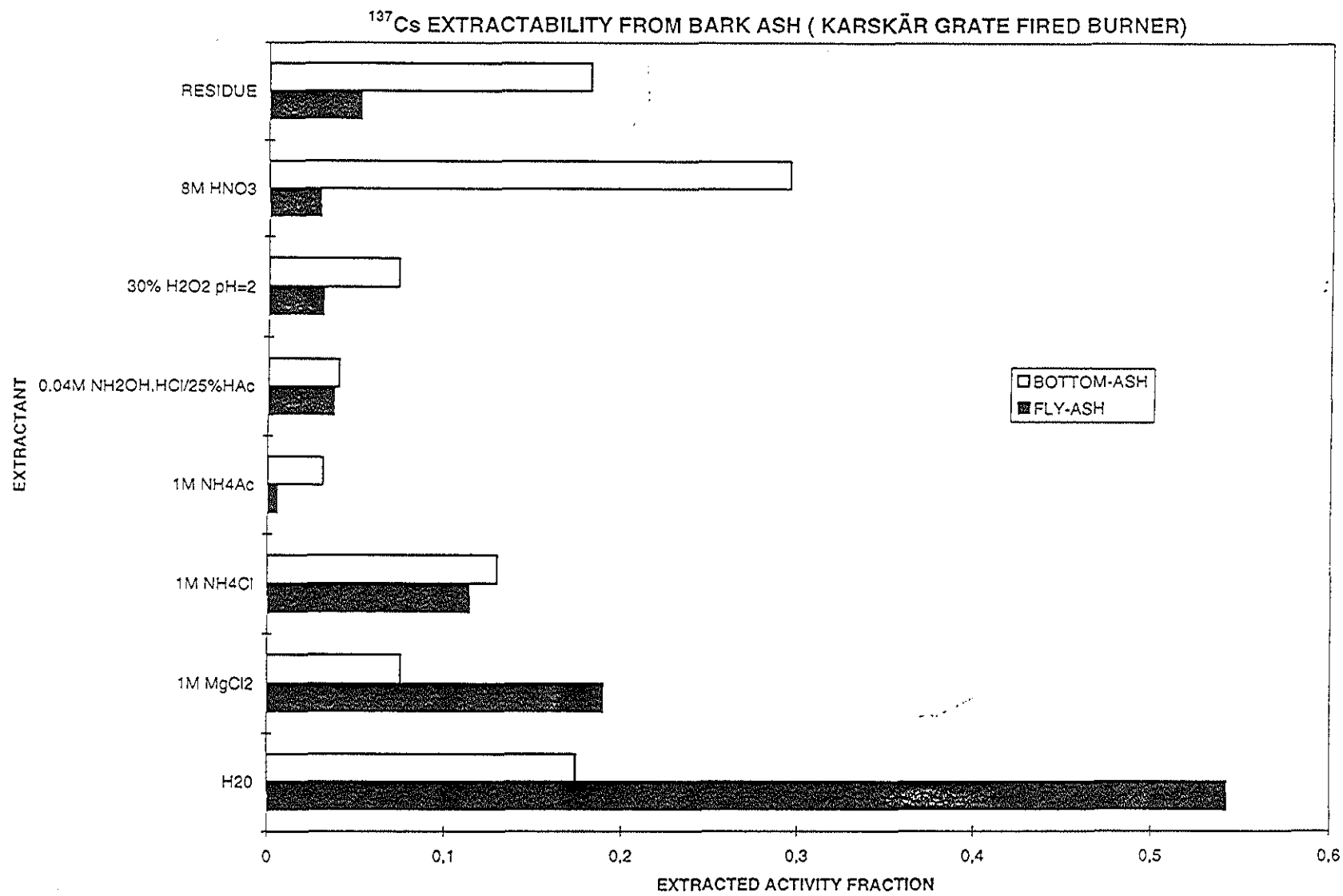


Figure 3. Radiocesium extractability from bark ash (fly-ash and bottom-ash) by sequential extraction. Ash from Karskär grate fired burner.

<sup>137</sup>Cs EXTRACTABILITY FROM BARK ASH (SKÄRBLACKA GRATE FIRED BURNER)

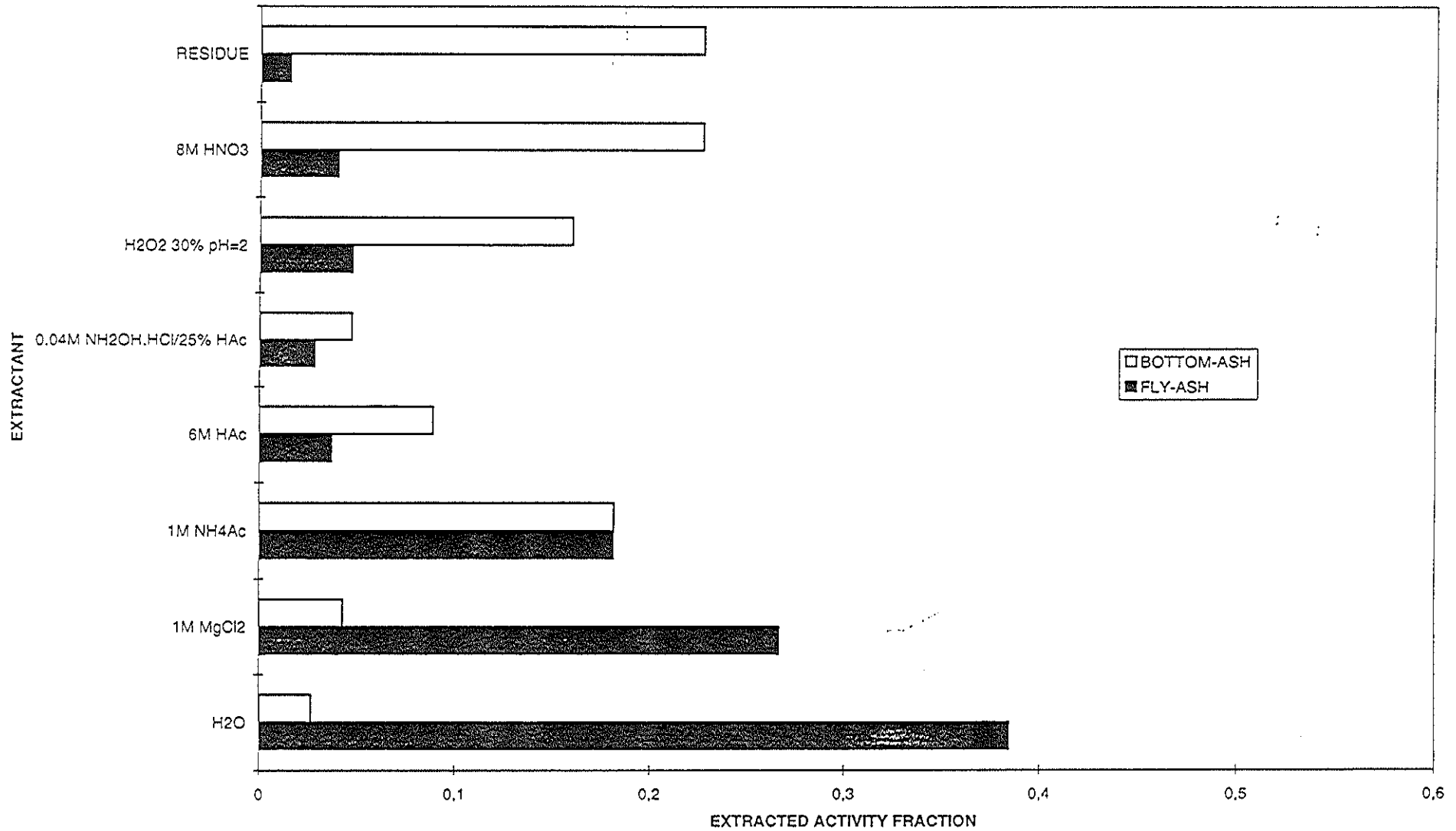


Figure 4, Radiocesium extractability from bark ash (fly -ash and bottom-ash) by sequential extraction. Ash from Skärblacka grate fired burner.

<sup>137</sup>Cs EXTRACTABILITY FROM PEAT ASH (UPPSALA POWDER BURNER)

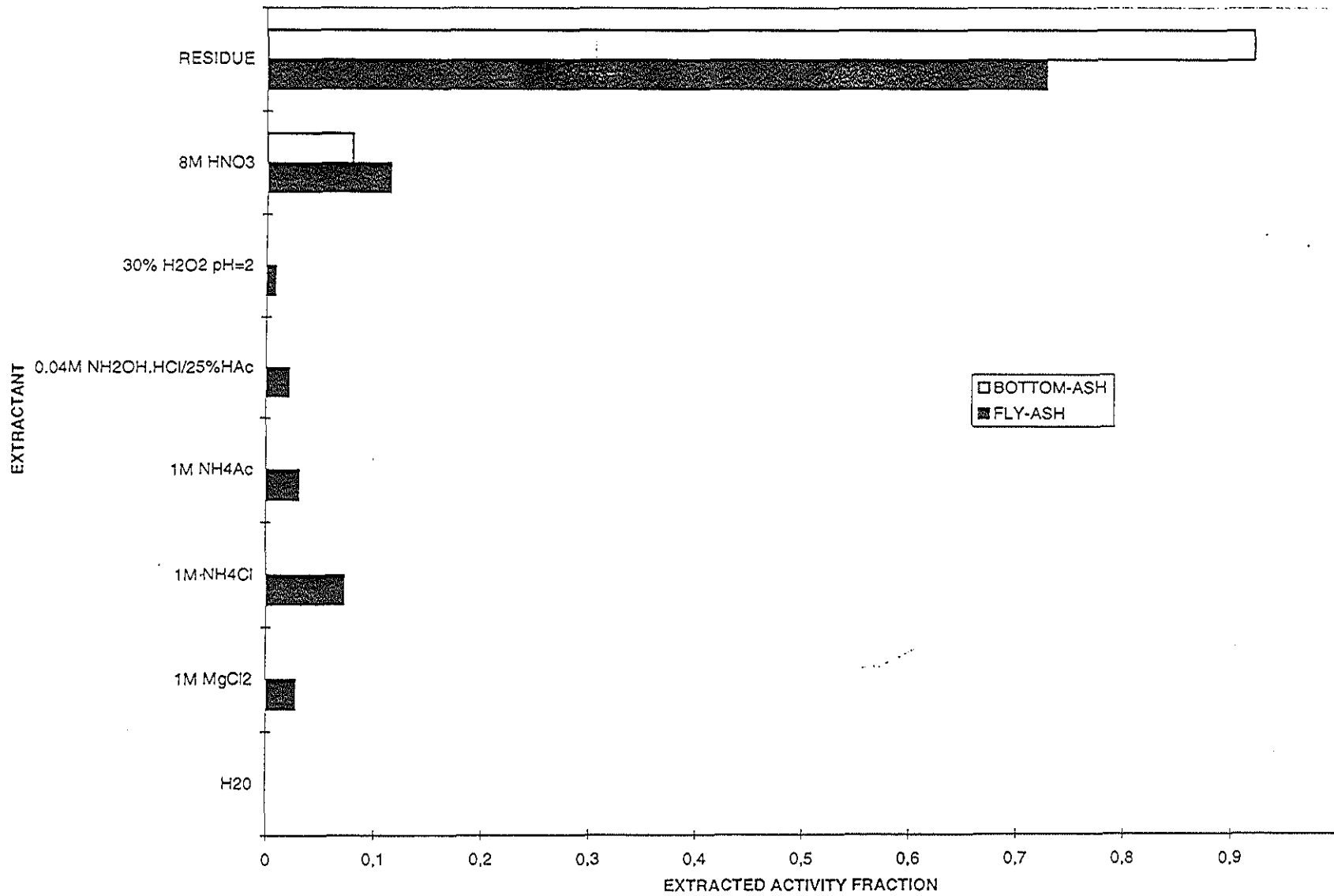


Figure 5, Radiocesium extractability from peat ash (fly-ash and bottom-ash) by sequential extraction. Ash from Uppsala powder burner.

<sup>137</sup>Cs EXTRACTABILITY FROM PEAT ASH (NÄSSJÖ CFB BURNER)

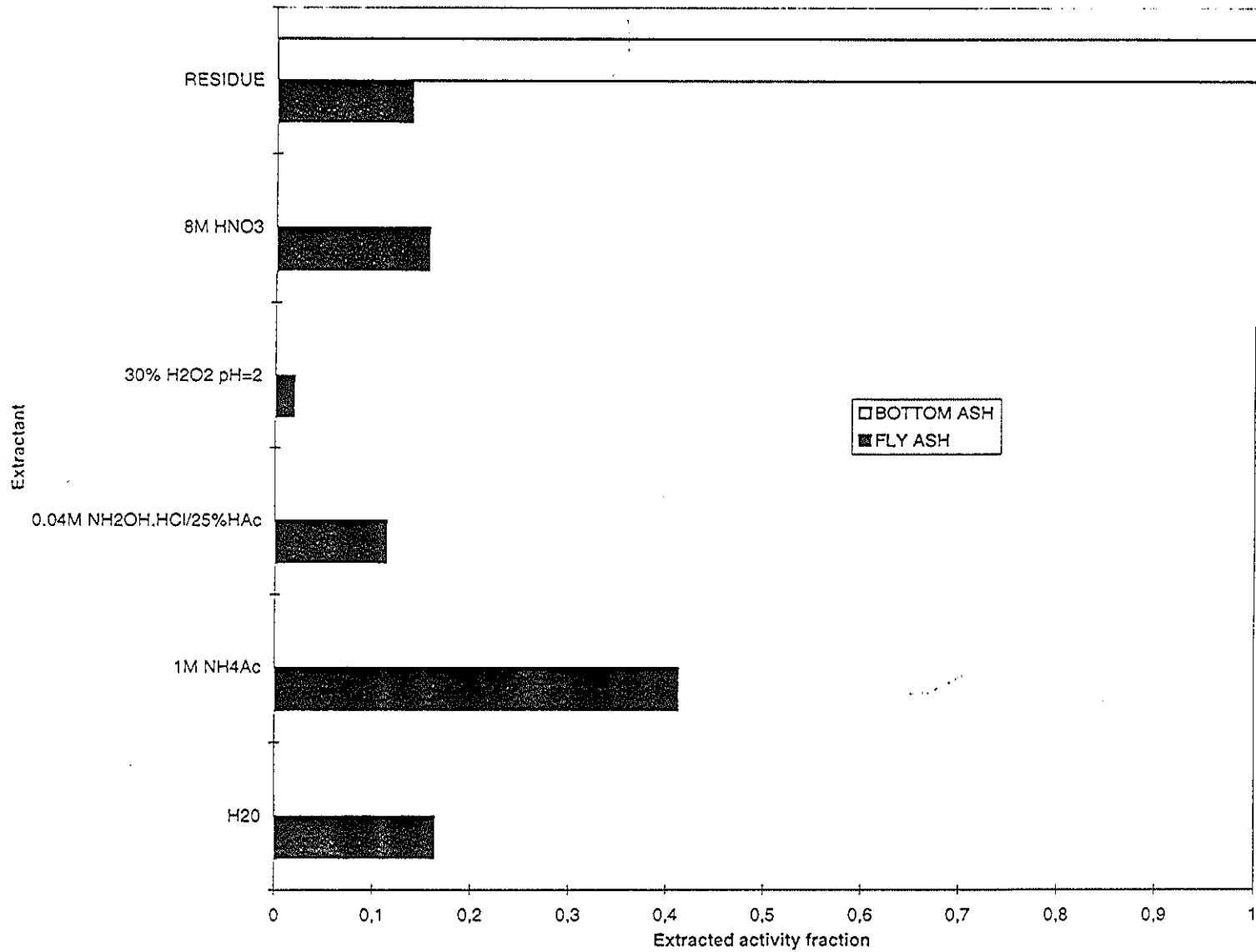


Figure 6, Radiocesium extractability from peat ash (fly ash and bottom ash) by sequential extraction. Ash from Nässjö continuous-fluidized-bed (CFB) fired burner.