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TOEGEPASTE BIOLOGISCHE WETENSCHAPPEN

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# PHYTOREMEDIATION OF LAND DISPOSED CONTAMINATED DREDGED SEDIMENTS: FATE OF HEAVY METALS

# FYTOREMEDIATIE VAN LANDGEBORGEN VERONTREINIGDE BAGGERSPECIE: GEDRAG VAN ZWARE METALEN

door

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# List of Abbreviations

| | | |
|---|---|---|
| AAS | : | Atomic Absorption Spectrometer |
| BCF | : | Bio Concentration Factor |
| DAW | : | Dry Ash Weight |
| DM | : | Dry Matter |
| DW | : | Dry Weight |
| DS | : | Disposal Site |
| EC | : | Electro Conductivity |
| FR | : | *Salix fragilis* 'Belgisch Rood' L. |
| GFAAS | : | Graphite Furnace Atomic Absorption Spectrophotometer |
| ICP-AES | : | Inductively Coupled Plasma–Atomic Emission Spectrometry |
| NDIR | : | Non-Dispersive Infrared |
| OM | : | Organic Matter |
| PAH | : | Poly Aromatic Hydrocarbon |
| RSD | : | Residual Standard Deviation |
| SRF | : | Short Rotation Forestry |
| TR | : | *Salix triandra* 'Noir de Villaines' L. |

# 1 General Introduction

## 1.1 Contaminated dredged sediments: a remediation problem

Due to poor national water management during the last decades and trans boundary industrial fluxes from Northern France, most fine-grained sediments of the Belgian inland waterways are enriched with contaminants such as heavy metals, poly aromatic hydrocarbons (PAHs), and mineral oil (Geuzens et al., 1998). The periodic dredging of these waterways is vital to ensure future navigation but it is a continuous source of large volumes of contaminated dredged materials which have to be treated or discarded (Forstner and Calmano, 1998). As more technical remediation techniques such as sediment washing, vitrification, and thermal treatment are often not yet economically and technologically feasible (Rulkens et al., 1998; Mulligan et al., 2001), the current option for treatment of contaminated sediment is disposal in confined landfills. This results in the establishment of fertile but contaminated sites with little beneficial uses. In Flanders, each year about 135 to 160 ha of land are theoretically needed to dispose of the 4,000,000 $m^3$ of sediment dredged from inland waterways (Demoen, 1989). However, such areas are not available and the lack of options for storage, remediation, and re-use of dredged sediments are currently limiting required and planned dredging activities. As a result of uncontrolled sediment disposal in the past extended areas along our waterways were used for the disposal of contaminated dredged sediments. For example, more then 425 ha of contaminated sediments are located along the shores and in alluvial plains of the main Flemish waterways Schelde and Leie. Currently, many of upland disposed dredged sediments are used for agricultural purposes and natural habitat creation (Vandecasteele et al., 2002; Vandecasteele et al., 2003), resulting in risk for food chain contamination and spreading of contaminants to the surroundings through plant uptake and erosion (Gambrell, 1994). These pathways are of particular concern as it was shown that metals in sediment derived soils are highly plant available and susceptible to run off (Tack et al., 1996; Singh et al., 1998).

Even if unpolluted topsoil is applied on contaminated dredged sediment, metal concentrations in agricultural crops grown on these sites are often above environmentally acceptable limits (Van Driel et al., 1995). Metal leaching to the groundwater on the other hand, is of lesser environmental concern (Ruban et al., 1998; Ross, 1994; Singh et al., 2000).

Extensive eco-technological techniques such as phytorestoration and -remediation can be interesting remediation options for the existing areas of land disposed dredged sediments and for the future treatment of the large volumes of contaminated dredged sediments. They are emerging technologies to restore, stabilize, and clean large areas of moderately contaminated substrates (Goldsmith, 1998). Trees have been suggested as a low cost, sustainable, and ecologically sound solution for phytoremediation of heavy metal contaminated land (Vangronsveld et al., 1998; Dickinson et al., 2000). The use of energy crops, such as willow and poplar species, as phytoremediation crop in this context is promising (Duncan et al. 1995; Robinson et al., 2003). Willow can accumulate heavy metals in their above ground biomass compartments which can be regularly harvested. In addition, they are easy to propagate, fast growing, metal tolerant perennial crops which can stabilize pollutants with an extensive root system and high evapotranspiration. The long remediation time, which is often associated with phytoremediation technologies, can be rendered less important if phytoremediation can be combined with a profit making operation, such as forestry and bio-energy production (Robinson et al., 2003).

In several European countries such as Sweden and Finland, willow stands managed in Short Rotation Forestry (SRF) systems are an increasingly used practice for the production of renewable energy and heat (Ledin, 1996; Schwaiger and Schlaladinger, 1998). However, large scale cultivation of energy crops has not yet started in other parts of Europe (Hanegraaf et al., 1998). Unstable markets and high prices of land negatively influence the financial feasibility of projects, and wide spread social acceptance of these crops is still lacking (Roos et al., 1999; Rösch and Kaltschmitt, 1999). A possible option to reduce the impact of these problems is combining the cultivation of energy crops with other possible functions of the land. In this context, SRF plantations have been planted on sanitary landfills, in mining areas, and on disposal sites of organic wastes (Ettala, 1988; Steer and Baker, 1997; Bungart and Hüttl, 2001).

The combined land use of dredged sediment disposal and biomass production for energy purposes with the potential for phytoremediation could thus be an economically and ecologically valuable land use option on historic and future sediment disposal sites if care is taken to minimize metal transfer to other compartments of the ecosystem. While in the last years the general principles and scientific groundwork of phytoremediation of contaminated sites with willow cultures were established, several gaps in knowledge on feasibility, management options, and faith of contaminant in the system remain.

With the introduction of a vegetative cover on a contaminated substrate it is important to consider the impact on the fate and behavior contaminants during the remediation and the subsequent handling of the produced biomass. Phytoremediation technologies should be operated in a risk based land management approach to ensure acceptable ecological and environmental risks. The assessment of exposure is an important step in this context of risk assessment. It encompasses the determination of the emissions, pathways and rates of movement of a substance and its transformation or degradation, in order to estimate the concentration/dose to which human populations or environmental spheres are or may be exposed (Vindimian, 2002). The main concern with planting trees on metal contaminated soils is the effect this may have on ecosystem mobility of metals, and the possibility of dispersion of toxic metals into the wider environment. New pathways for contaminated dispersal can be created through leaf fall, root activity, and biomass conversion. Knowledge on the amount of metals which reach the environment through these pathways is essential in assessing the sustainability and risk susceptibility of the system.

The second eco-technique investigated in this work is the multi-layered dredged sediment disposal in afforested disposal sites. The planting of a dense willow stand on contaminated dredged sediment surfaces results in stabilizing the substrate and rendering the site more esthetically attractive. If multiple layers of sediment can be brought in the same afforested disposal site, larger volumes of sediment can be stored on the same surface while the two previously beneficial properties of the stand are retained. Multi-layered dredged sediment disposal is already practiced in traditional dredged sediment disposal sites. A new layer of sediment is brought into the site after the previous layer has dewatered and ripened. Applying this technique in afforested sediment disposal sites could result in shortening the time between sediment applications, as it can be hypothesized that the presence of willow stems and the formation of a new root system in the new sediment layer could increase the speed of sediment dewatering and ripening.

## 1.2 Objectives

The general objective of the research in this thesis is to evaluate the possibilities and limitations of the use of *Salix* stands for the phytorestoration and -remediation of land disposed contaminated dredged sediments and to assess the fate of heavy metals in this system. The second general objective is to study the technical feasibility of multi-layered sediment disposal in afforested disposal sites.

This work has the following specific research objectives:

- To evaluate dredged sediment as a substrate for the growth of *Salix* and to describe the stand development of *Salix* stands on dredged sediment disposal sites.
- To investigate the feasibility of restoring and cleaning contaminated dredged sediment with willow cultures, and to determine which management options should be applied to maximize efficiency and minimize risks.
- To assess the impact of *Salix* based eco-technological techniques on metal mobility and availability in the ecosystem, with emphasis on the behavior of heavy metals in the foliage and the root zone of *Salix*. The study aims at quantifying heavy metal fluxes and pathways in such remediation schemes.
- To investigate the behavior of heavy metals during the conversion of heavy metal enriched willow wood to electricity and heat.
- To study the technical feasibility of multi-layered sediment disposal in afforested disposal sites.

### 1.3 Outline

This work presents applied and multi faceted research on the different aspects of a contaminated dredged sediment phytoremediation technology with willow cultures, ranging from the introduction, dynamics and development of *Salix* stands on contaminated dredged sediments, to stand management, metal uptake and translocation, risk assessment, and the conversion of *Salix* biomass to electricity and heat. An important part of this work will focus on the fate of contaminants in the phytoremediation system and the risk of dispersal of contaminants to the surroundings. In addition, the practical feasibility of multi-layered sediment disposal is assessed.

This work consists of a number of chapters submitted or published in international journals. Each of the chapters highlights particular aspects of the use of willow in the phytorestoration and –remediation of contaminated dredged sediments. Chapters are not intended to be stand alone entities but are steps to the intended aim of the study: the evaluation of willow stands in SRF system for the phytoremediation of contaminated dredged sediment in the final chapter of this thesis.

Chapter 1 presents the general introduction, objectives, and outline of this work.

Chapter 2 provides a short description and literature overview on the concept of phytoremediation of contaminated sites with willow cultures.

Chapter 3 describes the dynamics, development, and biomass production of willow stands grown on contaminated dredged sediment over a period of six growing seasons. In addition, the nutritional status and tree health are used to evaluate the suitability of dredged sediment as a substrate for willow growth.

In Chapter 4, the metal uptake and translocation by different willow clones grown on contaminated sediment in the different biomass compartments is assessed. The seasonal variations in metal concentrations in two clones in four different growing seasons is described to provide management guidelines to maximize metal export with harvest and to minimize metal losses to the environment.

Growing crops on metal contaminated substrates can change the availability and mobility of heavy metals in the root zone. Therefore chapter 5 describes two trials which investigate the short- and longer-term impact of willow root growth on metal extractability in both oxic and anoxic contaminated dredged sediments.

Chapter 6 deals with the conversion of heavy metal enriched willow wood to electricity and heat. It describes several gasification trials of willow, grown on contaminated dredged sediment, in a 100 kW pilot scale fixed bed downdraft gasification unit and presents results on the distribution of heavy metals in this system.

The 7$^{th}$ Chapter presents findings on the pilot scale test of the multi-layered sediment disposal technique in afforested sites. It describes the sediment dynamics in such a system and the influence of the sediment application on the *Salix* stand structure and development. Guidelines are provided to ensure the success of this technique with future applications.

Chapter 8 consists of the general discussion and conclusions. Results and insights from the previous chapters are combined to discuss the feasibility, management options, risks, and other aspects involved in the phytoremediation of land disposed contaminated dredged sediments with willow cultures.

# 2 Background: the use of *Salix* species in phytoremediation

## 2.1 Introduction

Phytoremediation is an emerging technology for cleaning and/or stabilizing large areas of contaminated land. Trees feature a range of characteristics which makes them suitable for use in this technology. Especially fast growing biomass species, such as *Salix* species, have been suggested as interesting tree species as they are easy to propagate, fast growing, metal tolerant species that are able to accumulate metals and/or provide physical stabilization. In addition, harvested biomass can be used to produce electricity and heat. This chapter provides a short description on the use of trees in phytoremediation, with emphasis on willow.

## 2.2 Phytoremediation

Over the last years, the focus in dealing with contaminated land is gradually shifting away from the traditional removal, disposal, and capping techniques to more integrated in-situ approaches. Efforts to develop such integrated approaches have resulted in a shift in attention from the assessment of problems to the formulation of solutions that meet the requirements of society. Possible sustainable solutions, such as phytorestoration and –remediation, focus on the restoration of the usability and the social and economical value of the land. Phytoremediation is the name given to a set of technologies in which plants are used to remediate the environment. It encompasses the direct use of living green plants for *in situ* risk reduction for contaminated soil, sludges, sediments, and ground water, through contaminant removal, degradation, or containment (Cunningham and Berti, 1993; Salt et al., 1995; Salt et al., 1998). Growing and, in some cases, harvesting plants on a contaminated site as a remediation method is an aesthetically pleasing, solar-energy driven, passive technique that can be used to clean up sites with shallow, low to moderate levels of contamination. Phytoremediation can be used along with or, in some cases, in place of mechanical cleanup methods. However, it is still an emerging technology in which aspects and knowledge of a wide range of environmental and biological research fields have to be combined to come to a sustainable tool in the remediation and restoration of large areas of contaminated land (Khan et al., 2000).

Based on the chemical and plant processes involved, phytoremediation techniques can be classified in three broad categories: phytostabilisation, phytoextraction, and phytodegradation.

Phytostabilisation is the use of plant species to immobilize contaminants in the soil and ground water and reduce their environmental impact and risk of dispersal (Bradshaw, 1979; Vangronsveld et al., 1995; Vangronsveld and Cunningham, 1998). Phytorestoration is often referred to in the same context as the establish of a vegetative cover at sites where natural vegetation is lacking due to high metals concentrations or were a particular vegetation is desired. The stabilization of contaminants is a result of several chemical and physical processes occurring at the soil-plant interface. The plants protect the soil from wind and water erosion and reduce the water percolation through the soil thus preventing leaching of contaminants (Vangronsveld et al. 1995). The soil can be physically stabilized through stronger aggregation, increased OM content, the formation of a dens root systems and a litter layer (Wilkinson et al., 1995). Chemical processes can include the absorption and accumulation by roots, adsorption onto roots, and chemical changes in the rhizosphere of plants (Mcgrath, et al., 2001). These chemical and physical processes reduce the mobility of the contaminant and prevent migration to the ground water or air, and they reduce bio-availability for entry into the food chain. Plants should be tolerant to the conditions prevailing on the site to ensure sufficient growth (Bradshaw, 1979). Soil amendments such as phosphate, lime, zeolites, organic matter (OM), Mn oxides, and Fe compounds are sometimes needed to immobilize toxic metals, allow plant growth, and reduce the risk of soil erosion and dispersal (Vangrondsveld et al., 1995). Vangronsveld and Cunningham (1998) list the main objectives for successful in situ inactivation with plants are: i) to change the trace element speciation in the soil in order to reduce the easily solulable and exchangeable fraction of these element, ii) to stabilize the vegetation cover and limit trace element uptake by crops, iii) to reduce the direct exposure of soil heterotrophic living organisms, and iv) to enhance biodiversity.

When applied on a waste disposal site or on a landfill, a vegetative cover can be considered as a long-term, self-sustaining cap composed of soil and plants. As such, vegetative covers are an alternative to composite clay or plastic layer caps (Ettala et al., 1988; Schnoor, 2000; Nixon et al., 2001). Plants control erosion and minimize seepage of water that could otherwise percolate through the landfill and form contaminated leachate. In addition, vegetative caps can be designed and managed not only to control erosion and percolation of water, but to remove or enhance the degradation of contaminants in the landfill.

Phytoextraction refers to the uptake and translocation of heavy metals into the aboveground portions of the plants, which can be subsequently harvested (Kumar et al., 1995; Salt et al., 1995; Chaney et al., 1997; Garbisu and Alkorta, 2001). Metal uptake by plants is determined by the availability of the metal in the substrate, which in its turn is dependent on the physical, chemical and biological factors (Ernst, 1996; Brummer, 1986). Brooks et al. (1977) identified an extreme form of metal accumulators, described as hyperaccumulators, in which tissue metal concentration can exceed 1000 mg metal per kg. The use of hyperaccumulating plants to actively reduce the metal content in the soil was suggested by Baker et al. in 1988. The first hyperaccumulators characterized were members of the *Brassicaceae* and *Fabaceae* families. Much on the previous work on phytoextraction with hyperaccumulators has involved the species *Thlaspi caerlescenc* (Kumar et al., 1995; Salt et al., 1995; Knight et al., 1997; Robinson et al., 1998). However, low yields, slow growth rate and harvesting problems limit the potential for effective phytoremediation with these plants (Salt et al., 1995; Ebbs and Kochian, 1997).

An alternative to hyperaccumulators is the use of plants with lower accumulation characteristics, but which are characterized by a higher biomass production, such as trees and agronomic crops. In this respect, several authors have studied the metal uptake capabilities of *Salix* species, cultivated *Brassica* (mustard) species, corn and sunflower (Landberg and Greger, 1994; Kumar et al., 1995; Blaylock et al., 1997). It has been suggested that their use can be accompanied with manipulations of soil conditions to increase the bio-availability and plant uptake. This is called induced phytoextraction. Most attention has thus far been directed to synthetic chelating agents such as Ethylenediamineteracetic acid (EDTA) (Huang and Cunningham, 1997). Although the use of these agents can significantly increase metal uptake, several negative consequences can be identified. Plants and soil micro-organisms often react negatively to this treatment, and there is the possibility of leaching large fraction of the metals to ground or surface waters (Sun et al., 2001; Römkens et al., 2002).

Phytodegradation is the breakdown of contaminants taken up by plants through metabolic processes within the plant, or the breakdown of contaminants external to the plant through the effect of compounds (such as enzymes) produced by the plants or microbial activity in the rhizosphere (Shimp et al., 1993; Cunningham et al., 1996; Burken and Schnoor, 1997; Burken and Schnoor, 1999). Riparian corridors or buffer strips are applications of phytoremediation that also may incorporate aspects of phytostabilisation, phytodegradation, and rhizodegradation to control, intercept, or remediate contamination entering a river or ground-water plume (Dix et al., 1997). Riparian corridor refers to plants that may be applied along a stream or river bank, while buffer strips may be applied around the perimeter of landfills.

## 2.3 The use of trees in the phytoremediation of metal contaminated land

The potential use of trees as a vegetation cover for heavy metal contaminated land has received increasing attention over the last 10 years. Trees feature a range of characteristics which makes their use in the restoration of contaminated land an interesting option: trees reduce the risk of contaminant dispersal by decreasing water and wind erosion with extended perennial root systems and the production of litter and organic layers on the contaminated surface (Stomp et al., 1993; Lepp and Dickinson, 1998). Several tree species are known to be tolerant to elevated heavy metal levels and can accumulate metals in their above ground biomass parts (Turner and Dickinson, 1993). Planting phreatophytic trees, such as *Salicaceae*, may further contribute to the stabilization by preventing the vertical migration to groundwater as a result of hydraulic control through interception and evapotranspiration (Schnoor, 2000). The most important requirements for trees intended for phytoremediation are that they must be easy to propagate, fast growing, metal tolerant species that are able to accumulate metals and/or provide physical stabilization (Punshon and Dickinson, 1997b). Contrary to food crops, higher metal contents are acceptable in trees as long as physiological activity is not affected (Labreque et al., 1995). Trees have thus been suggested as a low cost, sustainable, and ecologically sound solution to the remediation of heavy metal contaminated land (Glimmerveen, 1996; Dickinson et al., 2000), especially when it is uneconomic to use other treatments or there is no time pressure on the reuse of the land.

For trees to be used in phytoremediation systems it is essential that they are suited to the conditions occurring at the contaminated site. Tree survival, growth and physiological function can be affected detrimentally by many contaminants (Burton et al., 1983; Arduini et al., 1998), but physical conditions and nutrient deficiencies can also severely limit tree growth. Suitable rooting conditions and nutrient supply are of prime importance for the establishment of trees on contaminated sites. Poor water holding capacity and aeration, compaction, acidity, shallow ground water tables, and salinity can all negatively influence tree growth (Bending and Moffat, 1999). Other factors such as weed growth and site neglect can also result in unsatisfying growth (Dickinson, 2000).

Once the trees have become established, the vegetation cover results in the physical stabilization of the substrate. Through the development of a high-density perennial root system and the accumulation of OM and litter on the stand surface, the dispersal of contaminants by wind or runoff can be prevented (Ross et al., 1990; Stomp et al., 1993; Wilkinson, 1999).

While tolerance to heavy metals in herbaceous species was studied intensively, woody plants received less attention. Initial research on metal tolerance of trees and their use for the revegetation of contaminated land started at the end of seventies. Attention then was focused on the use of trees for the restoration and stabilization of metalliferous mine wastes. McCormack and Steiner (1978) tested the aluminium tolerance of eleven trees in solution culture. They identified resistant species from sensitive ones and made recommendations for the use of trees for the revegetation of mine spoils. In general, trees are generally absent from metalliferous sites (Ernst, 1990; Turner, 1994). However, Eltrop et al. (1991) reported the pioneer species *Salix* and *Betula* growing on metalliferous spoil and suggested that they have evolved tolerant ecotypes in response to constant exposure to heavy metals. Several other authors already reported tolerant *Betula* ecotypes on contaminated sites (Brown and Wilkins, 1985; Denny and Wilkins, 1987). They found that trees from contaminated sites were more tolerant to high concentrations of Zn: findings which were similar to the tolerance characteristics identified for herbaceous plants.

However, other research failed to demonstrate the existence of tolerance traits in pioneer species such as *Salix* (Dickinson et al., 1991; Landberg and Greger, 1996), implying that the adaptation of individual mature plants through phenotypic plasticity may be the most significant factor which determines the ability to survive pollution (Turner and Dickinson, 1993). This is supported by the fact that trees not specially selected for metal tolerance can generally survive in metal contaminated soil, but often at reduced growth rates. Dickinson et al. (1992) described tolerance and survival of plants on metal contaminated soils as arising from "an orchestrated multiplicity of physiological and biochemical responses, including both avoidance and true resistance mechanisms", which implies both genotypic and phenotypic adaptation. In addition, trees and especially *Salix* and *Betula* species, are known to be strongly mycorrhizal, a characteristic which can greatly influence metal tolerance (Harris and Jurgensen, 1977; Denny and Wilkins, 1987; Wilkinson, et al., 1995).

An important mechanism of tolerance is the immobilization of the contaminant through binding with cell walls, sequestration in vacuoles, or complexation with metallothionein-like proteins in the cytoplasm (Kahle, 1993). This immobilization is often most pronounced in the roots (Dickinson et al., 1991). Other tolerance strategies in trees include avoidance, excretion and exclusion (Baker, 1981). Especially avoidance of high pollutant concentrations by tree roots of is an important mechanism of facultative tolerance, through which trees can survive on heavy metal contaminated land (Dickinson et al., 1991; Watmough and Dickinson, 1995).

Tree species differ greatly in their ability to accumulate heavy metals. A variety of studies investigated the metal uptake and compartmentalization in trees for a range of different pollution conditions (Gretza, 1980; Gretza, 1982). Initially most of these were focused on forest ecosystems affected by aerial pollution in the vicinity of metalliferous industry or smelters (Clarke et al., 1980; Heinrichs and Mayer, 1980; Martin and Coughtrey, 1981, Martin et al., 1982). Recently, more attention has been paid to trees planted on contaminated land for remediation purposes (Turner and Dickinson, 1993; Riddel-Black et al., 1997; Hasselgren, 1999; Alriksson and Eriksson, 2001; Rosselli et al., 2003).

In general, *Salix* and *Betula* are characterized with a high uptake of Cd and Zn respectively compared to other tree species (Nissen and Lepp, 1997; Alriksson and Eriksson, 2001; Rosselli et al., 2003). Compared to these two species, most other tree species feature a low accumulation of heavy metals. Mertens et al. (2004) investigated the metal uptake of five tree species growing on brakish dredged sediments and found elevate concentrations of Cd and Zn in *Populus*, while concentrations in *Acer*, *Alnus*, *Fraxinus*, and *Robinia* could be considered as normal. A similar study by Rosselli et al. (2003) reported low metal concentrations in *Alnus*, *Fraxinus*, and *Sorbus*.

While the majority of metals taken up by trees are immobilized in the roots, the translocation of toxic metals to aboveground biomass compartments of trees varies widely between different metals. In general, higher Cd and Zn concentrations are found in actively growing tissue as leaves and shoots compared to the wood, while the differences for Cu and Pb are often less profound between biomass compartments (Ross, 1994; Riddel-Black et al., 1997; Nissen and Lepp, 1997). Heinrichs and Meyer (1980) found higher Cu concentrations and lower Pb concentrations in wood compared to leaves in beech. Bark metal concentrations are in general higher than wood concentrations. When compartment concentrations are converted to stocks taking into account the compartment biomass, the largest metal stocks are found in the wood. More on the distribution of heavy metals in trees is provided in Chapter 4.

## 2.4 The use of *Salix* in the phytoremediation of contaminated land

While a number of different tree species, such as *Betula* (Borgegard and Rydin, 1989), *Pinus* (Berry, 1982), *Alnus* (Dickinson, 2000), *Acer* (Turner and Dickinson 1993), and *Populus* (Schnoor, 1995; Steer and Baker, 1997), have been considered in studies on the restoration of contaminated substrates, most attention has recently been given to fast growing species such as willow (Pulford and Watson, 2003). Willow trees easy to propagate, fast growing, metal tolerant species that are able to accumulate metals. They can provide physical stabilization and are characterized with an extensive root system which makes them suitable candidates in phytoremediation projects (Keller et al. 2003). In addition, additional economical, social, and ecological benefits can be generated through the production of biomass for renewable energy purposes if the *Salix* stand is managed as an energy crop for the production of electricity and heat (Ledin, 1996; Robinson et al., 2003). When willow wood is harvested at regular intervals, contaminated sites with little other beneficial use can thus be made useful through the production of biomass for energy purposes.

The genus *Salix* is a large, taxonomically complex genus. Depending on the taxonomic school about 350 to 500 different willow species can be distinguished worldwide (Pohjonen, 1991; Argus, 1999). Willows are early successional trees with characteristics of pioneer species: a high initial growth rate, light seeds, and a relatively short life span compared to other species (Verwijst, 2001). *Salix* species can easily be propagated vegetatively, and most species resprout vigorously after cutting (Sennerby-Forsse et al., 1992; Ledin, 1996). The tree can thus be frequently harvested by coppicing every three three to five years in a SRF system, which makes it suitable for use in phytoremediation. The management of SRF plantations for the production of electricity and heat, is an already well established practice in several European countries, especially in Sweden and Finland (Christersson et al., 1993; Willebrand and Ledin, 1995; Ledin, 1996). *Salix* species are tolerant to a wide range of climatic and soil related factors and the large number of existing species and clones allows selection of those best suited to specific conditions. Several willow species are known to colonize edaphically extreme soils such as metaliferous sites, particularly *Salix caprea*, *Salix cinerea*, and *Salix viminalis* (Harris and Jurgensen, 1977; Turner and Dickinson, 1993; Eltrop et al., 1991). Grime et al. (1988) documented mining waste disposal sites as ecological niches for *Salix caprea* and *Salix cinerea*. Willow was also found to colonize metal contaminated river sediments (Mang and Reher, 1992, Vandecasteele et al., 2002).

Interest on the use of *Salix* in phytoremediation began in the beginning of the nineties. Research then focused on the use of willow stands for the production for energy purposes, often combined with the treatment of waste water in vegetation filters (Perttu, 1993; Riddel-Black, 1994a; Perttu and Kowalik, 1997; Elowson, 1999). At that time, several European countries started developing bio-energy production systems using willow in SRF systems. Organic wastes, such as waste water and sewage sludges, were considered interesting alternative sources for fertilization of willow stands compared to inorganic fertilizers. The nutrient composition of wastewaters and sludges was found to be comparable with the nutrient demand of *Salix* (Perttu, 1999). The irrigation of *Salix* stands with sewage sludges and wastewaters increased growth and biomass production (Kutera and Soroko, 1994; Labrecque et al., 1997), and led to more uniform growth and greater shoot numbers (Hasselgren, 1998). However, the presence of heavy metals in the applied organic fertilizers resulted in elevated concentrations of heavy metals, especially Cd, in the aboveground biomass (Riddel-Black, 1994b; Labrecque et al., 1995). This prompted research on metal accumulation and tolerance of willows to be used for combined phytoextraction of heavy metals and energy production.

Landberg and Greger (1994) performed a large scale hydroponical screening of 94 willow clones of *Salix viminalis, dasyclados, daphnoides, triandra* and *purpurea* for their tolerance to Cd and Zn. Results showed that *Salix* clones have a large variations in metal uptake and tolerance. Some clones were tolerant to both Cd and Zn, while others were tolerant to only one of the metals. Both tolerant and sensitive clones were characterized by high or low accumulation, which indicates that net uptake and accumulation in *Salix* does not seem to be correlated to the tolerance. *Salix* clones were only affected by heavy metal concentrations which by far exceeded levels found in the environment. Similar conclusions were made for Cu (Punshon et al. 1995) and Zn, Cd, Cu and Ni (Punshon and Dickinson, 1999). The latter study also reported considerable interclonal variations in metal tolerance. Punshon and Dickinson (1997a) showed that *Salix* trees could gradually adapt to high metal concentrations in soils. While most tolerance studies were conducted in hydroponic systems, some studies were performed in pot experiments (Punshon and Dickinson, 1997b) and field trials (Punshon and Dickinson, 1997b; Riddel-Black et al., 1997; Landberg and Greger, 1996; Felix, 1997). Punshon and Dickinson (1997b) reported *Salix cinerea* trees growing on mine spoil with stem metal concentrations up to 76.4 mg Cd/kg and 157.4 mg Pb/kg. An overview of metal concentrations measured in *Salix* trees growing on contaminated substrates is presented in Table 2–1.

In general, Cd and Zn are translocated from the roots and subsequently accumulated in shoots and leaves, while the highest Cu concentrations are found in the roots (Nissen and Lepp, 1997; Punshon et al., 1995). However, Riddel-Black et al. (1997) identified several species which accumulated Cu and Ni in aboveground biomass, but these showed reduced survival and biomass production. The other group had relatively low Ni and Cu in the bark and high Cd and Zn in the wood, with a good survival rate and biomass production. Landberg and Greger (2002) investigated variation in interactions between Cd, Cu and Zn on toxicity and accumulation. They found that the uptake of Cu was decreased by the other metals in clones with high Cu accumulating properties. The accumulation of Cd was not changed by the presence of other metals.

The large variation in heavy metal tolerance accumulation between clones allows the use of specific clones for specific applications. Landberg and Greger (1994) and Dickinson et al., (1995) proposed different strategies for contaminated land restoration using willow crops. Metal tolerant clones with high metal accumulating properties can be used to clean contaminated soils through repeated harvest of metal enriched wood. The prospects of actively cleaning soils with willow are most promising for Cd. In most accumulation experiments, Cd is found to be the only metal that is truly accumulated, with Bio Concentration Factors (BCF) > 1 (BCF = metal concentration in plant/metal concentration in soil). Greger et al. (1995) calculated that it would take 12 years to remove the Cd added to the soil with fertilizers in the last 100 years. Riddel-Black (1994) reported that *Salix* could remove 400% of the added Cd in sewage sludge.

Recently several studies focused on management options to increase metal export through willow cropping. Robinson et al. (2000) investigated the impact of chelating agents such as EDTA, DTPA, and NTA on metal accumulation. Results were not encouraging as treatments resulted in reduced growth (0.5 g/kg EDTA), reduced stomatal conductance (0.5 g/kg EDTA; 0.5 g/kg , DTPA), and necrosis followed by leaf abscission (2 g/kg EDTA; 0.5 g/kg NTA). Klang-Westin and Perttu (2002) investigated whether increased fertilization would result in higher amounts of extracted Cd. In general, increased biomass led to higher amounts of Cd in the stem. Differences were however small and in most cases insignificant, as increased biomass resulted in lowered Cd concentrations as a result of biological dilution. Only for 1 year old coppiced plants did higher nutrient levels result in significantly larger amounts of Cd in the stem. They conclude that if *Salix* is to be used as a phytoextractor of Cd, the possibilities for significantly removal rate by increased biomass production appears to be limited.

Research on the possibilities for phytodegradation of organic contaminants with *Salix* is still very limited, although poplar is attracting more attention (Burken and Schnoor, 1997; 1999). Corseuil and Moreno (2001) showed the ability of willow to reduce ethanol and benzene concentrations in polluted aquifers. Vervaeke et al. (2003) reported increased dissipation of mineral oil in the root zone of *Salix*, while PAHs concentrations were not affected.

Table 2–1: Overview of research on heavy metal accumulation by willow grown on contaminated substrates. Minimum –maximum values are presented if multiple clones were tested. X: spiked substrate. Concentrations in mg/kg. na: below detection limits.

| Author | *Salix* species | Site | pot/field | Metal | Substrate | Wood | Leaves | Other |
|---|---|---|---|---|---|---|---|---|
| Brieger et al., 1992 | *Salix spp* | fly ash disposal site | field | | | | | |
| Felix, 1997 | *Salix spp* | Cd rich calcareous soil | field | Cd | 7 | 22 | | |
| Good et al., 1985 | *Salix spp.* | Open cast coal sites | | | | | | |
| Goransson and Phillipot, 1994 | *Salix spp.* | Sewage sludge | pot | | | | | |
| Greger and Landberg, 1995 | *Salix viminalis* | Cd enriched agricultural soils | field | Cd | 0.6 | 1.1 | 5.5 | |
| Harris and Jurgensen, 1977 | *Salix spp.* | Mine tailings | | | | | | |
| Hammer et al., 2003. | *Salix viminalis* | Soil contaminated with smelter emissions | field | Cd | | 3.6 | 6 | |
| | | | | Zn | | 200 | 1110 | |
| Hasselgren, 1999 | | | | | | | | |
| Klang-Westin and Perttu, 2002 | *Salix dascyclados* | Soil | pot X | Cd | 0.6 | 7.1 | | |
| Klang-Westin and Perttu, 2003 | *Salix viminalis* | Cd enriched agricultural soils | field | Cd | 0.45 | 4.1 | 7.3 | |
| Mertens et al., 2001 | *Salix fragilis* | Contaminated dredged sediment | field | | | | | |

| Author | *Salix* species | Site | pot/field | Metal | Substrate | Wood | Leaves | Other |
|---|---|---|---|---|---|---|---|---|
| Nissen and Lepp, 1997 | 8 *Salix* varieties | Unpolluted soil | field | Cu | 8.95 | 11.1 | 8.63 | 6.2 |
| (other = bark) | | | | Zn | 47.3 | 52.4 | 296.2 | 208.04 |
| Östman, 1994 | *Salix viminalis* | Cd enriched agricultural soils | field | Cd | 0.24 | 3.3 | | |
| Punshon and Dickinson, 1997b | *Salix cinerea* | Mine spoil | field | Cu | 197.20 | 4.60 | 4.20 | |
| | | | | Cd | 254.8 | 76.4 | 43.9 | |
| | | | | Pb | 12,840 | 157.4 | 17.3 | |
| | | | | Zn | 1,259 | 77.3 | 87.1 | |
| Riddel-Black et al., 1994 | 4 *Salix* varieties | Sewage sludge amended soil | field | Cu | 140 | 5.7-8.2 | 10.4-15.8 | |
| | | | | Cd | 6 | 3.3-7.7 | 5.8-11.6 | |
| | | | | Cr | 358 | na | na | |
| | | | | Ni | 93 | 0.9-1.4 | 7-11.5 | |
| | | | | Pb | 200 | na | na | |
| | | | | Zn | 419 | 95.4-156.1 | 259-412 | |

| Author | *Salix* species | Site | pot/field | Metal | Substrate | Wood | Leaves | Other |
|---|---|---|---|---|---|---|---|---|
| Riddel-Black et al., 1997 | 20 *Salix* varieties | Sewage sludge amended soil | field | Cu | 300 | 1.2-24.2 | | 11.4-50.6 |
| (other = bark) | | | | Cd | 30 | 1-12.3 | | 7.8-35 |
| | | | | Cr | 1500 | na | | 1-65.6 |
| | | | | Ni | 500 | 3.2-7.1 | | na |
| | | | | Pb | 700 | na | | 13.8-71.6 |
| | | | | Zn | 2000 | 30.1-223 | | 215-476 |
| Robinson et al., 2000 | *S. matsudana x S. alba* | Soil | potX | Cd | 60.6 | 167 | | |
| Rosselli et al., 2003 | *Salix viminalis* | Sewage sludge contaminated compost | field | Cd | 1.8 | 1.30 | 0.05 | |
| | | | | Cu | 557 | 0.05 | 0.50 | |
| | | | | Zn | 620 | 0.50 | 0.00 | |
| Vervaeke et al., 2003 | *Salix viminalis* | Contaminated dredged sediment | field | Cu | 72.5 | 5.30 | 7.6 | 15.1 |
| (other = roots) | | | | Cd | 3 | 3.6 | 4.3 | 3.2 |
| | | | | Pb | 142.9 | 12.7 | 2.9 | 17.7 |
| | | | | Zn | 437.3 | 146.1 | 362.5 | 243 |

In addition to the possibilities of actively cleaning contaminated substrates, the use of willow stands in phytostabilisation and revegetation applications looks promising. The introduction of willow stands results in an effective 'green capping' of the contaminated site. The introduction of a dens willow stand has several positive environmental consequences (Ledin, 1998; Jug et al., 1999). Metals can be stabilised and prevented from leaching as water infiltration is reduced through plant mediated hydraulic control. This is the result of the increased evapotranspiration and the interception of rainwater in the stands canopy. The perennial willow root system demand of water acts as a filter and reduces the risk of contaminant leaching (Sander and Ericsson, 1999). Willow stands can transpire 400-700 mm a year or about 2/3 of the annual rainfall in Flanders (Grip et al., 1984). About 25% of the precipitation is intercepted in the stands canopy and does not reach the site surface. A poplar tree system, for example, allowed less percolation than a barren soil, a good grass cover and a clay cap according to Schnoor (2000). Robinson et al. 2003 presented a case study on the phytoremediation of a 3.6 ha sawdust pile that was leaching unacceptable amounts of boron (B) into local waterways. High water-use *Salicaceae* were used to control leaching to below local threshold levels. In addition, rhizosphere processes and the production of exudates and OM could result in the formation of precipitated and non soluble forms of pollutants further limiting the risks of the spreading of contaminants to the wider environment (Grigal and Berguson, 1998; Lombi et al., 2001).

In addition the the hydraulic control, the development of a high-density perennial root system and the accumulation of OM and litter on the stand surface can prevent the dispersal of contaminants by wind or runoff (Ross et al., 1990; Stomp et al., 1993; Wilkinson, 1999). In recent years willow were planted for the stabilization of radiocesium contaminated soils in the Belarus (Vandenhove et al., 2001), in post mining landscapes (Bungart and Hüttl, 2001), on sanitary landfills (Ettala, 1988; Nixon et al., 2001), and contaminated dredged sediment disposal sites (De Vos, 1994; Vervaeke et al., 2003). In addition, *Salix* species have been used for motorway slope stabilization, the rapid production of natural screens and erosion control (Gray and Sotir, 1992; Verwijst, 2001). Maintenance of natural willow belts around downhill ski tracks improves safety and is used as an avalanche control measurement in several Nordic countries. Watershed management may also include willow planting and maintenance in riparian buffer strips that function as a nutrient catch (Verwijst, 2001). With the introduction of a forest cover, the contaminated site can be transformed to more aesthetically appealing elements in the landscape. However, willow plantations will change the appearance of an earlier open landscape and can limit the visibility. The crop will grow 6-7 m in height before the harvest and, although the willow shed their leaves in winter, the view is disturbed by stems and twigs. This can, however, be seen as an advantage when the plantation is used as a natural screen or buffer between hard to combine land uses or to limit the visibility of disturbing elements in the landscape (Gray, 1992; Luyssaert et al., 2001). In addition, these buffers can reduce the level of noise and the amount of dust and chemicals in the atmosphere (Beckett et al., 1998).

## 2.5 Conclusions

Willow appears a valuable crop for use in phytoremediation and the interest of is growing for their use in extensive remediation projects. However, it is important to determine whether tree planting under any phytoremediation strategy will contaminate the wider environment. An important concern with planting trees on metal contaminated soils is the effect this may have on ecosystem mobility of metals, and the possibility of dispersion of metals into the wider environment. New pathways for contaminated dispersal can be created through leaf fall, root activity, and biomass conversion. Translocation of large amounts of metals to the leaves, for example, may be an undesirable source of food chain accumulation of metals.

# 3 Biomass production and development of *Salix* stands on contaminated dredged sediment disposal sites

Adapted from:
Vervaeke[1], P., Luyssaert[1], S., Mertens[1], J., De Vos[2], B., Speleers[3], L., Lust[1], N. 2001. Dredged sediment as a substrate for biomass production of willow trees established using the SALIMAT technique. Biomass and Bioenergy 21: 81-90.

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**Abstract**

The periodic dredging of inland waterways and the subsequent disposal of the dredged sediment result in the continuous establishment of contaminated sites. As this dredged sediment is rich in nutrients, occupies extended areas, and is often unsuitable for agriculture and public works due to the presence of contaminants, planting energy crops is one option for the remediation of this waste material. To evaluate dredged sediment as a substrate for growing willows, a 20 x 150 m disposal depot was successfully planted using rolls of connected willow rods (SALIMAT). Rods of a *Salix fragilis* clone and a *Salix triandra* clone were equally mixed in each mat. This SALIMAT proved to be an economic and effective planting technique for large areas of wet substrate. Leaf nutrient contents were determined to identify potential limiting growth factors and the biomass production and tree survival over 4 years of stand development were assessed for three different planting spacings (10, 20 and 40 cm). Results of the foliar analyses indicated that both species were supplied with sufficient N, P, K, and Ca to ensure optimal growth. The introduction of SALIMAT resulted in the rapid development of a high-density fast growing stand characterized by shoot densities of up to 54 shoots/$m^2$. An average annual production of 12.7 ton DM/ha was measured. The mixture of the two clones did not result in a polyclonal stand as *Salix triandra* was suppressed by *Salix fragilis*. The development of a willow stand was unsuccessful on parts of the depot with a sand fraction of 60%.

## 3.1 Introduction

In Europe, the percentage of total energy production provided by renewable energy should reach 12% in the year 2010. About 8% should be derived from the production off biomass (White Paper for a Community Strategy and Action Plan – Energy for the Future: Renewable Sources of Energy, 1997). Belgium aims at doubling the production of renewable energy to 3% of the total energy production. SRF with fast growing tree species, such as willow and poplar, is a promising alternative to substitute fossil fuel and it is an increasingly used practice for the production of energy in different European countries such as Sweden and Finland. However, large scale cultivation of energy crops has not yet started in other parts of Europe. Unstable markets, high prices of land negatively influence the financial feasibility of projects, and wide spread social acceptance of these crops is still lacking (Hanegraaf et al., 1998; Garcia Cidad et al., 2003). A possible option to reduce the impact of these problems is combining the cultivation of energy crops with other possible functions of the land (Aronsson and Perttu, 2001).

The extensive reclamation of derelict and contaminated sites by the introduction of a vegetation cover has received increased attention in recent years (Glimmerveen, 1996; Lepp and Dickinson, 1998; Dickinson, 2000). The focus in dealing with the reclamation of contaminated land is gradually shifting away from the traditional 'removal and disposal' techniques to more integrated in-situ approaches such as phytoremediation. The use of a vegetation cover may allow a complete long-term rehabilitation of extended contaminated sites to be achieved. When energy crops, such as willow trees, are used for the revegetation of contaminated sites with few alternative uses, additional income can be generated through the production of biomass for energy.

In Flanders, large areas along waterways were historically used to dispose dredged sediment and this practice is still continuing. Currently, the disposal on land is typically in the form of a complete containment or a landfill with few other functions. However, the shortage of available land for such disposals is becoming an increasingly important problem. As land disposed dredged sediments are rich in nutrients, occupy extended areas and often is unsuitable for use in agriculture and rural works due to the presence of contaminants, planting energy crops could be a possibility for the revalorization of this waste material.

Due to the wet conditions of hydraulically confined dredged sediment, the generally used planting methods with cuttings cannot be used to introduce willow stands (De Vos, 1994). Field trials showed that the introduction of loose plant material (cuttings, seeds) was generally not successful as the plant material floats away due to rainfall or superficial draining before rooting occurred. The vertical planting of cuttings into the sediment, using a small boat, showed acceptable results but this method is expensive and highly labor intensive. To overcome these problems, the Laboratory of Forestry of the Ghent University and the firm De Vos '*Salix*' developed a technique for planting willow on wet, inaccessible substrates such as dredged sediment. This technique, called SALIMAT, is based on the vegetative reproduction of willow from horizontally inlayed willow rods. Willow rods with a length of 2 m are tied together with biodegradable string and subsequently rolled around a central disposable tube. Different planting densities can be achieved with this technique as the length of the string used to hold the rods together can be adjusted. The technique offers multiple advantages (De Vos, 1994): SALIMATS i) can be mechanically manufactured off site, ii) are easy to store and transport and iii) are a practical, low-cost, mechanized planting method.

This chapter reports on the experiences with the SALIMAT technique for the introduction of willow on wet substrates. It evaluates the use of dredged sediment as a substrate for the growth of fast growing willow species based on leaf nutrient contents. The biomass production and tree survival over six years of stand development are reported for three different planting densities.

## 3.2 Materials and methods

### *3.2.1 Site description*

In March 1993, a 150 by 20 m depot at the experimental site in Menen (Belgium) was raised 2 m with dredged sediment from the adjacent river Leie. The dredged sediment was mixed with water and pumped hydraulically into the depot. Excess water was removed through an overflow collector at the end of the depot. One week later, the depot was planted with willow using the SALIMAT technique. The SALIMATS were unrolled horizontally by dragging the tube right across the width of the depot. Three different spacings between the rods were tested, 10, 20, and 40 cm, with four replications of each planting density over the length of the depot. Two indigenous species, *Salix triandra* L., Almond willow, (clone 'Noir de Villaines') and *Salix fragilis* L., Crack willow, (clone 'Belgisch rood') were equally mixed in each mat. After the establishment of the stand a 22-point grid was defined. No additional management inputs such as herbicides and fertilizers were used in the trial.

### *3.2.2 Sampling and measurements*

After the first growing season, every grid point (n = 22) was sampled down to 25 cm to determine the substrate's main chemical and physical characteristics. Leaves were sampled in the first, second, and sixth growing season. In the first and second growing season, all leaves from at least two trees were collected at each of the 22 grid points, mixed and sub-sampled. The time of sampling was the second week of august. In the sixth growing season, the same procedure was repeated but only on the 17 grid points in the *Salix fragilis* stand. After each growing season, from 1993 to 1998, at least 12 circular plots (four for each spacing) with a radius of 1 m were randomly chosen and cut from the stand at ground level to determine above ground biomass.

Trees were subsequently cut in pieces and weighed on the site. Sub-samples of the wood were taken to determine the moisture content. Samples were dried in a forced air oven for three days at 105°C. Shoot density was counted after the first, third , and sixth growing season in randomly chosen 3.14 $m^2$ sample plots.

### *3.2.3 Chemical analyses*

The soil samples were analyzed for soil pH ($H_2O$) and electrical conductivity (EC). Total nitrogen was determined using the modified Kjehldahl method (Bremner, 1996); the soil carbon content was analyzed using the Walkley and Black method (Nelson and Sommers, 1996). Nutrients (P, K, Mg, Ca) and metals (Cd, Pb, Zn, Cu, and Ni) were extracted from 3 g sub-samples with an *aqua regia* extraction of HCl and $HNO_3$, and were subsequently determined on ICP-AES (Varian Vista-axial, Varian, Palo Alto, CA). The particle size distribution of the dredged sediment was analyzed using the pipette method based on Stokes sedimentation law as proposed by Gee and Bauder (1986).

The sampled leaves were ground with a mortar and pestle, and dried at 70°C for three days before analyses. Leave samples from the first two growing seasons were digested in a nitric acid mixture after ashing at 450°C, samples from the 6$^{th}$ growing season were digested using microwaves. Leaf nutrient concentrations of P, K, Mg, and Ca in the digests were determined on ICP-AES. Leaf nitrogen concentrations were determined using the modified Kjehldahl method (Bremner, 1996).

## 3.3 Results

### *3.3.1 Substrate characteristics*

The hydraulic filling of the depot resulted in the establishment of a swampy, impassable terrain, which was waterlogged at several places. Due to the different sedimentation characteristics of the sediment fractions two areas could be observed in the depot: close to the inlet of the depot a sand plate developed as the heavier sand fraction settled fast while the silt and clay fractions were transported further from the inlet as they remained in suspension. The length of this sand plate was about 10 m; the other 140 m was characterized by a slight texture gradient. Results of the physical and chemical analyses of the substrate samples are presented in Table 3–1. The minimum and maximum values give an indication of the texture-correlated nutrient and contaminant concentrations with minimal values describing the sand plate characteristics and maximal values representing the concentrations found in the most clayey parts of the depot.

### *3.3.2 Stand establishment*

By dragging the tubes across the depot the SALIMAT planted itself by slightly sinking into the sediment under its own weight. Establishment of the SALIMAT was successful as the rods sprouted one week after planting. SALIMATS on the sand plate (20 x 10 m) close to the inlet of the depot did not produce shoots, as rods did not sink into the substrate. It is thus vital that the rods are covered with a layer of sediment and water to prevent desiccation. After one month, a dense cover of small willow shoots covered the rest of the depot.

Table 3–1: Characteristics of sediment substrate samples (0 – 25 cm) at 22 grid points (n= 22).

| | | Mean | Standard error | Min. | Max. |
|---|---|---|---|---|---|
| pH-$H_2O$ | | 7.0 | 0.0 | 6.4 | 7.2 |
| EC | µS/cm | 1695.8 | 123.3 | 951.0 | 2980.0 |
| Carbon | % | 3.3 | 0.2 | 1.7 | 5.6 |
| $CaCO_3$ | % | 7.3 | 0.1 | 6.3 | 9.3 |
| Sand (>50 µm) | % | 27.9 | 2.6 | 10.2 | 64.2 |
| Silt (2-50 µm) | % | 46.0 | 1.9 | 22.8 | 60.3 |
| Clay (<2 µm) | % | 22.7 | 0.9 | 17.3 | 32.3 |
| N | g/kg | 2.9 | 0.2 | 1.7 | 4.6 |
| P | g/kg | 8.9 | 0.4 | 5.3 | 14.0 |
| K | g/kg | 4.3 | 0.2 | 2.8 | 5.7 |
| Ca | g/kg | 28.8 | 0.4 | 25.4 | 33.7 |
| Mg | g/kg | 3.4 | 0.1 | 2.9 | 4.0 |
| Zn | mg/kg | 577.0 | 21.7 | 441.2 | 818.6 |
| Pb | mg/kg | 121.4 | 4.1 | 86.9 | 159.2 |
| Cd | mg/kg | 4.6 | 0.2 | 3.0 | 6.8 |
| Cu | mg/kg | 75.4 | 2.7 | 56.9 | 101.4 |
| Ni | mg/kg | 45.1 | 2.3 | 28.1 | 72.1 |
| Cr | mg/kg | 107.7 | 3.9 | 82.6 | 148.5 |

### *3.3.3 Leaf nutrient concentrations*

The results of the foliar analysis are used in this study to identify potential limiting growth factors of the sediment. Rytter and Ericsson (1993) concluded that the most commonly used base for expressing the nutrient status of plants, i.e. nutrient amount per unit dry weight of leaves, gives an adequate description of the nutritional status of *Salix* trees on fertile soils. To evaluate the nutrient status of dredged sediment for the growth of willows the leaf nutrient contents on a leaf dry weight basis (Table 3–2) are compared with the threshold contents of nutrients in leaves for sufficient and optimal growth as postulated by van den Burg (1990) (Table 3–3). No visual indications of nutrient deficiency were observed in this trial.

Table 3–2: Mean values with standard errors for the foliar nutrient contents (g/kg) of *Salix fragilis* ‘Belgisch rood’ and *Salix triandra* ‘Noir de Villaines’ in the first, second, and sixth growing seasons (n = 22).

| | *S. fragilis* 'Belgisch Rood' | | *S. triandra* 'Noir de Villaines' | |
|---|---|---|---|---|
| 1993 | Mean (g/kg) | St. Error | Mean (g/kg) | St. Error |
| N | 27.91 | 0.82 | 35.52 | 0.42 |
| P | 2.57 | 0.07 | 2.99 | 0.10 |
| K | 21.45 | 0.78 | 19.45 | 0.64 |
| Ca | 17.66 | 0.76 | 11.92 | 0.40 |
| Mg | 1.68 | 0.04 | 1.55 | 0.03 |
| 1994 | Mean (g/kg) | St. Error | Mean (g/kg) | St. Error |
| N | 28.23 | 0.39 | 35.3 | 0.35 |
| P | 7.95 | 0.25 | 8.44 | 0.22 |
| K | 20.76 | 0.56 | 18.51 | 0.30 |
| Ca | 14.71 | 0.44 | 9.82 | 0.16 |
| Mg | 2.87 | 0.06 | 2.03 | 0.08 |
| 1998 | Mean (g/kg) | St. Error | | |
| N | 23.93 | | | |
| P | 1.94 | | | |
| K | 23.75 | | | |
| Ca | 28.53 | | | |
| Mg | 3.46 | | | |

Table 3–3: Nutrient concentrations (g/kg) in *Salix* leaves for sufficient and optimal growth of willow (van den Burg, 1990).

| | Sufficient (g/kg) | Optimal (g/kg) |
|---|---|---|
| N | 22.0 | 30.0 |
| P | 1.8 | 2.1 |
| K | 8.0 | 18.0 |
| Ca | 3.5 | 4.5 |
| Mg | 1.6 | 3.0 |

The concentrations of N in the *Salix fragilis* and *Salix triandra* leaves sampled in the first growing season were 2.79 and 3.55%, respectively, indicating that both species were well supplied with nitrogen (van den Burg, 1990). The amount of available N in the dredged sediment can be considered to be sufficient for *Salix fragilis* and optimal for *Salix triandra*. The N concentrations of both clones in the first and second growing season were comparable but this was not the case for the foliar P concentrations of both clones. Mean phosphorous concentrations in leaves of the 2 year old *Salix fragilis* and *Salix triandra* trees were 7.95 g P/kg, and 8.44 g P/kg, respectively, while the concentrations in the 1 year old stand were 2.57 g P/kg and 2.99 g P/kg.

In every growing season, the concentrations of phosphorous in the leaves of both clones surpassed the 2.1 g P/kg level for optimal P supply (van den Burg, 1990). Rytter and Ericsson (1993) reported the highest P content of 4-5 g P/kg in the second half of the season. After six years of growth the *Salix fragilis* stand is still sufficiently supplied with N and P.

Mean foliar potassium concentrations in the first growing season of 21 and 19 g K/kg in the *Salix fragilis* and *Salix triandra* leaves, respectively, were also higher than the threshold values for optimal growth. Van den Burg (1990) recommended 8 and 18 g K/kg as threshold values for sufficient and optimum growth. The fast growing willow stands on fertile arable soils in the study of Rytter and Ericsson (1993) featured concentrations between 15 and 20 g K/kg in their aerial tissue.

The willows growing on the dredged sediment were provided with a high level of Ca. Mean Ca concentrations in the *Salix fragilis* and *triandra* trees reached 17.7 g Ca/kg and 11.9 g Ca/kg, respectively, in the first growing season and far exceeded the critical Ca concentration for optimal growth of 4.5 mg Ca /kg reported by van den Burg (1990) although the second growing season Ca levels were lower (Table 2). According to Rytter and Ericsson(1993), vigorous *Salix viminalis* L. stands on fertile clayey soils where characterized by foliar Ca concentrations between 12 and 15 g/kg.

Foliar Mg concentrations were 2.87 g/kg and 2.03 g/kg for the *Salix fragilis* and *Salix triandra*, respectively, in their second growing season. Willows are well supplied with Mg if they contain between 2 and 2.5 g/kg of this element in their foliage (van den Burg, 1990; Rytter and Ericsson, 1993). Concentrations found in leaves sampled during the first growing season were below these threshold values, indicating an insufficient supply for this period, although no visual symptoms of Mg deficiency were observed

### *3.3.4 Stand density*

High densities of shoots per hectare were observed after the first growing season (Table 3–4). A distance of 10 cm between the rods resulted in the highest total shoot density of 545,000 shoots/ha with 20 or 40 cm spacings leading to 330,000 and 230,000 shoots per hectare, respectively. After the first growing season 20% of all shoots had died in the 10 cm spacing while these percentages were 5 and 20% for the 20 and 40 cm treatments, respectively. However, with 440,000 living shoots/ha, the number of living shoots in the 10 cm treatment was still 40% and 136% higher then the number in the 20 and 40 cm treatments. *Salix fragilis* showed the better stand establishment on dredged sediment as was shown by the higher shoot densities in all treatments. In the mats with 10 cm of spacing, one third of the total living shoots are of the *Salix triandra* clone resulting in a *triandra/fragilis* ratio of 0.5. This difference declined with increasing rod spacing with a ratio of 0.6 at the 20 cm spacing and 0.7 at 40 cm.

Two growing seasons later the total number of trees (dead and living) was reduced by 53%, 25%, and 20% for the 10, 20, and 40 cm treatments, respectively. After three years the effect of the rod spacing on the density of living trees was negligible, as the number of living trees in all treatments had decreased to about 110,000 per ha with no significant differences between the treatments. The density of dead shoots however still reflected the spacing density. Shoot densities of *triandra* trees were just below those of *fragilis* in each treatment. In the 10 and 40 cm treatments the *triandra/fragilis* ratio was 0.66, whereas in the 20 cm treatment slightly more *triandra* then *fragilis* trees were found as indicated by a ratio of 1.16. From the 5$^{th}$ growing season *Salix triandra* trees disappeared from the stand as a result of the competition with the faster developing *Salix fragilis* trees. The density of living *Salix fragilis* trees was further reduced to about 32,000 per ha, while the dead wood density was 100,000 trees per ha. After the $6^{th}$ growing season, no significant difference in living and dead tree density could be observed between the different spacings.

Table 3–4: Shoot densities of *Salix fragilis* 'Belgisch Rood' and *Salix triandra* 'Noir de Villaines' in their first, third and sixth growing season at 3 different rod distances (shoots/$m^2$). Characters in superscript indicate homogenous sub-groups with no significant differences between means according to Tuckey's post hoc test ($\alpha$ = 0.05).

| Year | Rod distance | *S. triandra* shoots/$m^2$ | *S. fragilis* shoots/$m^2$ | Sum living shoots/$m^2$ | Dead shoots/$m^2$ | Living + dead shoots/$m^2$ |
|---|---|---|---|---|---|---|
| 1993 | 10 | $15.25^{a}$ | $28.50^{a}$ | $43.75^{a}$ | $10.75^{a}$ | $54.50^{a}$ |
| | 20 | $11.75^{ab}$ | $19.25^{ab}$ | $31^{ab}$ | $1.75^{b}$ | $32.75^{ab}$ |
| | 40 | $7.50^{b}$ | $11^{b}$ | $18.50^{b}$ | $4.75^{ab}$ | $23.25^{b}$ |
| 1995 | 10 | $4.25^{a}$ | $6.25^{a}$ | $10.50^{a}$ | $15^{a}$ | $25.50^{a}$ |
| | 20 | $6.50^{a}$ | $5.50^{a}$ | $12^{a}$ | $12.75^{a}$ | $24.75^{a}$ |
| | 40 | $3.75^{a}$ | $5.75^{a}$ | $9.50^{a}$ | $8.75^{b}$ | $18.25^{b}$ |
| 1998 | 10 | / | $3.26^{a}$ | $3.26^{a}$ | $12.27^{a}$ | 15.43 |
| | 20 | / | $3.25^{a}$ | $3.25^{a}$ | $8.75^{a}$ | 12.02 |
| | 40 | / | $3.02^{a}$ | $3.02^{a}$ | $9.95^{a}$ | 12.97 |

### *3.3.5 Biomass production*

The annual and cumulative production rates are presented in Figure 3–1. The mean annual production measured on the site was 12.7 ton DM/ha. After the first growing season, 10.3 ton DM/ha of total standing biomass was measured over the whole of the depot. Tree growth was the most vigorous in the second growing season with an increment of 17.5 ton DM/ha/year. Figure 3–2 shows the biomass production for both the investigated *Salix* stands and the dead wood biomass in the first four growing seasons of stand establishment. In the first growing season, the yield dropped from 11.97 ton DM/ha to 8.23 ton DM/ha with increased spacing between the rods from 10 cm to 40 cm. Dead wood constituted about 14-15% of the total biomass in all treatments, indicating that the amount decreased proportionally with increased rod spacing. With the 10 cm spacing the amount of *Salix fragilis* biomass was more than double the biomass of *Salix triandra*. This difference was smaller at lower planting densities. The amount of living and dead biomass increased by 17 and 0.5 ton DM/ha, respectively. The percentage dead wood was lower than in the first growing season as only about 5 to 8% (for 40 and 10 cm spacings) of the above ground biomass was found to be dead. If the stand was harvested after three years, the mean yield of the three treatments would reach 43.1 ton DM/ha of which 8.5% was dead. Only one quarter of the biomass consisted of *Salix triandra* indicating inferior growth compared to the *Salix fragilis* clone. This percentage decreased to 15% after the fourth growing season. Four years of stand development resulted in a standing above ground biomass of 55.7 ton DM/ha, representing a mean annual biomass production of 13.9 ton DM/ha/year. From the fifth growing season, the *Salix triandra* trees almost completely disappeared from the stand. Some individuals were left on the border of the disposal site. After the sixth growing season, a total production of 76.4 ton DM/ha was measured. In the fifth and sixth growing season, the percentage of dead wood was to 15% of the total biomass.

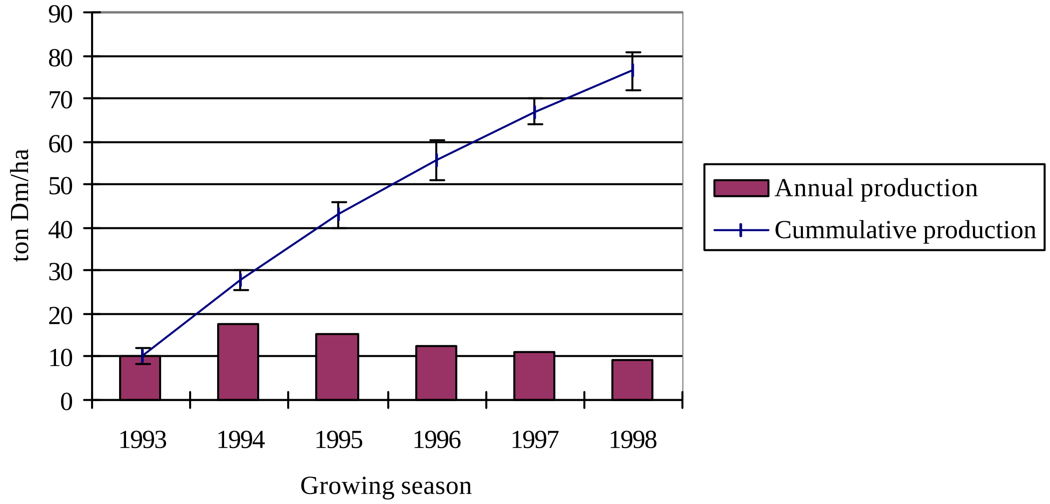


Figure 3–1: Annual and cumulative biomass production of the investigated *Salix* stand

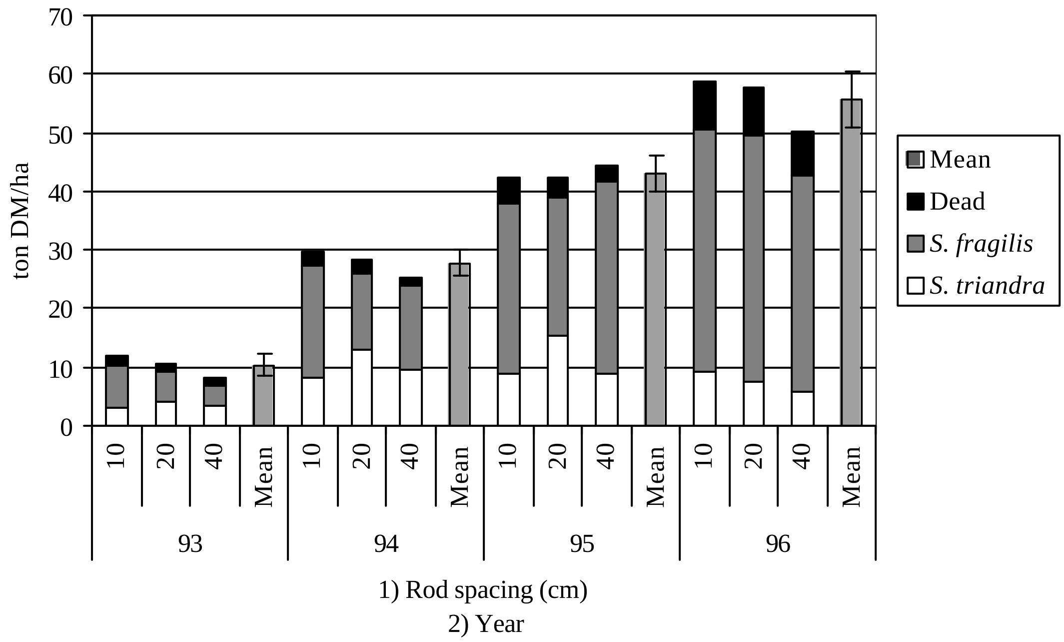


Figure 3–2: Biomass determined after each growing season of a mixed stand of *Salix triandra*, 'Noir de Villaines' and *Salix fragilis*, 'Belgisch Rood' on dredged sediment (ton DM/ha)

## 3.4 Discussion

The SALIMAT planting technique proved to be successful for the rapid introduction of a dense willow stand on land disposed, dredged sediment. Within a few weeks after introduction, the dredged sediment depot was covered by a dense willow stand, with a number of positive consequences already described by several authors (Perttu and Kowalik, 1997; Glimmerveen, 1996; Punshon and Dickinson, 1997). Owing to the production of a large amount of litter there is, with time, an increase in the humus content of the substrate that favors the biochemical stabilization of the dredged sediment by increased nutrient cycling and the activation of a soil biotic community leading to the initiation of soil formation and creation of a forest microclimate (Ledin, 1998). Through the development of a high-density, perennial root system and the accumulation of OM and litter on the soil surface, the dispersal of contaminants by wind or runoff is greatly reduced (Riddel-Black, 1994). Nutrients and metals are stabilized against leaching as water infiltration is reduced by increased evapotranspiration and the interception of rainwater by the canopy (Persson and Lindroth, 1994; Ledin, 1998). In addition, the high evaporation rates increase the dewatering speed of the sediment. At the same time the site is landscaped and integrated into its environment. In this way, confined dredged sediment disposal sites, which were previously derelict can be transformed to more aesthetically appealing elements in the landscape. Considering the above mentioned beneficial influences of growing fast growing energy crops, the introduction of the SALIMATS can be regarded as a phytostabilization step in the remediation of dredged sediment depots. In addition to the use of willows for phytostabilisation they can also be used for phytoextraction of heavy metals. Studies have shown that there is a relatively large uptake of cadmium into the shoots of *Salix* plants (Punshon and Dickinson, 1997; Ericsson, 1994; Östman, 1994). This implies a potential to clean dredged sediment of cadmium through the export of metals with the repeated harvest of biomass. This aspect will be further discussed in Chapter 4 of this work.

An important factor for the success of the SALIMAT technique is the moisture content of the substrate. The substrate should be wet or saturated with water to allow optimal rooting of the *Salix* rods. It is vital, therefore, that the SALIMAT sinks slightly into the substrate to avoid desiccation. The technique is not suited to gravel, sandy textured soils or consolidated sediment (crusts). Based on the results of the particle size analysis (Table 3–1) it can be concluded that the introduction of SALIMAT will not be successful on mineral substrates with a sand fraction around 60%. Only a small area of the depot close to the inlet had such a high sand fraction, the rest of the depot being filled with medium textured, dredged sediment. The medium texture across the majority of the depot and the neutral pH of the dredged substrate can be considered optimal for willow growth and nutrient availability (Heilman and Norby, 1998; Ledin and Willebrand, 1995). In addition, the high buffering capacity of the sediment due to the high amounts of $CaCO_3$ present will prevent acidification and reduce metal leaching. It is possible to apply the SALIMATS on dry surfaces if the precautions necessary to prevent desiccation of the rods are followed. On dry surfaces, the SALIMATS can be unrolled with a tractor or by hand and should then be covered with a thin layer of soil. Another limitation is that the SALIMAT introduction is restricted to the period from November until the end of April. Activities should be planned to finish dredging and land filling during this period to optimize field conditions for SALIMAT application.

The results of the foliar macronutrient levels indicate that the *Salix* species were growing under favorable conditions for the production of biomass. To summarize the comparison of leaf nutrient concentrations with those of Van den Burg (1990), the amounts of available P, K, and Ca present in the dredged sediment were sufficient to ensure optimal growth of willow. In addition, the foliar N, P, K, Ca, and Mg concentrations of both clones in this experiment were comparable with the nutrient concentrations of willows growing on fertile arable soils in Sweden as reported by Rytter and Ericsson (1993). The N concentration of the *Salix fragilis* trees was slightly below the 3% N threshold for optimal growth. The amount of available N in the dredged sediment can thus be considered sufficient for *Salix fragilis* and optimal for *Salix triandra*. In general, nitrogen is the element most limiting the production of biomass in SRF when all other factors are favorable (Heilman and Norby, 1998). Rytter and Ericsson (1993) determined foliar nutrient concentrations of 2 year old *Salix viminalis* stands on very fertile arable soils in Sweden during August and September, and recommend 30 g N/kg as optimal for growth in accordance with van den Burg (1990). Jug et al. (1999) also concluded that concentrations above 3% are needed for optimum growth as they observed that willows supplied with N fertilizer only showed superior yields when foliar concentrations were between 3 and 4%. Concentrations above 4% indicated luxury uptake.

With an increment of 13.9 ton DM/ha/year in the first 4 years after establishment, the willow stand on dredged sediment was highly productive. The high biomass production is additional evidence for the suitability of dredged sediment as a substrate for the growth of fast growing willow species. In SRF, yields normally vary from 10 to 15 ton DM/ha/year depending on management and site characteristics, while exceptional productions up to 20 ton DM/ha/year have been reported (Ledin and Willebrand, 1995). Biomass yields in this study were achieved with clones that had not been selected for high biomass production, probably underestimating the potential biomass production with selected *Salix viminalis* clones. After the first growing season there were differences in yields between the different spacings tested as the yield increased with increasing planting density. These differences became smaller in later growing seasons especially between the 10 cm and 20 cm treatments. The biomass production over 4 years obtained with these two planting densities was about 58 ton DM/ha. Using 40 cm between the rods resulted in a lower yield of 50 ton DM/ha after 4 years. In each of the four growing seasons the amount of dead wood decreased with decreasing planting density. Competition between trees is most intense when higher plant densities are used. Mortality in the first year after introduction was greatest, as shoots were vulnerable to stress and competition. In the second growing season mortality was reduced due to the selection that had occurred during the first growing season. Following the second growing season the percentage of dead biomass increased again, indicating mortality due to increased competition between trees combined with lower increments of living biomass. All treatments featured the same percentage of dead wood after four growing seasons (15%) indicating a proportional increase of dead and living biomass with increased plant density. Willebrand et al. (1993) concluded for SRF that the dependence of yield on initial planting density disappears at higher densities and becomes weaker at low densities in later rotations. As very high densities of shoots are obtained using the SALIMAT technique it is likely that after several more growing seasons, yields would be similar for all three treatments. The differences between treatments would also disappear if the stand was coppiced after for example 4 years. This is indicated by the similar densities of living trees after three years for each of the three treatments. After coppicing, the stools of these trees will grow the shoots for the next rotation.

The mixture of *Salix triandra* and *Salix fragilis* in the SALIMATS did not result in a polyclonal stand as the *Salix triandra* was suppressed by the *Salix fragilis*. After four years, only 15% of the living biomass consisted of *Salix triandra*. From the fifth growing season, the *Salix triandra* trees almost completely disappeared from the stand. Some individuals were left on the border of the disposal site. *Salix fragilis* is known to be rather undemanding of soil type, and to grow well in locations with elevated moisture content or in dry valleys. It is one of the tallest tree-like willows as it can attain a height of 20 m. *Salix triandra* is a shrub or small tree up to 9 m high and is one of the easiest rooting willows (Pohjonen, 1993). Only on the borders and on a small patch next to the inlet of the depot did *Salix triandra* trees survive. This patch was the transition zone between the sand plate and the rest of the disposal site and was characterized with a coarser texture compare to the rest of the disposal site. *Salix fragilis* rods failed to root in this zone as they were not covered by a sediment layer and subsequently desiccated. The fact that *Salix triandra* established on this part can be explained by its good rooting capabilities, even when the rods did not sink entirely into the dredged sediment. This highlights another advantage of the SALIMAT technique. Clones, which grow in different soil and moisture conditions, can be incorporated into one SALIMAT. In this way, surfaces with a great variability in soil and moisture conditions, which is often the case with larger disposal sites for dredged sediment, can be successfully planted over their entire area. If only one clone was used, spots with unfavorable growth conditions would remain as open gaps in the stand. This would result in an ineffective capping of the site and in a lower biomass production per hectare.

### 3.5 Conclusions

The SALIMAT planting technique proved to be successful for the rapid introduction of a dense willow stand on land disposed dredged sediment, and was highly efficient and cost effective compared to traditional planting techniques. However, success of the planting technique is highly dependent on the moisture content and particle size distribution of the sediment. The applied willow rods should sink into the sediment to allow proper rooting to take place. From the leaf analysis and yield results it can be concluded that this dredged sediment provided a suitable substrate for the growth of fast growing trees for biomass production. Biomass production results were comparable and often higher than production reported in traditional willow plantations. Very high stem number densities were achieved in the first growing seasons after planting which decreased rapidly as a result of natural thinning The different planting designs tested did not result in significantly different biomass production values after several growing seasons. SALIMATS with larger spacings between the rods should thus be considered to reduce application costs. The introduction of SALIMATS results in an effective 'green capping' of the polluted site through the development of a high density, fast growing stand with a long growing season. The introduction of the SALIMATS can thus be regarded as a phytostabilization step in the remediation of dredged sediment disposal sites. Through the development of a high density, perennial root system and the accumulation of OM and litter on the soil surface, the dispersal of contaminants by wind or runoff can be reduced.

# 4 Seasonal changes of heavy metals in biomass compartments of *Salix* stands growing on contaminated dredged sediment: potentials and limitations for phytoremediation

Vervaeke[1], P., Mertens[2], J., Lust[2], N., Tack[1], F.M.G. 2004. Seasonal changes of heavy metals in biomass compartments of *Salix* stands growing on contaminated dredged sediment: potentials and limitations for phytoremediation. Environmental Science and Technology, submitted.

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## 4.1 Introduction

In the previous chapter it was shown that hydraulically raised dredged sediment can be successfully planted with *Salix* species and is a suitable substrate for the production of willow wood. However, sediments dredged from waterways are often polluted with metals, PAHs, and mineral oil. This limits the possibilities for the re-use of this material in public works and agriculture. As traditional remediation techniques are often not economically feasible, the current remediation option for contaminated sediment in Belgium is disposal in confined landfills. This results in the establishment of fertile but contaminated sites with little beneficial uses. In addition, the shortage of land for disposal is becoming an increasingly important problem. A lack of options for storage, remediation and re-use of dredged sediments limits the planned dredging activities required. The combined land use of dredged sediment disposal and biomass production for energy purposes, with the potential for phytoremediation, could thus be an economically and ecologically valuable land use option on historic and future sediment disposal sites.

While willows are excellent producers of biomass, they are also characterized by an array of characteristics that make these species promising for phytoremediation applications. It is recognised that certain willow clones have a strong potential for heavy metal uptake (Landberg and Greger, 1994). This characteristic is, as with metal tolerance, species and clone dependent (Dickinson et al. 1994). Table 2–1 presents a list of research papers on metal accumulation by willow species with the measured metal concentrations in the investigated biomass compartments. Especially the uptake of Cd by selected *Salix* species and clones is already well documented. *Salix* can be defined as a high accumulator rather then a hyper accumulator. Contents of 0.4–3.9 mg/kg stem-wood have been measured in a range of *Salix* clones growing on Cd enriched agricultural land (Ledin, 1998). Punshon and Dickinson (1997) reported high Cd concentrations up to 44 mg/kg in leaves and 76 mg/kg in stems of *Salix cinerea* growing on mining spoil. SRF with metal accumulating trees could thus be used to remove heavy metals from the substrate through repeated harvest of the woody biomass. (Dickinson, 1996; Punshon and Dickinson, 1997). Greger et al.

(1997), for example, reported that 12 years of willow growth would be required to remove the Cd accumulated in Swedish soils during the last century.

Optimizing management practises, such as the rotation length and harvest time, can increase the efficiency of the phytoremediation process (Ensley et al., 1997). In this context, seasonal variations of heavy metal concentrations in the different aboveground biomass compartments and changes with stand age can be important parameters to optimize the management of a phytoextraction system to ensure maximal metal export with harvest, and to correctly measure metal fluxes in the ecosystem (Ross, 1994). In addition, seasonal changes in leaf metal concentrations can be important in assessing the risk of planting willow on contaminated land. An important concern with planting trees on metal contaminated soils is the effects this may have on ecosystem mobility of metals, and the possibility of dispersion of toxic metals to the environment. An important pathway of metal dispersal in such ecosystems is leaf fall. After autumn, leaves can be blown from the stand, which disperses heavy metals further from the contaminated site. More importantly, the produced litter layer is an essential carbon and nitrogen source in the contaminated ecosystem. The litter decomposition can thus result in the introduction of heavy metal in the food chain, as many soil (micro-)organisms contribute to this process.

The aim of the experiment reported in this chapter was to assess the seasonal variations and changes with stand age in metal concentrations of two willow clones grown on contaminated dredged sediment. Subsequently, metal stocks were calculated with the help of biomass results of the different tree compartments. Results from this experiment will allows an evaluation of the feasibility of removing heavy metals from dredged sediments with a willow based phytoextraction system and assess metal losses to the environment with leaf fall. The experiment was performed on tree stands of four different ages to investigate if the harvesting cycle could influence the amount of exported metals.

## 4.2 Methods and Materials

### *4.2.1 The experimental site and design*

The experimental dredged sediment disposal site in Menen (Belgium, 50°48' N, 3°08' E) was established in 1991 along the river Leie. The site covers an area of 4 ha and consists of 18 dredged sediment disposal sites: six large disposal sites with an area of 150 x 20 m and 12 isolated small disposal sites with an area of 10 x 20 m. All the disposal sites (DS) were hydraulically filled with dredged sediment from the adjacent river Leie from 1992 to 1998, and were subsequently planted with *Salix*. For this experiment, four plots were selected in different dredged sediment disposal sites based on tree species and the time of stand establishment. Trees in these four plots were in their first, second, fourth, and sixth growing season in 1999, the year of sampling. An overview of the sampled plots is presented in Table 4–1.

Table 4–1: Overview of the sampled disposal sites and plots

| Disposal site | Area | Raised | Planted | Species | Plot area | Label |
|---|---|---|---|---|---|---|
| DS6 | 150 x 20 m | 1992 | End 1992 | *Salix fragilis* | 10 x 20 m | FR6 |
| DS4 | 10 x 20 m | 1994 | End 1994 | *Salix fragilis* | 10 x 20 m | FR4 |
| DS2 | 50 x 20 | 1995 | Start 1997 | *Salix fragilis*<br>*Salix triandra* | 20 x 20 m with eight 25 $m^2$ sub-plots of each species | FR2<br>TR2 |
| DS1 | 100 x 20 m | 1995 | Start 1998 | *Salix fragilis*<br>*Salix triandra* | 40 x 20 m with eight 50 m2 sub-plots of each species | FR1<br>TR1 |

DS6 was filled in 1992 and was planted the same year with *Salix fragilis* 'Belgisch Rood' (FR) using the SALIMAT technique (Vervaeke et al., 2001). Trees on this DS were in their sixth growing season at the time of sampling. A 10 by 20 m plot was selected and tree samples from this plot will be labeled FR6 in the remainder of this chapter. DS4 was raised and planted in 1994 with *Salix fragilis* 'Belgisch Rood', also using the SALIMAT technique. Trees on this disposal site were in their fourth growing season at the time of sampling. Samples from this plot were labeled with FR4 for this investigation. Another 150 x 20 m disposal site was raised in 1995 and subsequently split in two plots with an embankment. One plot was planted in 1997 (DS2), the other in 1998 (DS1), both with two willow species *Salix fragilis* 'Belgisch rood' and *Salix triandra* 'Noir de Villaines' (TR), using the SALIMAT technique. Eight separate sub-plots of both species were established in a checker pattern in both the main DS1 and DS2 plots. Samples from the 2 year *Salix fragilis* and *Salix triandra* sub-plots were labeled FR2 and TR2, respectively. Accordingly, the labels FR1 and TR1 were used for the samples from the 1 year old trees.

### *4.2.2 Sampling and analysis*

Dredged sediment in each of the four plots was characterized for its main chemical and physical characteristics. Soil samples were taken in March 1998 with an auger to a depth of 30 cm. The largest plots with the 1 and 2 year old willow were sampled 16 and 12 times, respectively. The smaller plots with the 4 and 6 year old trees were sampled 4 and 5 times, respectively. All soil samples were dried at 105°C, milled, passed through a 2 mm mesh, and mixed. The pH of the samples was measured in a 1:5 sediment:deionized water suspension. Total nitrogen was determined using the modified Kjehldahl method (Bremner, 1996), the Walkley Black method (Nelson and Sommers, 1996) was used to assess the amount of OM in each sample.

Other element concentrations (K, P, S, Cd, Cr, Cu, Ni, Pb and Zn) were extracted using a $HNO_3$/HCl/HF mixture during microwave digestion (CEM, MDS 2000). During a 14 minute time span, the power of the microwave system was increased from 250 W to 600 W while the pressure in the vessel was kept at a constant 25 bar. The vessel content was then filtered over a 0.45 µm membrane filter in a 50 ml flask, which was then filled up to 50 ml with deionized water. Extracts were subsequently analyzed for the investigated heavy metals on ICP-AES (Varian Vista-axial, Varian, Palo Alto, CA). The analytical quality of the measurements was checked by including a method-blank and laboratory controls sample every 10 samples. In addition to the determination of the total metal concentrations in the sediments assessment of the bio-available pool of heavy metals was made using an ammonium-acetate at pH 7 extraction (Tack and Verloo, 1995). Samples from DS1 were pooled (groups of four adjacent samples) and mixed throughoutly to obtain 4 composite samples before this procedure. The same was done with the 12 samples from DS2 (groups of three samples). For each of the four replicates, 10 gram of sediment was extracted after 2 hours of reciprocal shaking of a 1:5 sediment:extractant suspension. The resulting sediment paste was filtered under vacuum onto a Buchner funnel fitted with filter paper (Schleicher and Schuell $589^2$, White Ribbon) and the metal concentrations in the extracts were subsequently analyzed on a graphite furnace atomic absorption spectrophotometer (Varian AA-1475 with GTA-95, Palo Alto) or a flame atomic absorption spectrophotometer (Varian SpectrAA-10, Varian, Palo Alto), depending on required detection limits. The 4 composite samples from DS1 and DS2 and the original DS4 and DS6 samples were used for the determination of the particle size distribution. Particle fractions were determined using the pipette method as described by Gee and Bauder (1986).

Leaves, wood and bark from each of the plots were sampled from April to November 1998. Four replicates of each biomass compartment (wood, bark, leaves) were sampled every month in all the plots. At least 3 complete rods were cut from four of the eight sub-plots in the 1 and 2 year old *Salix fragilis* and *Salix triandra* sub-plots. The bark and leaves were removed immediately after sampling and the weight of the wood, the bark and the leaves were determined for each rod. In the 1 year old stands, bark was only removed from the 3rd month of sampling. The three wood samples originating from the same sub-plot were subsequently pooled together. The same procedure was followed for the bark and leave samples. In the 4 and 6 year stands, four complete trees were cut with every sampling. While in the younger stands the complete rods were processed for analysis, the size of the older trees made sub-sampling of the trees unavoidable. Wood samples from each of the cut trees were taken by cutting a stem disk at the center of gravity of the tree. Leaves samples were collected from at least 10 locations in the crown and pooled together for each tree. Leaves were rinsed at least three times in deionized water before analysis (Azcue and Mudroch, 1994). All *Salix fragilis* trees had lost their leaves by the second week of October, while *Salix triandra* leaf fall was concluded by the end of that month. All wood, bark, and leave samples were dried at 70°C to constant weight and subsequently milled. The moisture content was calculated after the drying step. The metals Cd, Cr, Cu, Ni, Pb and Zn were extracted from each of the biomass samples in an $HNO_3$ p.a. 65% during microwave digestion (CEM, MDS 2000). Extracts were analyzed for the investigated metals on ICP-AES (Varian Vista-axial, Varian, Palo Alto, CA). The method run on the ICP-AES was validated with the reference material CRM 60 containing *Lagarosiphon major* moss and CRM 281 containing *Elymus spp*. The analytical quality of the measurements was checked by including a method-blank and laboratory controls sample every 10 samples. Leaf nitrogen concentrations were determined with the modified Kjehldahl method (Bremner, 1996).

The dry ash to dry weight ratio was determined for wood and foliar samples. Samples were dried for 72 h at 70°C, and a known amount (*ca* 1 g) of ground and sieved sample was weighed into porcelain crucibles. The crucibles were gradually heated to 450°C and ashed for 4 hours. The crucibles were then transferred to a desiccator and left to cool down. Method blanks were included to control analytical quality. The metal concentrations were expressed on a dry ash weight (DAW) basis by dividing the metal concentration expressed on a dry weight (DW) basis with the ratio between DAW and DW.

The biomass production in the stands was measured or estimated to calculate metal stocks and fluxes. Wood and bark biomass production in the first and second year stands was calculated from the wood and bark biomass measured in the last sampling in November and the tree density. Stem dry weight and stem diameter at 0.55 m above the ground were determined for the sampled stems. The relationship between the two parameters was established with the model: dry weight = a x diameter$^b$. This equation was subsequently used to calculate the stands total biomass based on the diameter distribution and total stem number. The August measurements were used for the determination of the leaf biomass in these plots. Biomass production results reported in Chapter 3 were used for the calculation of metal fluxes in the 4 and 6 year old stands. The bark content for these stands was calculated as 15 and 10 % respectively of the total woody biomass. For these older stands, a leaf biomass percentage of 10% of the wood biomass was used which is common in willow stands (Geyer, 1981). The amounts of metals which could be exported by harvest or which reached the stands surface with leaf fall were calculated for a 12 year period. Hereby it was hypothesized that biomass production and metal accumulation would remain constant after each harvest for this period. The 1 year old stands would thus be theoretically harvested twelve times while for the 6 year old stand two harvests applied. Leaf biomass for each stand was cumulatively added over the duration of the rotation to obtain the total leaf production during that rotation. Metal concentrations measured in the different compartments in the last month of sampling were used for the calculation of the harvestable metal mass and amounts of metals which reach the surface with leaf fall. As there was no biomass and metal concentration data for wood, leaves and bark for the 3 and 5 year old *Salix fragilis* stands, the biomass and metal concentrations were interpolated between the data of the 2 and 4, and 4 and 6 year old stands respectively.

### *4.2.3 Statistical analysis*

The disposal site characteristics were compared with ANOVA using Tuckey's post-hoc test to identify differences between means. The same procedure was applied to compare bio-available metal fractions in the sampled sediments. Seasonal changes in metal concentrations were evaluated for the factors 'month' and 'stand' with ANOVA. The use of both dry weight (DW) and dry ash weight (DAW) as basis to express metal concentrations was evaluated using the relative standard variation (RSD), also called the coefficient of variation. The DW and DAW RSD's for each sampling month and stand were compared using a paired t-test. Multiple comparison of means was performed according to Tuckey's post hoc test. Statistical calculations were performed using the SPSS 11 software package.

## 4.3 Results

### *4.3.1 Dredged sediment characteristics*

Results from the dredged sediment analysis show that the chemical and textural characteristics of the sediments in the four investigated sites are relatively comparable (

Table 4–2). The pH off the sediments in all the investigated sites can be considered as neutral. While sediments in the disposal sites DS1, DS2 and DS3 feature comparable particle distributions, sediment in disposal site DS6 is characterized with a lower sand and higher clay content. DS6 sediment can also be appreciated as more fertile with significantly higher N and P concentrations but a lower K concentration while DS1 sediment is richest in OM and S. Sediment in disposal site DS6 features slightly different metal concentrations compared to the other sediments: the sediment in this disposal site is characterized by significantly higher Cd concentrations but lower Cr and Ni concentrations. There are no significant differences in Cu, Pb and Zn concentrations between the disposal sites. Thus, while the dredged sediment in the disposal sites DS1, DS2, and DS4 can be characterized as similar for the total metal concentrations, sediments from DS6 features some differences compared to the other depots. The sediment heavy metal concentrations can be compared with the threshold values contained the VLAREA legislation. This legislation described the decision of the Flemish government on the introduction of the Flemish guidelines of waste prevention and management. Only the Cd concentrations of the sediments in every disposal site are above the VLAREA thresholds for reuse of the sediment as soil. Cr is in excess in DS1, DS2, and DS4, while Zn exceeds these thresholds in DS1, DS4, and DS6.

Differences in the bio-available metal concentrations, as measured with the ammonium-acetate (pH 7) extraction procedure, did not follow the same trend as with the total metal concentrations (Table 4–3). Extracts from sediments from all disposal sites featured comparable Cr, Zn and Ni concentrations. Sediments from DS1 featured a larger bio-available Cd fraction, while Cu was less available in the sediments from DS6. Sediment from DS4 featured the largest bio-available Cu fraction. Differences were however small and bio-available concentrations for all the four disposal sites were in the same order of magnitude, which makes it possible to compare metal uptake from these sediments.

Table 4–2: Particle size distribution and chemical characteristics of the sediments in the 4 disposal sites (0-30 cm). Metal concentrations are compared against the VLAREA thresholds for reuse of the sediments as soil (appendix 4.2.3)

| Depot | Stand | N | >50 µm (%) | 50-20 µm (%) | 20-2 µm (%) | <2 µm (%) | | |
|---|---|---|---|---|---|---|---|---|
| DS1 | FR1, TR1 | 5 | 42 a | 29 a | 17 a | 12 a | | |
| DS2 | FR2, TR2 | 5 | 31 ab | 29 a | 27 a | 13 a | | |
| DS4 | FR4 | 4 | 36 ab | 25 a | 22 a | 16 ab | | |
| DS6 | FR6 | 5 | 22 b | 33 a | 25 a | 19 b | | |
| | | | OM (%) | pH ($H_2O$) | N (mg/kg) | P (mg/kg) | K (g/kg) | S (mg/kg) |
| DS1 | FR1, TR1 | 12 | 5.0 a | 7.1 a | 2130 a | 1870 a | 11.2 a | 1890 |
| DS2 | FR2, TR2 | 16 | 3.7 b | 7.0 a | 1530 a | 1460 a | 11.9 a | 1190 |
| DS4 | FR4 | 4 | 4.0 b | 7.1 a | 2000 a | 1560 a | 9.5 b | 1130 |
| DS6 | FR6 | 5 | 3.7 b | 6.9 a | 3180 b | 7490 b | 6.2 c | 1220 |
| | | | Cd (mg/kg) | Cu (mg/kg) | Cr (mg/kg) | Ni (mg/kg) | Pb (mg/kg) | Zn (mg/kg) |
| DS1 | FR1, TR1 | 12 | 4.6 a | 78.3 a | 127 a | 53.3 a | 91 a | 475 a |
| DS2 | FR2, TR2 | 16 | 3.5 a | 57.7 a | 136 b | 44.8 b | 74 a | 361 a |
| DS4 | FR4 | 4 | 5.0 a | 69.9 a | 138 b | 42.3 b | 102 a | 457 a |
| DS6 | FR6 | 5 | 9.4 b | 74.5 a | 67.4 c | 20.7 c | 117 a | 475 a |
| VLAREA thresholds | | | 1.6 | 118 | 85 | 65 | 138 | 385 |

Table 4–3: Mean available metal concentrations (± standard deviation) measured after an ammonium-acetate (pH 7) extraction (mg/kg)

| | Cd | | | | Cr | | | | Cu | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DS1 | 1.03 | ± | 0.06 | a | 0.54 | ± | 0.19 | a | 0.71 | ± | 0.10 | a |
| DS2 | 0.62 | ± | 0.06 | b | 0.67 | ± | 0.09 | a | 0.78 | ± | 0.14 | a |
| DS4 | 0.66 | ± | 0.01 | b | 0.54 | ± | 0.15 | a | 0.87 | ± | 0.07 | a |
| DS6 | 0.52 | ± | 0.04 | b | 0.38 | ± | 0.05 | a | 0.56 | ± | 0.05 | b |
| | Ni | | | | Pb | | | | Zn | | | |
| DS1 | 1.31 | ± | 0.15 | a | 0.77 | ± | 0.04 | a | 61.95 | ± | 10.82 | a |
| DS2 | 1.12 | ± | 0.14 | a | 0.75 | ± | 0.04 | a | 72.37 | ± | 6.93 | a |
| DS4 | 1.25 | ± | 0.12 | a | 1.00 | ± | 0.13 | b | 78.77 | ± | 4.82 | a |
| DS6 | 1.12 | ± | 0.22 | a | 0.68 | ± | 0.09 | a | 77.76 | ± | 11.59 | a |

### 4.3.2 *Biomass metal concentrations.*

The following paragraphs present the results on the seasonal variation in metal concentrations for the wood, bark, and foliar compartments of the different investigated stands. Seasonal variations of elements which featured concentrations below measurement detection limits in over 50% of the samples (total amount of samples: 192) are not graphically depicted.

#### 4.3.2.1 *Wood metal concentrations*

The Cd and Zn wood concentrations from the 1 and 2 year old stand increase strongly over the growing season (Figure 4–1 and Figure 4–2). Initial FR1 and TR1 Cd concentrations were 6.8 ± 1.8 and 8.4 ± 2.4 mg Cd/kg respectively, and increased to 15.8 ± 1.9 and 25.2 ± 1.7 mg Cd/kg at the end of the growing season. The same trend was observed for the 2 year old FR2 and TR2 stands, although the increase was less outspoken. The Cd concentrations of the 4 and 6 year old wood was fairly constant over the growing season, with mean concentrations over the coarse of the growing season of 5.6 ± 0.7 and 6.6 ± 1.9 mg Cd/kg for FR4 and FR6 respectively. Cd concentrations in the *Salix triandra* wood were consistently higher compared to *Salix fragilis* for the 1 and 2 year stands. Zn concentrations also increased in the 1 and 2 year stands. While Zn concentrations in the *triandra* wood were slightly higher compared to *fragilis*, no significant differences between the *triandra* and *fragilis* trees were observed. The Cu concentration of the 1 year old willow wood featured the opposite trend as observed for Cd and Zn; Cu concentrations decreased over the growing season from 17.4 ± 0.9 and 15.6 ± 1.2 mg Cu/kg for TR1 and FR1 respectively, to 5.8 ± 0.5 and 5.6 ± 0.3 mg Cu/kg (Figure 4–3). This significant decrease was not observed for the older stands, although slightly lower Cu concentrations were measured at the end of the growing season.

Measurements for the other heavy metals Cr, Ni and Pb were only were almost all below the detection limits (0.1 mg Cr/kg, 0.2 mg Ni/kg, and 0.2 mg Pb/kg). For Cr, only 14% of the 192 samples were above the detection limit and most of these measurements were made in September, when a mean concentration of 0.5 ± 0.2 mg Cr/kg for all stands was measured. For Pb, only 23% of the samples featured Pb concentrations above the detection limit. The highest concentrations, which amounted to 0.9 ± 0.4 mg Pb/kg, were measured in the wood of the 6 year *Salix fragilis* stand in August. Ni concentrations in the first and two last months of the measurements were almost all below detection limits. The highest Ni concentration in the wood, e.g. 0.5 ± 0.1 mg Ni/kg, was measured in July. Again, no significant differences between plots and tree species could be found.

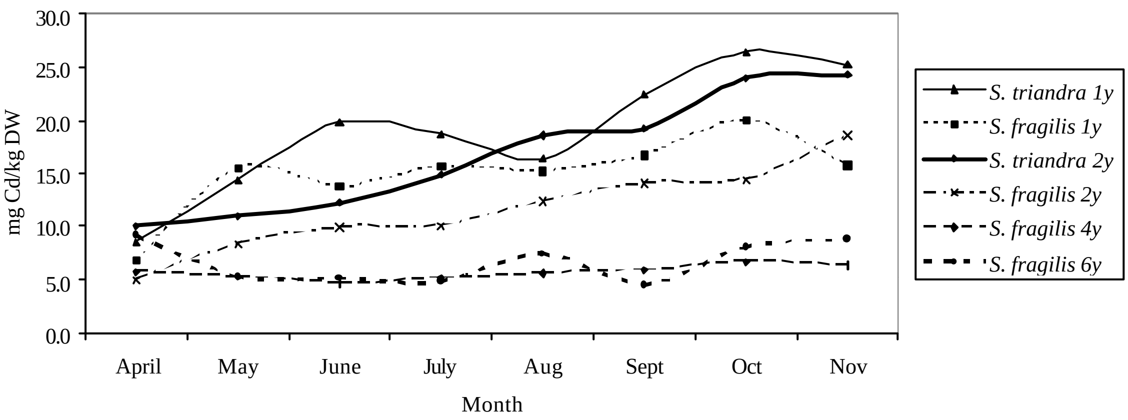


Figure 4–1: Seasonal changes in the wood Cd concentration

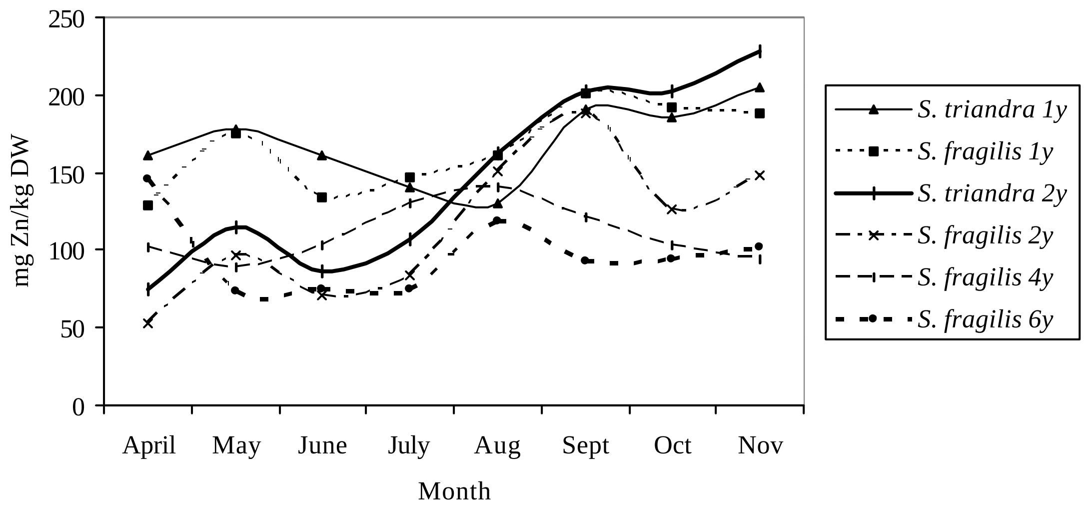


Figure 4–2: Seasonal changes in the wood Zn concentration

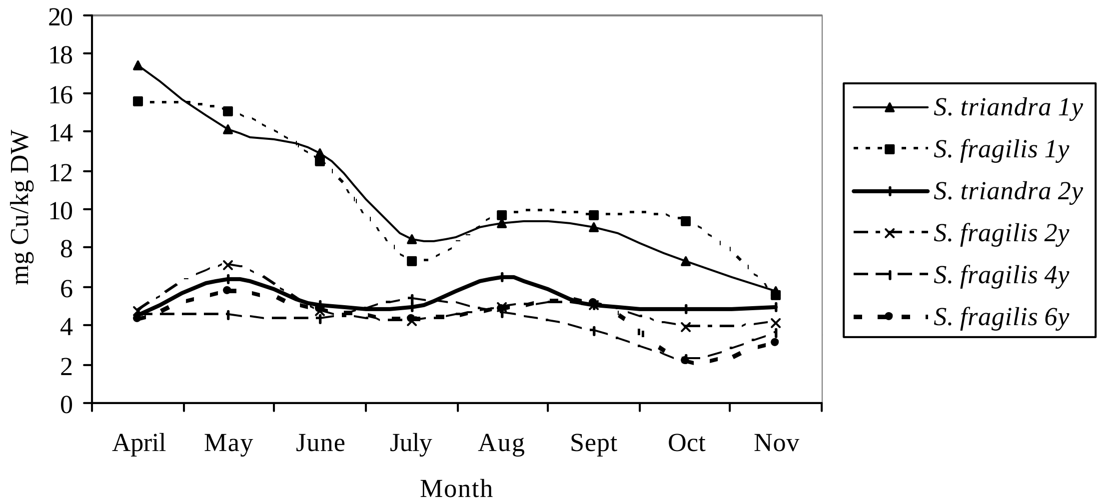


Figure 4–3: Seasonal changes in the wood Cu concentration

The changes in ash percentage for the investigated stands are presented in Figure 4–4. Only the samples from 1 year old TR1 and FR1 stands feature changes over the growing season; just after sprouting the shoots are characterized with ash percentages of about 8-10%. The following months this percentage decreases to levels found in the older stands of about 1.2 ± 0.2%. In the older stands no significant differences in ash percentages were found over the growing season.

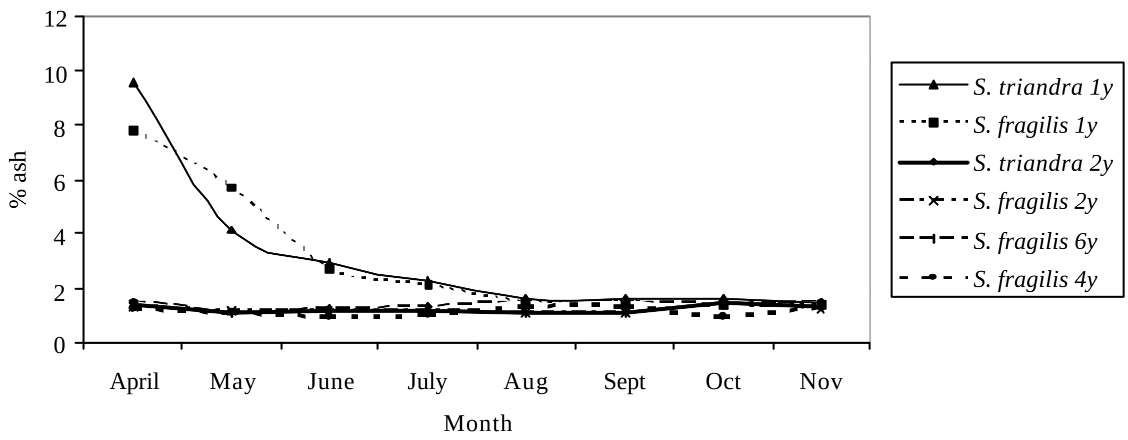


Figure 4–4: Changes in wood ash percentages over the growing season

When metal concentrations were expressed on DAW, the RSD increased for Cd, Cu, and Zn compared to when DW was used as a reference. Only 32%, 25%, and 29% of the RSD's for Cd, Cu, and Zn respectively were lower when DAW was used as a reference. Table 4–4 presents the results of the t-tests performed on the DW and DAW RSD's of each month and each stand. The mean RSD's of measurements expressed on a DAW basis are all significantly higher compared to the RSD's of measurements expressed on DW. The differences were largest for the Cu measurements and smallest for Cd.

Table 4–4: Mean RSD values for wood metal concentrations expressed on DW and DAW (n = 48), compared with a paired t-test.

| | Mean DW | Mean DAW | DW-DAW | St.deviation | t | deg freedom | sign. (2 tail) | Sign. Diff. |
|---|---|---|---|---|---|---|---|---|
| Cd | 17.61 | 20.31 | -2.7 | 7.66 | -2.44 | 47 | 0.018 | yes |
| Cu | 10.66 | 17.34 | -6.7 | 12.21 | -3.79 | 47 | 0.000 | yes |
| Zn | 15.53 | 20.1 | -4.6 | 11.35 | -2.79 | 47 | 0.008 | yes |

#### *4.3.2.2 Bark metal concentrations*

The seasonal changes in the bark Cd, Cu, Pb, and Zn concentrations are presented in Figure 4–5, Figure 4–6, Figure 4–7, and Figure 4–8respectively. Metal concentrations measured in the bark are consistently higher compared to the wood concentrations. As with the wood Cd and Zn concentrations, bark concentrations of the 2 year old stands increase over the course of the growing season. However, this increase is less outspoken for the 1 year old TR1 and FR1 stands. Concentrations up to 51 ± 8 mg Cd/kg and 901 ± 51 mg Zn/kg were measured at the end of the growing season in the TR2 and FR1 stands respectively. The Cd and Zn concentrations of the older 4 and 6 year stand remained fairly constant over the growing season. Mean Cd concentrations over the growing season were 19 ± 2 mg Cd /kg and 23 ± 4 mg Cd/kg for FR4 and FR6 respectively. For Zn these concentrations were 606 ± 77 mg Zn/kg and 573 ± 100 mg Zn/kg. The Cu concentrations of the FR2, TR2, FR4, and FR6 stands are fairly constant over the growing season with a slight decrease towards the end. Concentrations in FR1 and TR1 featured higher concentrations in the beginning of the growing season and a more pronounced decline towards the end. The same trends were also observed for the Cu wood concentrations.

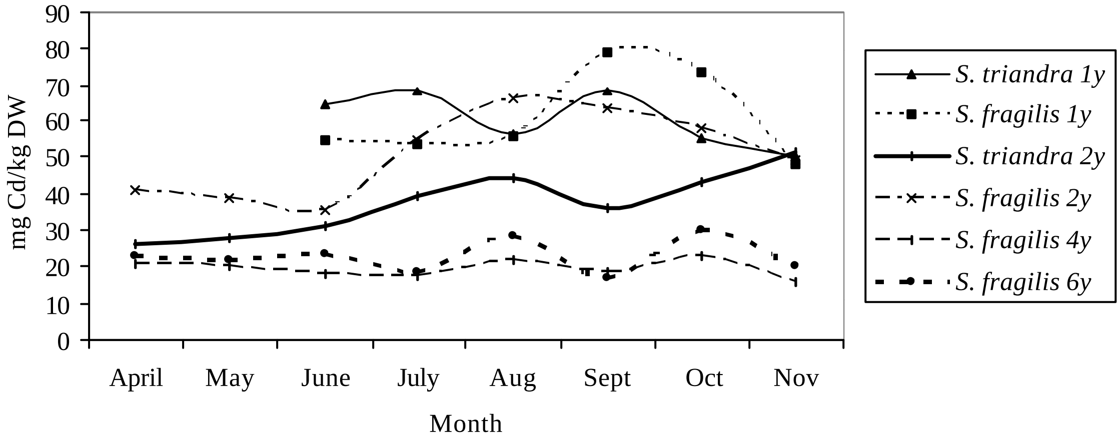


Figure 4–5: Seasonal changes in the bark Cd concentration

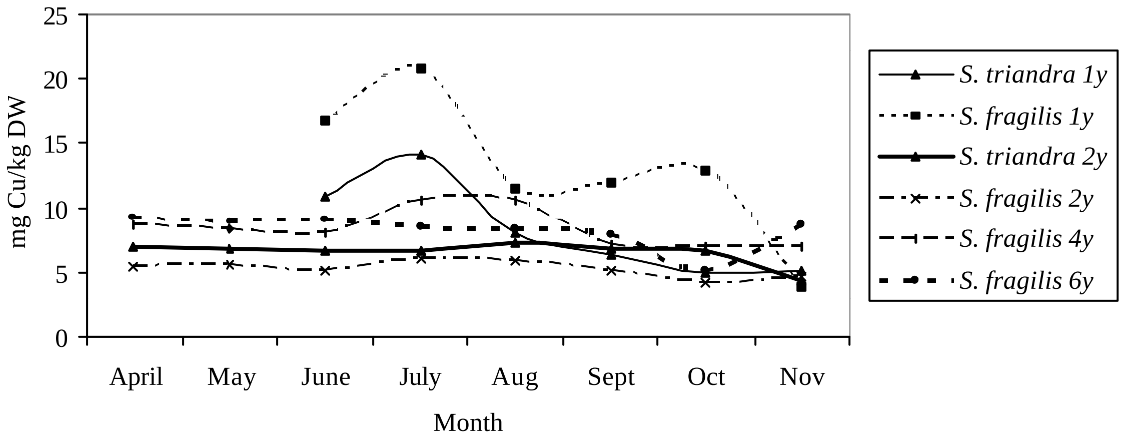


Figure 4–6: Seasonal changes in the bark Cu concentration

Bark Pb concentrations were all significantly higher in the 2 older FR4 and FR6 stand compared to the 1 and 2 year stands (Figure 4–7), but decreased towards the end of the growing season.

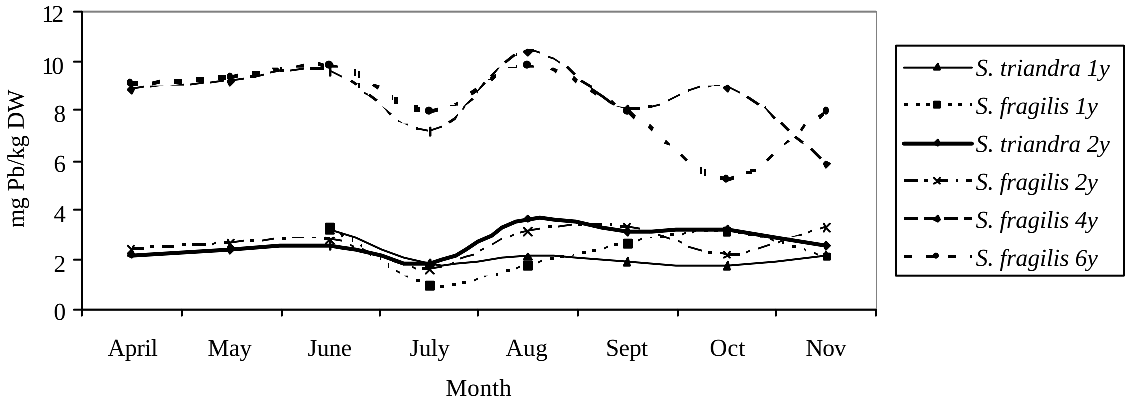


Figure 4–7: Seasonal changes in the bark Pb concentration

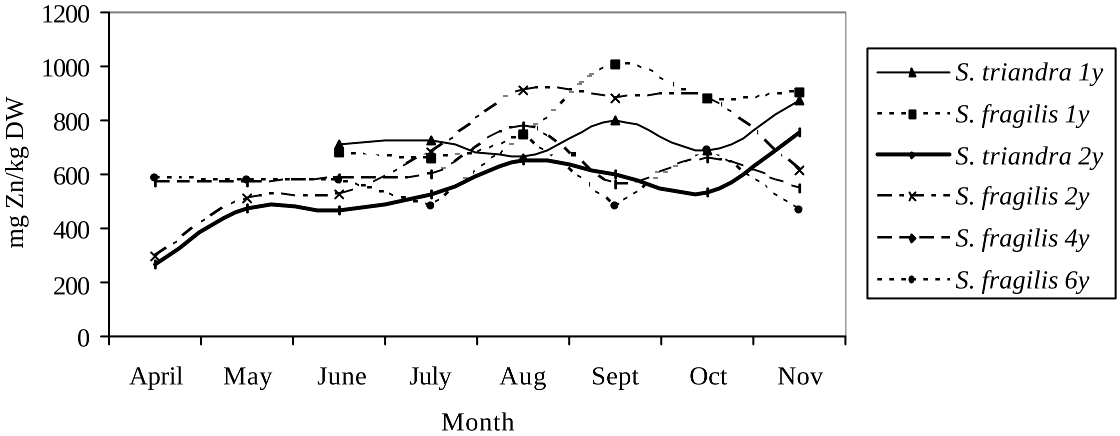


Figure 4–8: Seasonal changes in the bark Zn concentration

The bark was characterized with higher Cr and Ni concentrations compared to the wood. Cr concentrations ranged from 0.21 mg/kg to 0.91 mg/kg, for Ni the minimum and maximum values were 0.4 mg/kg and 2.0 mg/kg respectively. Measurements of both elements were however characterized with high RSD's and means strongly fluctuated over the growing season.

*4.3.2.3 Foliar metal concentrations*

The seasonal changes in the bark Cd, Cr, Cu, Ni, Pb, and Zn concentrations are presented in Figure 4–9, Figure 4–10, Figure 4–11, Figure 4–12, Figure 4–13, and Figure 4–14 respectively. Leaf metal concentrations can be compared to the threshold values for normal and critical foliar metal concentrations in plants postulated by Kabata-Pendias en Pendias (1984) (Table 4–5).

Table 4–5: Normal and critical concentrations of metals in leaves and soil (mg/kg DW) (Kabata-Pendias en Pendias, 1984)

| | | Cd | Zn | Cu | Pb | Cr | Ni |
|---|---|---|---|---|---|---|---|
| Normal | Substrate | 0,1 | 50 | 60 | 10 | 60 | 40 |
| | Leaf | <0,5 | 27-150 | 8 | 3 | 0,1-0,5 | 0,1-5 |
| Critical | Leaf | 8 | 100-400 | 20 | 35 | 5-30 | 10-100 |

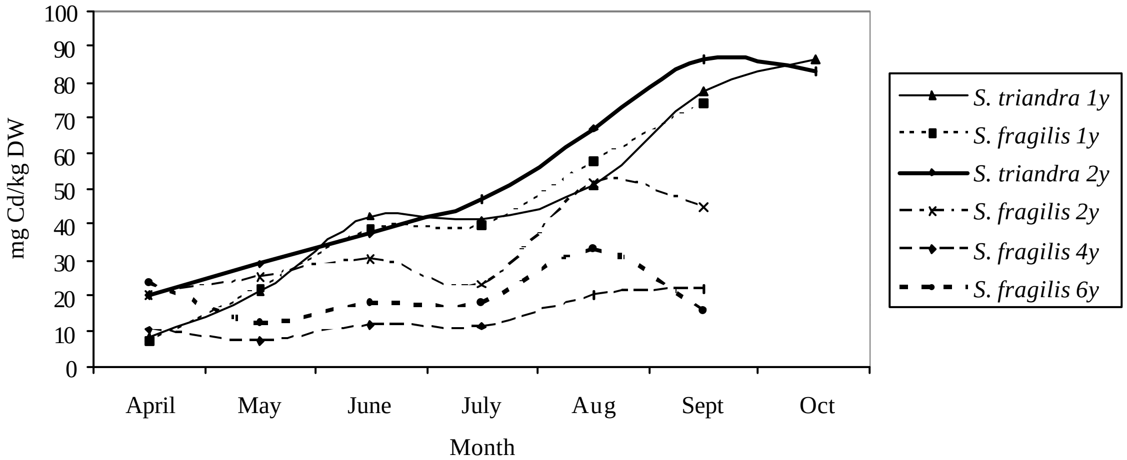


Figure 4–9: Seasonal changes in the foliar Cd concentrations

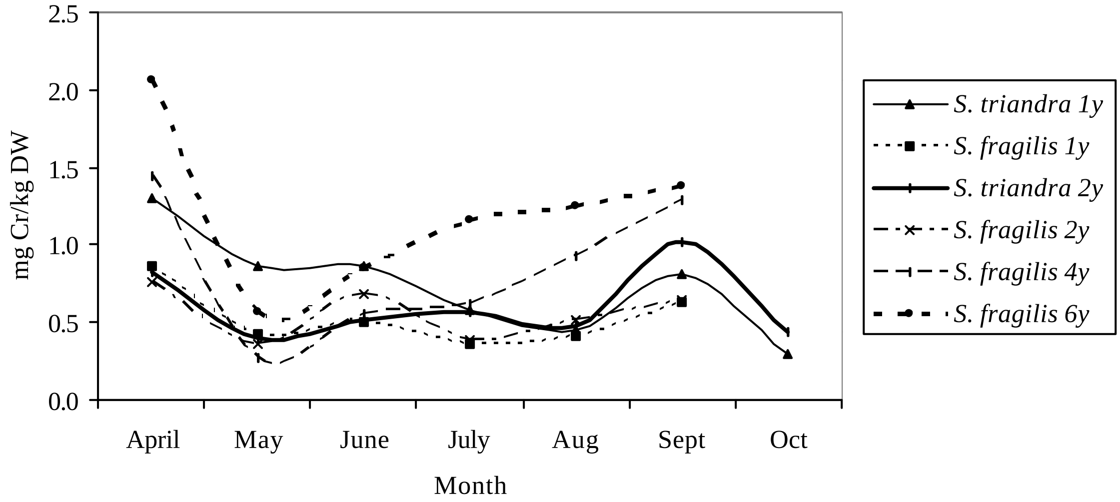


Figure 4–10: Seasonal changes in the foliar Cr concentrations

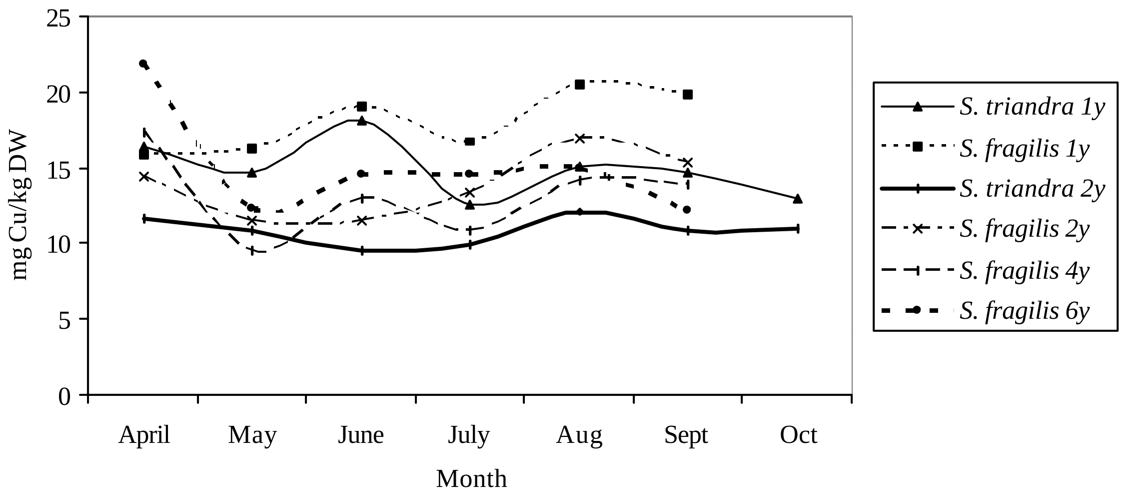


Figure 4–11: Seasonal changes in the foliar Cu concentrations

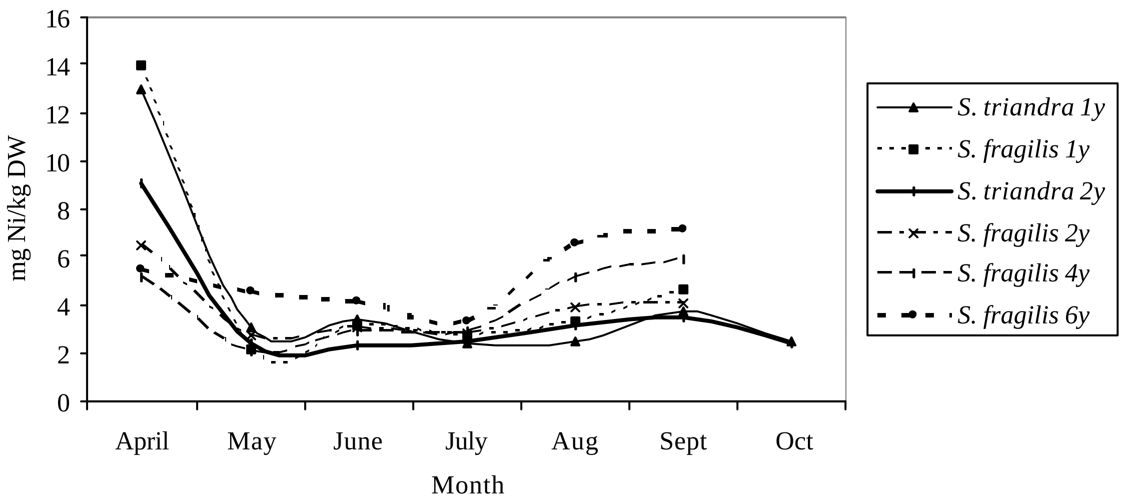


Figure 4–12: Seasonal changes in the foliar Ni concentrations

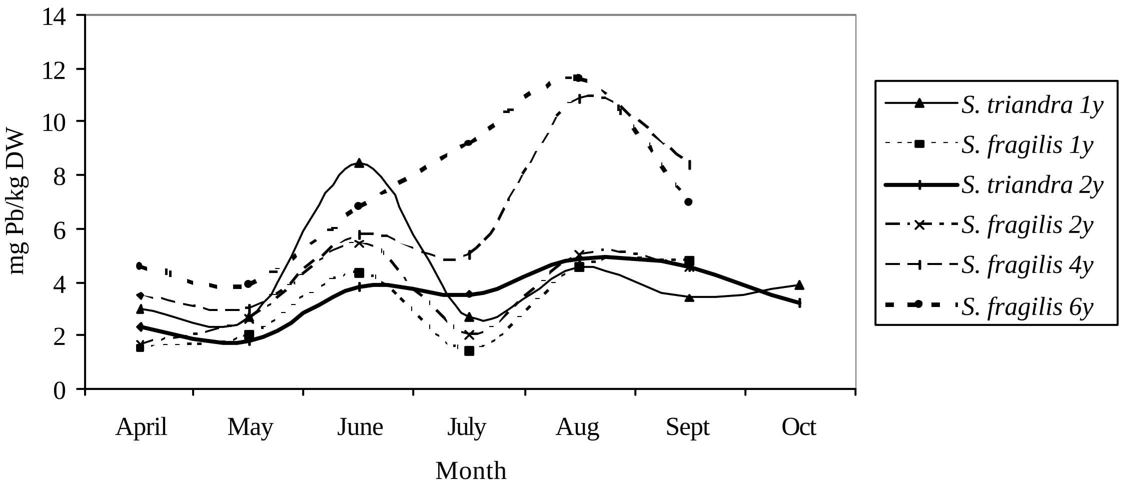


Figure 4–13: Seasonal changes in the foliar Pb concentrations

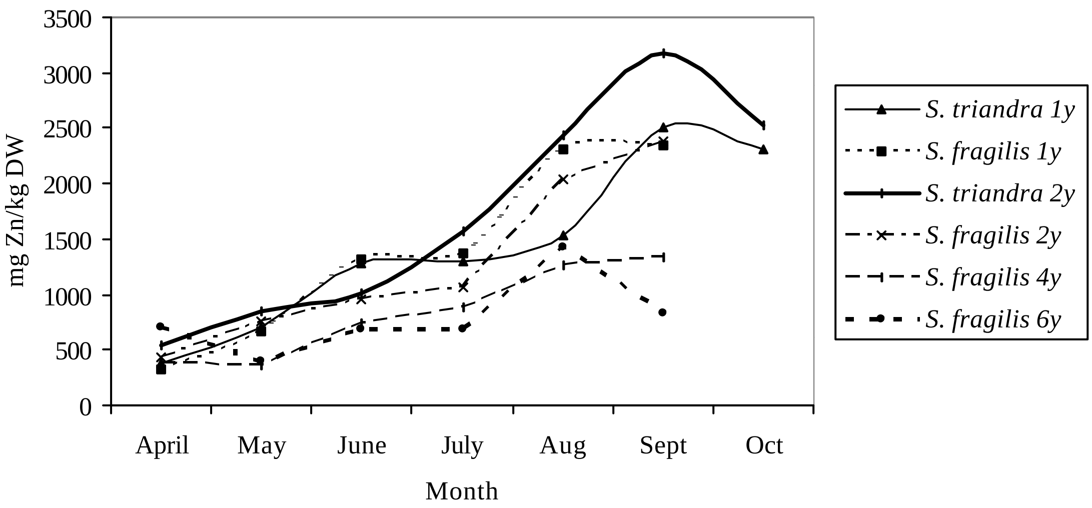


Figure 4–14: Seasonal changes in the foliar Zn concentrations

All metal concentrations measured in the leaves were higher compared to the wood and bark concentrations. The differences in metal concentrations over the growing season are more outspoken compared to the trends observed for the wood concentrations. Especially the foliar Cd and Zn concentrations increase towards the end of the growing season. This was observed for all investigated stands but was most outspoken in the 1 and 2 year old stands. The Cd concentration in FR1 and FR2, for example, increased from respectively 7.4 ± 1.8 mg Cd/kg and 20.1 ± 2.6 mg Cd/kg to 74 ± 21 mg Cd/kg and 44.8 ± 4.4 mg Cd/kg. At the end of the growing season the Cd and Zn concentrations decrease slightly before leaf fall. Cd and Zn concentrations were higher in *Salix triandra* leaves for most months compared to *Salix fragilis*. The trends for the Cd and Zn concentrations in the leaves are remarkably similar.

Table 4–6 presents the correlation coefficients between Cd and Zn and Cd and Pb concentrations. The correlations are strongest ($R^2$ = 0.997 for FR1) in the youngest stands and decrease with stand age. Such correlations were not observed for wood Cd and Zn concentrations.

Table 4–6: Correlation coefficients between foliar Cd and Zn and Cd and Pb concentrations in *Salix fragilis* (n = 24) and *Salix triandra* stands (n = 28).

| | Cd-Zn | Cd-Pb |
|---|---|---|
| *S. triandra* 1y | 0.984 | 0.113 |
| *S. fragilis* 1y | 0.997 | 0.724 |
| *S. triandra* 2y | 0.987 | 0.636 |
| *S. fragilis* 2y | 0.989 | 0.638 |
| *S. fragilis* 4y | 0.938 | 0.955 |
| *S. fragilis* 6y | 0.883 | 0.668 |

The greatest increase in the Pb concentration towards the end of the growing season was observed in the 4 and 6 year old stands. This is opposite to Cd and Zn where the youngest stands showed the greatest increase. The foliar Pb concentrations declined again after August.

High foliar Cr and Ni concentrations were observed in the beginning of the growing season for all stands. These concentrations rapidly declined in the second month of sampling and stayed fairly constant over the next months until summer. Before leaf senescence both Cr and Ni concentrations increase in the oldest FR4 and FR6 stands, and to a lesser extend in the younger *Salix fragilis* stands. On the other hand, Cr and Ni concentrations decrease in the last month before total leaf fall in the 1 and 2 year old *Salix triandra* stands. Cu concentrations in all stands stay fairly constant over the course of the growing season.

The changes in foliar ash percentages are presented in Figure 4–15. Ash contents of *Salix triandra* trees are always higher compared to *Salix fragilis*. The ash contents of the 1 and 2 year old stands change little over the course of the growing season and are situated between 8 and 11%. However, leaves from the two older stands show considerable variation in ash concentration. After an initial decline in the beginning of the growing season, FR4 and FR6 ash contents steadily rose until August. For example, the ash concentration of the FR6 stand almost doubled from 7 to 14% between the months of May and August. Towards the end of the growing season ash contents decline again. A similar decline was observed at the end of the growing season of the 1 and 2 year *Salix triandra* stands.

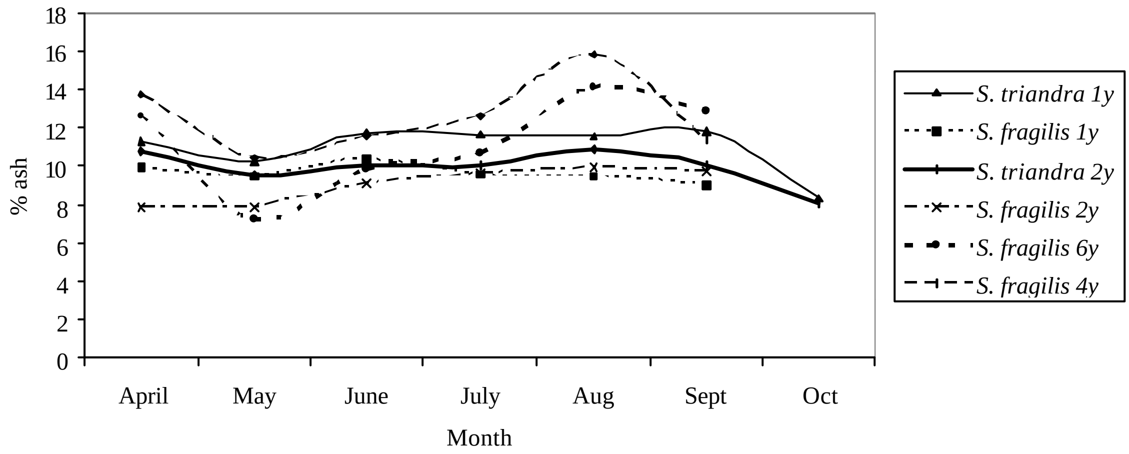


Figure 4–15: Changes in foliar ash percentages over the growing season

The small change in ash content of the 1 and 2 year old stands results in little changes in the metal concentrations trends if these are expressed on a DAW basis compared to the previously described DW trends. Only for the 1 and 2 year old *Salix triandra* stands does the decline in ash content at the end of the growing season result in higher metal concentrations when expressed on a DAW basis. For example, Cd and Zn concentrations on DW basis declined in the last month of sampling for *Salix triandra*, but when expressed on a DAW this decline is not observed. Expressing Cu concentrations on a DAW basis also results in an increase towards the end of the growing season. The changes in Cd, Cu, and Zn concentrations expressed on a DAW basis over the growing season are presented in Figure 4–16, Figure 4–17, and Figure 4–18 respectively as an illustration of the effect of expressing foliar metal contents on a DAW basis. As a result of the high foliar ash contents in the beginning and the increase towards the end of the growing season growing season of the FR4 and FR6 stands, the previously increasing trends in metal concentrations toward the end of the growing season are less outspoken.

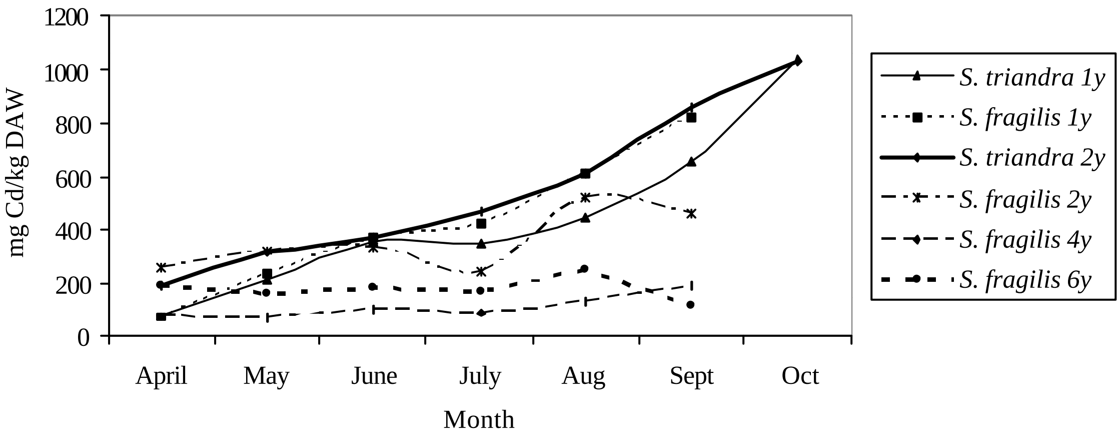


Figure 4–16: Seasonal changes in the foliar Cd concentrations expressed on DAW basis

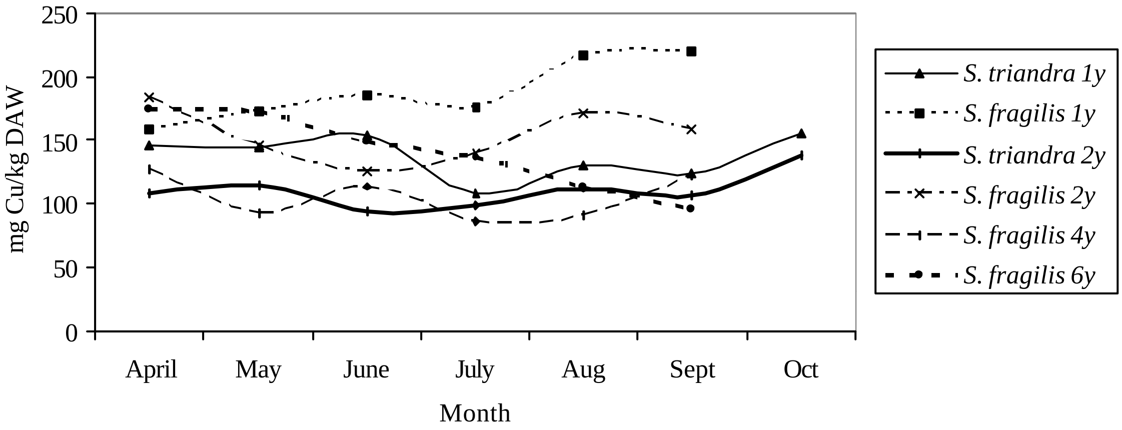


Figure 4–17: Seasonal changes in the foliar Cu concentrations expressed on DAW basis

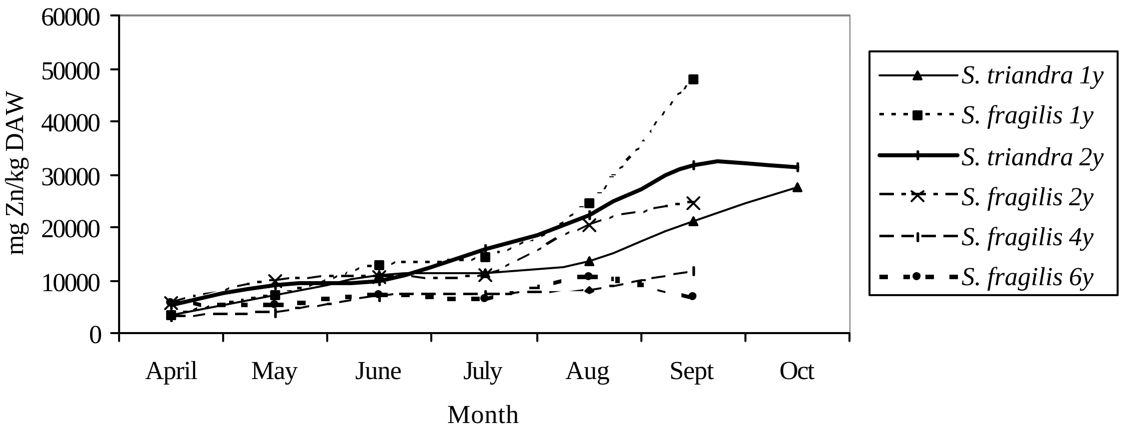


Figure 4–18: Seasonal changes in the foliar Zn concentrations expressed on DAW basis

The mean RSD's of measurements expressed on a DAW basis were all higher compared to the RSD's of measurements expressed on DW. Table 4–7 presents the results of the t-tests performed on the DW and DAW RSD's of each month and each stand. However, these differences were only significant for Ni and Pb. When DAW was used as a reference, 44.7, 39.5, 44.7, 34.2, 28.9, and 39.5% of the RSD's for Cd, Cr, Cu, Ni, Pb and Zn respectively were lower compared to when DW was used as a reference.

Table 4–7: Mean RSD values for foliar metal concentrations expressed on DW and DAW (n = 38), compared with a paired t-test.

| | Mean DW | Mean DAW | DW-DAW | St.deviation | t | deg freedom | sign. (2 tail) | |
|---|---|---|---|---|---|---|---|---|
| Cd | 17.01 | 18.23 | -1.23 | 5.14 | -1.47 | 37 | 0.15 | no |
| Cr | 22.9 | 24.83 | -1.93 | 7.67 | -1.55 | 37 | 0.129 | no |
| Cu | 11.11 | 12.9 | -1.79 | 4.78 | -1.91 | 37 | 0.064 | no |
| Ni | 17.19 | 20.13 | -2.23 | 6.6 | -2.07 | 37 | 0.046 | yes |
| Pb | 18.15 | 20.56 | -2.41 | 5.47 | -2.71 | 37 | 0.01 | yes |
| Zn | 15.05 | 16.51 | -1.47 | 5.54 | -1.63 | 37 | 0.112 | no |

The seasonal changes in leaf/wood concentration ratios for the three metals Cd, Cu, and Zn are presented in Figure 4–19, Figure 4–20, and Figure 4–21 respectively. These figures give a more detailed picture of the relationship between wood and foliar metal concentrations over the course of the growing season. For the three considered metals the foliar/wood concentrations ratios increase towards the end of the growing season, indicating that leaves get enriched with heavy metals compared to the wood. This enrichment is most outspoken for Zn: the ratios generally increased with factor 4 from the beginning of the growing season towards leaf senescence. For Cu, the ratio first declines after bud break, indicating a retranslocation of Cu from newly formed leaves towards wood, bark, or roots. This decline is most outspoken for the oldest stand en becomes less with decreasing stand age. For the 1 year old stand only an increase is observed over start to finish of the growing season which indicates Cu is solely tranlocated from the wood to leaves, as was observed for Cd and Zn.

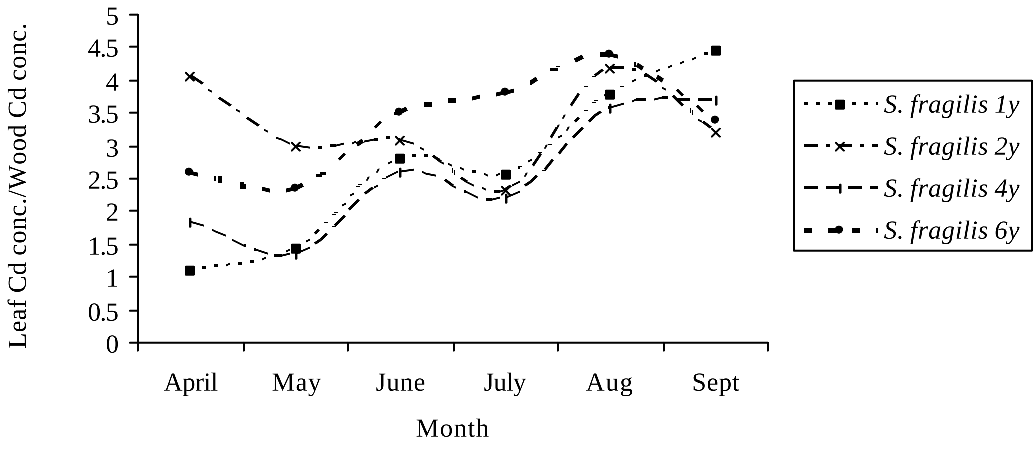


Figure 4–19: Foliar/wood Cd concentrations ratio in *Salix fragilis* trees of different stand ages over the course of the growing season.

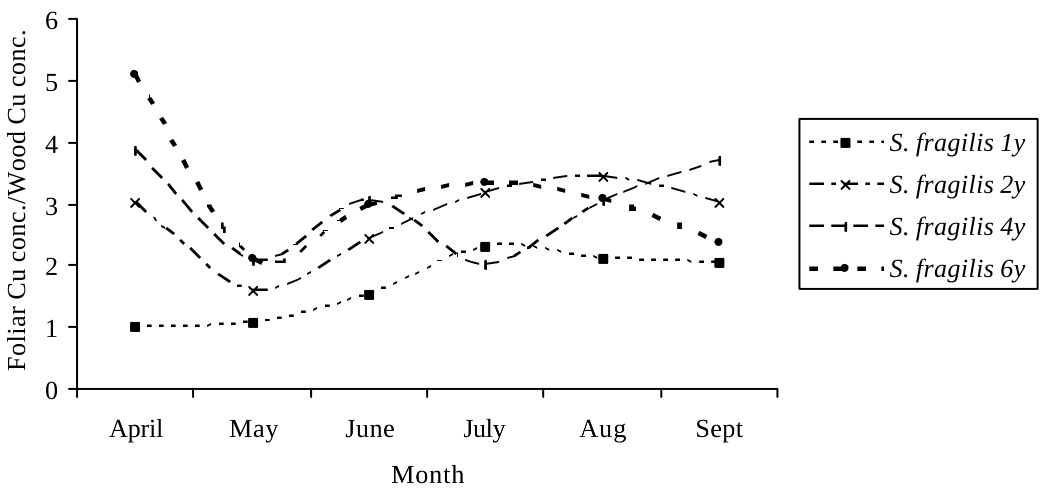


Figure 4–20: Foliar/wood Cu concentrations ratio in *Salix fragilis* trees of different stand ages over the course of the growing season

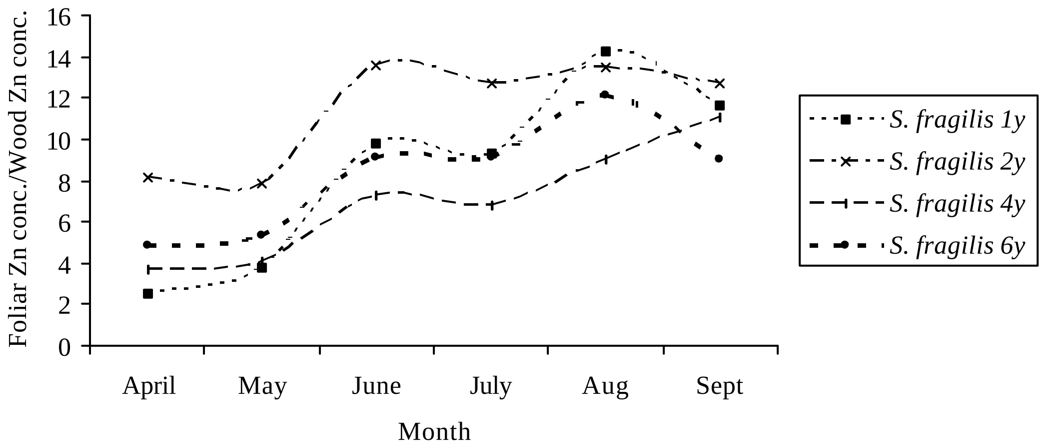


Figure 4–21: Foliar/wood Zn concentrations ratio in *Salix fragilis* trees of different stand ages over the course of the growing season

### *4.3.3 Metal stocks in biomass compartments*

Compartment concentrations can be converted to stocks taking into account the compartment biomass. This allows an estimation of the amount of metals which can be exported from the site with harvest or which will be recycled to stand surface with leaf fall. The wood, bark, and leaf biomass production of the investigated stands is presented in Table 4–8. Stem numbers per ha in the 1 year old stand were high as a result of the SALIMAT planting. Densities for FR1 and TR1 were 487,000 and 636,000 shoots/ha respectively. While the stem number of *triandra* trees was higher, the biomass production was lower compared to the *Salix fragilis* for the two investigated growing seasons. *Salix triandra* trees were characterized with higher bark contents compared to *fragilis trees*: FR1 and TR1 bark contents were 25 and 27% respectively. Leaf biomass was for both the 1 and 2 year stands were about 15% of the total aboveground biomass. Biomass productions for FR4 and FR6 were obtained from Chapter 3.

Table 4–8: Wood, bark, and leaf biomass (mean value ± standard deviation) values of the different stands (ton DM/ha). Biomass values for the 4 and 6 year old *Salix fragilis* stands were obtained from Chapter 3.

| | Wood | | Bark | | Wood and Bark | | Leaf | |
|---|---|---|---|---|---|---|---|---|
| FR1 | 8.8 | ±1.2 | 2.2 | ±0.3 | 10.9 | ±2.1 | 1.7 | ±0.2 |
| TR1 | 7.3 | ±1.1 | 2.0 | ±0.3 | 9.2 | ±1.7 | 1.4 | ±0.2 |
| FR2 | 15.8 | ±3.1 | 3.3 | ±0.4 | 19.1 | ±3.5 | 2.7 | ±0.4 |
| TR2 | 13.6 | ±2.8 | 3.1 | ±0.5 | 16.7 | ±2.9 | 2.4 | ±0.3 |
| FR4 | 47.3 | | 8.4 | | 55.7 | ±4.1 | 5.6 | |
| TR4 | 68.8 | | 7.6 | | 76.4 | ±4.2 | 7.6 | |

As could be expected from the high Cd concentrations in all biomass compartments, considerable quantities of Cd are incorporated into the aboveground biomass. Table 4–9 presents the amounts of metals which are exported from the site with the harvest of the stem biomass (wood and bark), the amount of metals which reach the stand surface with leaf fall, and the total amount of extracted metals by the trees for different rotation scenarios over a period of 12 years. Between 3.2 kg and 5.7 kg of Cd are removed from the sediment through the accumulation in the trees over a 12 year period. The amounts of Zn are situated between 76 and 104 kg. The stem and foliar Cd and Zn stocks for the 1 and 2 year old *Salix triandra* trees are higher than for *Salix fragilis*. Twelve annual harvests of the *Salix triandra* stand would deplete the sediment profile of 16% of the total Cd amount. For Zn this percentage was 4%. The amount of metals was calculated from the mean metal concentration for the 4 disposal sites in a 0.5 m profile with 1.3 g/cm$^3$ bulk soil density. With increasing rotation length the amount of Cd which is removed from the sediment profile decreases. Stocks of Cr, Cu, Ni and Pb are low (< 1%) compared to the amounts of these metals present in the soil profile

While a large percentage of soil Cd in accumulated in the *Salix* stands, considerable amounts of metals are recycled to the stand surface with leaf fall. The amounts of Cd in the foliage are of the same order of magnitude and often higher compared to the amount present in the stems. For example, applying 4 or 6 year rotation results in more Cd distributed through leaf fall than Cd that can be removed through the harvest of the stems. For Zn almost four times more Zn reaches the stand surface compared to the amount of Zn in wood and bark.

Table 4–9: Amounts of metals (kg) which are removed from the site with harvest of the stem biomass (wood and bark), the amount of metals which reach the stand surface with leaf fall, and the total amount of extracted metals by *Salix fragilis* and *Salix triandra* trees for different rotations scenarios over a period of 12 years. The highest total amount (stem and stem and leaves) are evaluated against the amount of metal present in a 0.5 m profile and assuming a bulk soil density of 1.3 ton/$m^3$.

| | Cd | | | Cr | | | Cu | | | Ni | | | Pb | | | Zn | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Stem | Leaf | Total | Stem | Leaf | Total | Stem | Leaf | Total | Stem | Leaf | Total | Stem | Leaf | Total | Stem | Leaf | Total |
| *S. fragilis* | | | | | | | | | | | | | | | | | | |
| 12 1-year rotations | 2.51 | 1.89 | 4.40 | 0.01 | 0.01 | 0.02 | 0.58 | 0.33 | 0.91 | 0.05 | 0.08 | 0.13 | 0.13 | 0.08 | 0.21 | 37.60 | 38.83 | 76.42 |
| 6 2-year rotations | 2.42 | 1.58 | 4.00 | 0.00 | 0.01 | 0.02 | 0.42 | 0.40 | 0.82 | 0.05 | 0.10 | 0.15 | 0.13 | 0.11 | 0.24 | 23.52 | 55.14 | 78.67 |
| 3 4-year rotations | 1.30 | 1.88 | 3.18 | 0.01 | 0.04 | 0.05 | 0.69 | 0.56 | 1.25 | 0.09 | 0.19 | 0.28 | 0.27 | 0.26 | 0.53 | 26.95 | 77.36 | 104.30 |
| 2 6-year rotations | 1.52 | 1.73 | 3.24 | 0.01 | 0.06 | 0.07 | 0.56 | 0.73 | 1.29 | 0.08 | 0.32 | 0.40 | 0.24 | 0.38 | 0.63 | 21.20 | 78.51 | 99.71 |
| *S triandra* | | | | | | | | | | | | | | | | | | |
| 12 1-year rotations | 3.96 | 1.71 | 5.67 | 0.01 | 0.01 | 0.02 | 0.74 | 0.26 | 1.00 | 0.06 | 0.05 | 0.11 | 0.15 | 0.08 | 0.23 | 44.42 | 45.40 | 89.82 |
| 6 2-year rotations | 3.32 | 2.28 | 5.60 | 0.01 | 0.01 | 0.02 | 0.55 | 0.32 | 0.87 | 0.06 | 0.07 | 0.12 | 0.14 | 0.09 | 0.23 | 36.72 | 66.04 | 102.76 |
| kg metal/ha soil | 37 | | | 762 | | | 456 | | | 262 | | | 626 | | | 2884 | | |
| % export soil | 11 | | 16 | 0 | | 0.01 | 0.16 | | 0.28 | 0.03 | | 0.15 | 0.04 | | 0.10 | 2 | | 4 |

## 4.4 Discussion

### *4.4.1 Metal distribution*

Cd and Zn are easily transported to aboveground biomass compartments of both investigated *Salix* clones, resulting in elevated wood, bark, and leaf concentrations while Cr, Cu, Ni, and Pb are less easily accumulated. These latter elements are known to be strongly absorbed on the substrate or are accumulate in the roots, which prevents them to be transported to aboveground biomass parts (Landberg and Greger, 1994; Nissen and Lepp, 1997; Punshon et al., 1995; McGregor et al., 1996). When compared to similar reports, the Cd and Zn concentrations measured in all considered biomass compartments in this study were very high (Table 2–1). For Cd, the highest concentrations in the 1 and 2 year old stands were 26.4, 79, and 74 mg Cd/kg DW for wood, bark and leaves respectively. Cd was the only metal with a BCF > 1 in all compartments, showing a pronounced bioaccumulation. Zn featured BCF > 1 for the bark and leaves (Table 4–10). Foliar Cd and Zn concentrations of both investigated species are well above the critical threshold values of 8 mg Cd/kg and 100-400 mg Zn/kg for toxicity. (Table 4–5). Both the *Salix fragilis* and *triandra* species showed no visible signs of phytotoxicity, indicating that they are both tolerant to high Cd and Zn concentration levels in their tissues. For comparison, Vandecasteele et al. (2002) reported baseline foliar Cd and Zn concentrations in willows grown on unpolluted substrates of 0.5-2.9 mg Cd/kg DW and 130-340 mg Zn/kg DW respectively. Baseline Cd concentrations in a Swedish study by Eriksson and Ledin (1999) were between 0.31 and 1.96 mg Cd/kg DW. The range for foliar Zn in several UK willow species was between 82 and 296 mg Zn/kg DW (Nissen and Lepp, 1997). The highest Cd concentrations so far were reported by Punshon and Dickinson (1997), who measured foliar and wood concentrations for *Salix cinerea* growing on heavily contaminated mine spoil of and 44 and 76 mg Cd/kg DW respectively.

Table 4–10: Bio concentration factor of the different biomass compartments of the 4 year old *Salix fragilis* stand (August samples). Na: not available, wood concentrations between detection limits.

| | Leaves | Bark | Wood |
|---|---|---|---|
| Cd | 3.99 | 4.35 | 1.12 |
| Cu | 0.20 | 0.15 | 0.07 |
| Cr | 0.01 | 0.003 | Na |
| Ni | 0.12 | 0.05 | 0.01 |
| Pb | 0.11 | 0.10 | Na |
| Zn | 2.76 | 1.70 | 0.32 |

Metal concentrations decreased in the following order: leaf  bark > wood, with bark and leaves often characterized with similar metal concentrations. The distribution of heavy metals over the different tree compartments presented in this investigation corresponds to observations made in previous research on metal uptake by willow species. Several studies have shown that accumulation preliminary occurs in actively growing tissues such as shoots and young leaves (Riddel-Black, 1994, Nissen and Lepp, 1997; Riddel-Black et al., 1997; Hasselgren, 1999).

Wood showed considerable lower concentrations than leaf and bark, especially for Cd and Zn. Bark Cd concentrations were on average 3.5 times higher compared to the wood concentration, for Zn and Cu this factor was 5.3 and 1.5 respectively. These ratios changed little over the course of the growing season. This is consistent with findings on the distribution of plant nutrients and metals in willow, which are generally higher in bark than in wood (Hytönen et al., 1995; Riddel-Black et al., 1997). The combined sampling of wood and bark for the determination of metal exports in willow phytoremediation systems can thus result in significant errors as heavy metal concentration will strongly depend on the sampling height which influences the wood/bark ratio. Sander and Ericsson (1998) reported that Zn concentrations doubled and Cd concentrations increased by 20% from the lowest to the highest sampling level along the trees stem. Most studies on heavy metal uptake by willow do not discern between wood and bark in their sampling strategies, making it difficult to assess and compare their findings.

Leaf and bark were characterized by measurable Pb and Cr concentrations, while almost all wood samples featured concentrations below detection limits. Wood can thus be considered a bad sink for these elements. Similar observations were made by Riddel-Black (1994) and Riddel-Black et al. (1997). This may indicate that these metals are accumulated in larger amounts through processes in addition to root uptake and xylem transport, most probably through aerial deposition in the months and years prior to sampling. Both elements are known to be adsorbed and accumulated by leaves (Little, 1973). The downward transport through the phloem and depositions on the bark itself could explain the measured concentrations in the bark. To eliminate the effect of direct aerial deposits on foliar metal concentrations in this study, leaves were rinsed prior to analysis. However, no such procedure was followed for bark. Alriksson and Eriksson (2001) cite Balsberg (1971), who separated outer and inner bark of *Betula pendula* and found that Pb concentrations were many times higher in the outer bark than in the inner bark, while for Zn the opposite was true. This indicated that a high proportion of the Pb in the biomass can originate from direct deposition rather than trough root uptake. Chappelka et al. (1991) showed that root uptake and transport to other aboveground compartments was of minor importance for biomass concentrations of Pb in *Pinus*. With aerial deposition the main factor determining the Pb concentrations in bark and leaves, it is possible to explain the significantly higher bark Pb concentrations in the 4 and 6 year old stand compared to the younger *fragilis* plantations in this study. However, for Cr no such differences between stand ages were observed. The low wood Pb concentrations for both the Salix *fragilis* and *triandra* clones in this trial are in contrast with the concentration reported for *Salix viminalis* 'Orm' grown on contaminated dredged sediment by Vervaeke et al. (2003), who reported mean Pb concentrations in the wood of 12.7 mg Pb/kg. But here it has to be mentioned that bark and wood were sampled together. However, Punshon and Dickinson (1997) also reported very high Pb concentrations of 157 mg Pb/kg in willow stems grown on mine spoil, which is difficult to attribute only to aerial deposition.

Leaf Cu concentrations were a factor two to four higher compared to wood Cu concentrations depending on clone and stand age. In this trial Cu thus appeared to be fairly mobile for translocation from stem to leaves and bark. It is generally accepted that Cu is an immobile element in plants and is mostly retained in the roots. As such, only a small percentage of soil Cu is generally translocated to above ground biomass parts, as also observed in this trial (Table 4–10). This is explained by several mechanisms: storage in the root tissues (Alloway, 1995; Marchner, 1995), and the low mobility of Cu in plants as a result of the strong binding with the xylem (Nissen and Lepp, 1997). The strong correlation between shoot Cu concentration in 1 year old trees with the declining ash percentage is probably also explained by this strong Cu retention in mineral rich tissue. As this study did not investigate root metal concentration, it is difficult to discern whether these mechanisms also applied in the two *Salix* clones used in this trial.

### *4.4.2 Seasonal changes in metal concentrations*

Foliar metal concentrations of both investigated willow clones showed an increase towards the end of the growing season. This increase was most outspoken for Cd and Zn, but also noticeable for Cu. Results from the foliar/wood Cd and Zn concentration ratios show that this increase in foliar metal accumulation occurs over the course of the growing season for all the investigated stands. This implies that the foliage of willow can be considered as a sink of metals which were supplied to the leaves through the wood. Over the course of the growing season the foliar Cd and Zn concentrations were well correlated ($R^2$ up to 0.997) which points to similar translocations mechanism for these elements to the leaves and possibly comparable sequestration characteristics in the leaves. Cd in leaves is generally accumulated in vacuoles to protect vital compounds of the cell. For Zn this mechanism is still little understood (Lasat, 2002). A similar large increase in foliar Pb concentrations was also observed in the 4 and 6 year old *Salix fragilis* stands.

From the leaf/wood concentration ratios it was shown that at the start of the growing season Cu is translocated from the leaves to the wood, at the end the opposite occurs and leaves get enriched compared to wood. Our results on Cu and Zn concentrations in leaves differ from those of Kim and Fergusson (1994) and Nissen and Lepp (1997). Both studies reported strong positive correlations between foliar Cu and Zn content, which Nissen and Lepp (1997) argued indicated a common pathway of movement. Kim and Fergusson (1994) on the other hand explained a common decrease in Cu and Zn concentrations towards the end of the growing season in *Aesulus hippocastanum* L. growing on unpolluted soil to a dilution effect caused by leaf growth. Such a correlation was not found in this study; while a drop in Cu concentrations was followed by a slight increase towards the end of the growing season, Zn concentrations increased over the whole of the growing season.

However, foliar Cu however showed similar seasonal patterns with Cr and Ni concentrations. The Cr and Ni concentrations dropped sharply in the beginning of the growing season for all stands after which they increased again towards leaf senescence. For absolute Cu concentrations this trend was only observed in the 4 and 6 year old *fragilis* stands, while concentrations in the younger stands were much more constant over the growing season. However, a clearer decrease is noticed when expressed as the leaf/wood concentrations ratio. The decrease in Ni concentration was largest in both the 1 year old *fragilis* and *triandra* stands, while Cr concentrations dropped most significantly in the foliage of the 4 and 6 year old *Salix fragilis* stands. A 2 year study of the metal concentrations in leaves of a mature birch stand by Ehlin (1982) showed that Cu and Ni contents decreased at the beginning of the growth period. This author attributed this to a dilution effect resulting from increased dry weight of the leaves. Similarly, Dinelli and Lombini (1996) reported higher whole plant Cu, Cr, Ni, and Zn concentrations in the early vegetative growth stage of *Salix* growing on mine spoil. They attributed this to a relatively high metal uptake compared to growth rate in the beginning of the growing season. This was followed by a period of vigorous growth, which diluted the concentrations.

Other studies have confirmed this concentration of metals in leaves of deciduous trees prior to shedding. Riddel-Black (1994) reported consistent increases in foliar heavy metals concentrations shortly before senescence in willow grown on metal contaminated substrate. Guha and Mitchell (1966) reported seasonal changes in foliar heavy metal concentrations in 18 deciduous tree species. They found clear evidence of metal accumulation in actively growing tissues, such as shoots and young leaves and showed that species such as sycamore, beech, and horse chestnut accumulated Fe and Zn at the end of the growing season. A marked accumulation of Zn in sycamore, beech, horse chestnut and hazel leaves at the end of the growing season has been noted by Ross (1994). Martin and Coughtrey (1982), found generally higher Cd and Pb in leaves of field maple at the end of the growing season. Hasselgren (1999) reported a tendency of increased willow leaf Cu content in autumn. A sharp increase in foliar Zn concentration was observed in a *Salix cinerea* stand growing on dredged sediment (Vandecasteele et al., 2002). This increase in metal concentrations is generally interpreted as metal shunting occurring in the plant tissues prior to senescence and that this phenomenon might be part of an excretion mechanism of excess metals by the tree (Baker, 1981; Riddel-Black, 1994; Hasselgren, 1999).

In the 1 and 2 year stand of both clones an increase of the wood Cd and Zn concentrations was observed over the course of the growing season. This increase was largest for the 1 year old trees, while in the older stand wood Cd and Zn concentrations remained fairly constant. This would imply that in these younger stands Cd was progressively accumulated throughout the growing season. The same trend was observed when wood Cd and Zn concentrations of these stands were expressed on a DAW basis. One explanation for this can be that the fast developing root systems in these young stands explores more substrate with large pools of available Cd with time. Another could be that Cd and Zn in the sediment became more available over the course of the growing season. However, sediments used in the trial were completely oxidized thus further oxidation could not be an explanation. As this trial only assessed the metal availability in the beginning of the growing season it is not possible to assess changes in metal availability over the course of the growing season. During dormancy, Cd and Zn concentrations should then decrease again as a result of a sharp reduction in the xylem flow. However, this could not be discerned in this study. These seasonal changes in biomass metal concentrations in wood should be considered to determine the sampling time. If shoot analysis aims at determining the removal of metals, sampling should be done at harvest. For the determination of metal loads in leaf litter for the purpose of risk analysis, sampling should be performed with leaf fall.

#### *4.4.3 Stand age*

Our results suggest that metal concentrations in willow biomass compartments decrease with stand age. Several other studies found similar results when investigating Cd accumulation over several growing seasons. Hammer et al. (2003) reported decreasing stem and leaf Cd and Zn concentrations with increasing stand age over a 5 year period at two different sites. Hasselgren (1999) also reported lower stem metal concentrations with the aging of the investigated willow stands. This may be attributed to the general notion that metal accumulation preliminary occurs in actively growing tissues such as shoots and young leaves. Another explanation could be that accumulated metals are diluted with increased biomass production. Klang-Westin and Perttu (2002) reported an opposing and very consistent relationship between stem biomass and stem Cd concentration. Our finding and these reports suggests that the potential to remove metals from contaminated site declines with tree age. Several factors such as dilution, metal availability in the root zone, and root activity can have an influence on this trend. Identifying these factors is a most needed task in further research.

#### *4.4.4 Metal concentrations expressed on DW versus DAW*

All RSD values for both DW and DAW concentrations in this study were below 20%, except for Cr wood concentrations which were slightly higher (24%). All RSD values are within the intervals defined for element variation between individual plants sampled at the same location (Djingova and Kuleff, 1994). According to Ernst (1990) RSD values lower than 20% can be considered normal, while higher values indicate to environmental stress in the stand. Spatial variability in this study was thus in the normal range indicating that the applied sampling procedure was representative for each of the investigated stands.

The constant dry ash percentages for wood over the growing season for the 2, 4, and 6 year old stands did not result in a clearer explanation of changes in wood metal concentrations. Only for the 1 year old stand there was a decrease in ash percentage from just after shoot break up to August when the constant level observed in the older stand was reached. This decrease in ash percentage corresponded with an decrease in wood Cu in the 1 year old stands of both investigated clones. This may indicates a close affinity for Cu with ash forming mineral material in the wood. Using DAW as a basis for wood metal concentration significantly increased the mean RSD values for Cd, Cu, and Zn concentrations for all sampling times and locations

Also for foliar metal concentrations did the use of DAW as a reference result in generally higher RSD's. For Cd, Cu, and Zn these differences were small and not significant, while the only significant differences found were for Ni and Pb. This is in contrast with findings by Claussen (1990) and Luyssaert et al. (2002) who reported lower RSD values when concentrations were expressed on a DAW reference. Vandecasteele et al. (2002) reported that 64% of the samples featured lower RSD values for Cd concentrations when expressed on a DAW basis.

### *4.4.5 Possibilities and limitations for phytoremediation*

The calculation results of the metal stocks in the different willow biomass compartments show that considerable amounts of Cd can be extracted from the contaminated sediment. For the other investigated elements the amount of metal accumulated in aboveground biomass is too low to ensure a timely remediation. Thus, only for Cd there are prospects of actively cleaning land disposed dredged sediments through phytoremediation, leaving other metals in place. As contaminated sediment is mostly contaminated with a range of heavy metals, the use of *Salix* to actively remediate this sediment to threshold values for all metals for reuse of the sediment as soil or building material is limited.

The highest theoretical export of Cd would be achieved with twelve annual harvests (stems and leaves) of the *Salix triandra* stand. This would deplete the sediment profile of 16% of the total Cd amount. However, a considerable period of time would be needed to reach the Cd threshold concentrations for reuse of the sediment as soil. To reduce the heavy metal concentration from 4.6 mg Cd/kg to the threshold value of 1.6 mg Cd/kg a period of 41 years would be needed (VLAREA, 1998). If only the stems would be harvested, this period needed would increase to 60 years.

However, for these calculations several assumptions were made which merit further discussion. It was hypothesized that both metal accumulation and biomass production would remain constant after each harvest. In reality the dynamics of the processes governing the uptake of Cd in *Salix* have to be taken into account. As available metals are accumulated by the tree, it can be expected that with time the amount of plant available Cd will decrease. The rate of this decline is poorly known and will depend on the rate at which Cd is mobilized from the less soluble soil fractions. The mobilization of Cd from the less solulable fractions to available form is in turn influenced by the root activity. There are scarce and contradictory reports on the availability of heavy metals in the root zone of *Salix*. Eriksson and Ledin (1999) found that long-term cropping of *Salix* resulted in a 30 to 40% decrease in plant-available Cd, although the effects on concentrations of total Cd were negligible. Their data on exchangeable Cd also showed that uptake occurred throughout the soil profile and that the involved Cd pool was large. Cd is generally present in exchangeable form in soils. In this trial a mean 15% of the total Cd was in available form. Results in this work (Chapter 5) suggest that metal availability in the vicinity of willow roots can increase compared to unrooted bulk soil. Pulford et al. (2002) also showed that the concentrations of EDTA-extractable Cd, Cu, Ni, and Zn in sewage sludge-amended soil were higher under willows than in unplanted areas. This increased availability can probably guarantee a continuous supply of available Cd to the roots for uptake. A *Salix* crop can therefore probably take up a large portion of Cd in the substrate before the readily available fraction is substantially reduced.

The other assumption made in this trial was that biomass production would be constant for every rotation period over the 12 years. From 3 to 6 year rotations it can be expected that this will be true, based on reports on traditional SRF practices (Willebrand and Ledin, 1995). Short rotation forests managed with such rotation periods are generally characterized with constant biomass production for every rotation as long as soil fertility is maintained. Only towards the end of the 20 year period in which SRF stands are generally operated a decline in production can be expected as a result of root and stump dieback. Reducing the rotation time to one year can however result in the decline of biomass production. Kopp et al. (1997) reported significantly lower yields in 3 years of annual willow harvesting compared to the production measured when a 3 year rotation is applied. Likewise, the cumulative production from two biennial harvests was significantly larger than the cumulative production from 4 annual harvests. Results from Sweden suggest that rotation lengths from four to six years result in the largest mean annual increments (Willebrand et al., 1993). The reduced biomass production with shorter rotations can be attributed to larger increments in the later stages of multi-year rotation compared to the production of the stand in the first year after harvest. This was also observed in willow stands growing on dredged sediments as reported in Chapter 3. In addition, stump mortality due to repeated harvests is another reason for decreasing yields (Harrington et al., 1984). The calculations on the potential exportable amounts of metals exported for 1 and possibly 2 year rotations should thus be regarded as a most optimistic assessment and are probably an overestimation.

Large amounts of metals, especially Cd and Zn, are recycled to the ecosystem if leaves are left on the site (Table 4–11). Klang-Westin and Eriksson (2003) reported also high amounts of Cd compared to the shoots in willow stands grown on contaminated agricultural land: about 21 to 48% of the shoot Cd was found in the leaves. These and our findings indicate that large percentages of accumulated Cd are recycled with leaf fall to the stands surface. Such translocation of large amounts of metals to the leaves may be an undesirable source of food chain accumulation of metals. In addition, high metal concentrations in the litter can negatively affect the litter decomposition (Zwolinski, 1994; Kohler et al., 1995). This was shown in several studies on forest ecosystems close to metal smelters. However, Key et al. (1988) and Vervaeke et al. (2003) reported an accumulation of Cd in the litter layer on dredged sediment disposal sites planted with willow but in neither of these studies it was reported that this affected litter dynamics. Vandecasteele et al. (2002) investigated the litter decomposition in old willow stands which had spontaneously colonized dredged sediments. Also in that study no negative effects of the contamination on litter decomposition were observed.

Table 4–11: Amounts of metals in litter in a 2 year *Salix fragilis* and a 2 year *Salix viminalis* stand (Vervaeke et al., 2003) compared with the annual atmospheric deposition in rural reference areas in Flanders (Van Grieken, 1996).

| | Amount in FR2 litter (g/ha/y) | Amount in *Salix viminalis* litter[a] (g/ha/y) | Atmospheric deposition (g/ha/y) |
|---|---|---|---|
| Cd | 106 | 11.8 | 7.3 |
| Cu | 38.5 | 38.2 | 73 |
| Pb | 11.1 | 57.4 | 110 |
| Zn | 5900 | 795.1 | 440 |

[a]: according to Vervaeke et al. (2003)

Up to now, the recycling of heavy metals with leaf fall and the associated risks have received little attention in the literature on the evaluation of willow species for phytoremediation purposes, although recently Hammer et al. (2003) also discussed this topic. A possible management option is to harvest the leaves in addition to the wood. This would increase the amount of metals which can be exported from the site and reduce the risk of food chain accumulation. In general, willows in SRF systems are harvested in winter when leaves have already fallen (Willebrand and Ledin, 1995). One option to remove the leaves is to collect them from the site surface after the harvest of the wood. For rotations longer than one year this can result in practical problems as it implies that leaves have to be removed in the years between harvests. Another possibility is to harvest the trees at the end of the summer before leaves have fallen. In general it is accepted that cutting willow in an actively growing stage results in result in physiological disorders and that resprouting is severely affected (Sennerby-Forsse et al., 1992). Root systems can lack nutrient reserves to support root growth and the development of a new shoot system. Disturbances to ongoing physiological processes involving internal hormonal interactions might cause stress to the system and lead to reduced production (Sennerby-Forsse et al., 1992). However, Hammer et al. (2003) reported no negative effect of annual harvesting stems and leaves before the start of leaf senescence. They showed that *Salix* could be clear-felled every year prior to leaf fall and still produce an increasing annual biomass. The fact that willows in their study were grown on a fertile substrate which received additional fertilization may be an explanation for their findings. Harvesting before leaf fall can result in practical problems in addition to possible physiological disturbances. For example, the on site chipping of the wood would be severely hampered. In addition, large quantities of nutrients are exported from the ecosystem as a result removing the leaves from the site. This can in time result in N and P deficiencies which in turn endanger the productivity of the stand.

If the aim of the restoration project is not to remove the heavy metals but to stabilize the metals, planting willow clones with limited metal translocation to the foliage, should be considered. Vervaeke et al. (2003) reported that the amounts of metals that were annually recycled with leaf fall in a *Salix viminalis* 'Orm' stand were in the same order of the annual atmospheric metal deposition in rural reference areas in Flanders (Table 4–11). In such a case, the risk of contamination of the wider environment through leaf fall can thus be considered as minimal.

## 4.5 Conclusions

Results from this trial indicate that the use of willow for the extraction of heavy metals is only an option if Cd is the only element which has to be exported. Although very high Cd concentrations were measured in the investigated *Salix* species, the time needed to reach the threshold values for reuse as soil of the dredged sediment in this trial would be considerable. Other metal which exceed their threshold concentrations for reuse of the sediment can not be removed in a timely fashion. Thus only for dredged sediments which feature slightly elevated Cd concentrations compared to threshold values are eligible for remediation with metal accumulation willow clones. The amount of extractable Cd can be increased through the combined harvest of stems and leaves. This also reduces the risks of spreading large amounts of Cd and Zn to the surroundings with leaf fall. However, such practices can endanger the sustainability of the SRF system as yield may become negatively affected. While results suggested that Cd uptake and stand age were inversely correlated it was shown that the length of the rotation did not drastically change potential metal exports. The large seasonal changes in metal concentrations of the different aboveground biomass compartments indicate that sampling should be performed close to the harvest and leaf senescence in order to correctly assess the potential amount of exportable heavy metals and the recycling of metals with leaf fall. Wood and bark should be sampled and analyzed separately as they are characterized with different metal concentrations.

# 5 Short- and longer-term effects of the *Salix* root system on metal extractability in contaminated dredged sediment

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**Abstract**

Willow stands are often proposed as vegetation covers for the restoration and stabilization of contaminated and derelict land. Planting willows on dredged sediment disposal sites for biomass production can be an alternative to traditional capping techniques. However, with the introduction of willow stands on dredged sediment disposal sites, the possibility of increased contaminant availability in the root zone must be acknowledged as it can increase the risk of leaching. Two trials investigated the availability of Cd, Zn, Cu, and Pb in the root zones of willows grown on contaminated sediment. To assess the effects of willow root growth on metal extractability and mobility, bulk and rhizosphere sediment samples were extracted with deionized water, ammonium-acetate at pH 7, and ammonium-acetate-EDTA at pH 4.65. A rhizobox experiment was used to investigate the short-term impact of willow roots on metal availability in oxic and anoxic sediment. Longer-term effects were assessed in a field trial. The rhizobox trial showed that Cd, Zn, and Cu extractability in the rhizosphere increased while the opposite was observed for Pb. This was attributed to the increased willow-induced oxidation rate in the root zone as a result of aeration and evapotranspiration, which masked the direct chemical and biological influences of the willow roots. The field trial showed that Cu and Pb, but not Cd, were more available in the root zone after water and ammonium-acetate [pH 7] extraction compared to the bulk sediment. Sediment in the root zone was better structured and aggregated and thus more permeable for downward water flows, causing leaching of a fraction of the metals and significantly lower total contents of Cd, Cu, and Pb. These findings indicate that a vegetation cover strategy to stabilize sediments can increase metal availability in the root zone and that potential metal losses to the environment should be considered.

## 5.1 Introduction

The use of trees in phytoremediation of contaminated land is receiving increased attention. Dickinson (2000) argues that there is sufficient evidence to consider the use of trees in reclamation as part of a realistic, integrated, low-cost, ecologically sound, and sustainable strategy for contaminated land. Over recent years, research has focused on planting willows on land contaminated with heavy metals, radionucleides, and other pollutants (Perttu and Kowalik, 1997; Vandenhove et al., 2001; Pulford and Watson, 2003). Large areas of land disposed dredged sediment with little other possibilities for end use can be restored by planting willow stands for biomass production. A dense willow vegetation cover can be easily introduced on land disposed anoxic sediments using the SALIMAT technique (Chapter 3). In addition, about 20% of the area of historic sediment disposal sites in Flanders was spontaneously colonized by willow (Vandecasteele et al., 2002).

While the revegetation of contaminated sites has received increasing attention over recent years, little information is available on the impact of willow tree roots on metal availability and mobility. With the spontaneous or deliberate introduction of willow stands on contaminated substrates, such as dredged sediment disposal sites, it is important to consider the possibility of increased metal bio-availability in the root zone, as willow stands could increase the risk of metal leaching. The bio-availability of nutrients and heavy metals in the rhizosphere of plants growing on contaminated substrates is altered through changes in the pH, the redox potential, the ionic strength, and ligand concentrations of the soil solution. These changes can be attributed to element uptake and solution flow to the roots, changes in redox conditions, plant-induced changes in solution chemistry, increased sorption on living and dead plant material, and the exudation of organics by the roots (Nye, 1981; McLaughlin et al., 1998; Hinsinger, 2000). While multiple studies have characterized the fractionation of heavy metals in bulk and rhizosphere soil of agronomic and herbaceous species, similar data are rare for tree stands growing on contaminated substrates.

The drying of anoxic sediment, for example after upland disposal, results in changes in pH, redox conditions, and the solubility of trace elements (Tack et al., 1996; Singh et al., 1998). The introduction of a willow vegetation cover on hydraulically raised sediment can influence oxidation and drying through increased evaporation and aeration of the root zone. Thus, the presence of active roots in anoxic sediment can be expected to have a more pronounced impact on metal availability compared to roots present in regular soils or already dried sediment. The aim of this investigation was to assess the short- and long-term effects of willow trees on metal extractability in dredged sediment. The short-term impact of willow growth on metal behavior in dry sediment and during the ripening of fresh anoxic sediment was determined in the green house with a rhizobox experiment. Long-term effects were observed under field conditions.

## 5.2 Methods and Materials

### *5.2.1 Sediment characterization and effect of forced air-drying*

In the first experiment, the short-term impact of willow roots on the metal availability in sediments was assessed. Fresh anoxic sediment from the river Leie (Roeselare) was collected from a dredging barge and transported in 25 l containers for use in the rhizobox green house experiment. Part of this sediment was dried at 105°C in a forced air oven to constant weight while another part was kept immersed under a water layer to prevent oxidation. The dried and anoxic sediments were sampled (n = 4) for an initial characterization. The dried sediment was thoroughly mixed and subsequently sub-sampled with a spoon. Samples from the wet sediment were obtained with a small auger. Care was taken to minimize oxidation of the anoxic sediment by storing the samples in a $N_2$ atmosphere immediately after sampling and flushing glassware with $N_2$ prior to use. The dried sediment samples were ground, sieved (2 mm mesh), and analyzed for total nitrogen, carbon, and carbonate content and total Cd, Zn, Cu, and Pb content. Total nitrogen was determined with the Kjelhdahl method, carbon was measured using the Walkley and Black method (OM = C% x 1.72), and the amount of carbonates was determined gravimetrically. The total metal concentrations were determined with an acid extraction (aqua regia mixture). The particle size distribution of the sediment was determined using the pipette procedure proposed by Gee and Bauder (1986). The redox potential of the fresh sediment was measured with a platinum electrode and a saturated calomel electrode as the reference electrode. Measurements were made by inserting the electrodes directly into the sediment following stabilization.

A water extraction procedure was used to investigate metal leachability. Water extracts of the anoxic and dried sediment were prepared following 2 hours of reciprocal shaking of a 1:2 sediment/deionized water suspension. The resulting sediment paste was filtered under vacuum onto a Buchner funnel fitted with filter paper (Schleicher and Schuell $589^2$, White Ribbon), and subsequently through a 0.45 µm filter. Water extracts were subsequently analyzed for pH, electrical conductivity (EC), $SO_4^{2-}$, $NO_3^-$, dissolved organic carbon (DOC), Cd, Zn, Cu, and Pb. DOC concentrations were obtained by subtracting the inorganic carbon (IC) concentration from the total carbon (TC) concentrations of each extract. TC and IC were analyzed on a Shimazu TOC-5000 Analyzer. Concentrations of $SO_4^{2-}$ and $NO_3^-$ were determined on a Dionex 200 ion chromatograph. Readily exchangeable and more persistently bound metals were extracted with 1M ammonium-acetate at pH 7 and 0.5 M ammonium-acetate-EDTA at pH 4.65, respectively (2 hour reciprocal shaking of a 1:5 sediment:extractant suspension). Metal concentrations in all extracts were analyzed on a GFAAS (Varian AA-1475 with GTA-95, Palo Alto) or on a AAS (Varian SpectrAA-10, Varian, Palo Alto), depending on required detection limits.

### *5.2.2 Rhizobox experiment*

Two large rhizoboxes (40 cm x 30 cm x 30 cm [LWH]), modified from Youssef and Chino (1988), were filled with dry and fresh sediment (Figure 5–1). The dried sediment was previously brought to 30% water content with deionized water to allow plant growth. Each rhizobox featured a rhizosphere and two bulk soil compartments. Dimensions of the rhizosphere compartment were 40 cm x 2 cm x 30 cm (LWH). Nylon mesh (50 µm pore size) was used to separate the rhizosphere and bulk soil compartments. Two boxes with the same dimensions, but without compartmentalization were filled with fresh and dried sediment to act as wet and dry control treatments, respectively. The rhizoboxes were planted by horizontally placing three *Salix viminalis* ‘Orm’ L. cuttings (35 cm) on the sediment in the rhizosphere compartment. Shoot and root growth on the cuttings in this compartment started one week after planting. Plants were watered regularly with deionized water to keep the moisture content of the dried and fresh sediment around 30 and 40%, respectively. The moisture content of the sediment at field capacity was 35%. Water content was measured at regular intervals during the trial using a Time Domain Reflectrometry probe. Control boxes received the same amount of water as the corresponding rhizoboxes. The temperature in the greenhouse was kept at approximately 20°C, and mean relative humidity was maintained around 45% during the whole trial. A light regimen of 16 hours light and 8 hours dark was applied.

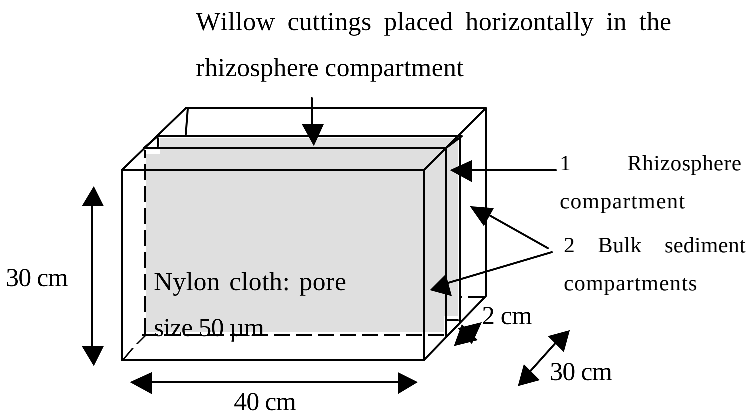


Figure 5–1: Rhizobox diagram.

The willows were grown for 2.5 months. After this period, the sediment in the rhizosphere compartment of the anoxic sediment rhizobox was densely penetrated with roots. Willows in the rhizobox filled with dry sediment, however, wilted and died 2.5 weeks after the start of the experiment. Only minimal rooting was observed in the dried sediment, and this was attributed to compaction and subsequent lack of aeration of the substrate. The compaction was the result of swelling and shrinking of the sediment after the repeated wetting of the dried sediment. We therefore decided not to sample the different compartments of this rhizobox and to consider only the rhizobox with initially anoxic sediment in the experiment. The redox potential was measured in situ before sampling the sediment from the rhizoboxes and control boxes. Roots were separated from the rhizosphere sediment with faucets. Only sediment from the center of each compartment or control box was used to determine metal availability. This sediment was sampled three times for each of the treatments. The rest of the sediment, which had made contact with the box or nylon, was discarded. Sampling and sediment preparation were performed under inert conditions (with $N_2$) in a glove bag. The sampled sediment was stored at 4°C in plastic bags flushed with $N_2$. Extraction and analysis of the sediments were performed within 3 days of sampling. Every sample was subsequently extracted with deionized water, ammonium-acetate at pH 7, and ammonium-acetate-EDTA at pH 4.65 as described earlier. The same parameters measured on the extracts of the initial dry and anoxic sediment were measured on each of the extracts as described above.

The different biomass compartments of the willows grown in the rhizobox were sampled after the experiment. From three of the 6 willows shoots that developed on the horizontal cuttings, wood, leaves, and roots were separated, dried at 70°C, ground, and subsequently digested in an aqua regia mixture. Concentrations of Cd, Zn, Cu, and Pb were determined on an AAS (Varian SpectrAA-10, Varian, Palo Alto).

### *5.2.3 Field trial design*

To assess long-term effects, the root zone in an existing stand of *Salix triandra* 'Noir de Villaines' was sampled in the field. This stand was planted 6 year ago and is located at the experimental site in Menen, Belgium (50°48' N, 3°08' E). After four years of stand development, a new layer (1.5 m) of sediment was placed between the trees, causing the trees to form adventitious roots in the newly dredged sediment layer (Figure 5–2). Two years after the sediment application, the dense new root systems had developed into small root mounds (30-40 cm) as the sediment ripened and settled. Sediment samples (n = 4) were taken in the root mounds and the unrooted bulk sediment using an auger as presented in Figure 5–2. The same metal extractions were performed and the same parameters were measured as described before. Wood and root samples of every sampled tree (n = 4) were also collected. Roots were washed three times in deionized water to remove attached sediment. These samples were processed and analyzed for heavy metal concentrations as in the rhizobox experiment.

### *5.2.4 Statistical analysis*

Means of the replicates and the evaluation of significant differences between treatments were determined with descriptive statistics and ANOVA, followed by Tukey's post hoc test ($\alpha$ = 0.05). Correlations between parameters measured in the water extracts were evaluated using Pearson correlation coefficients.

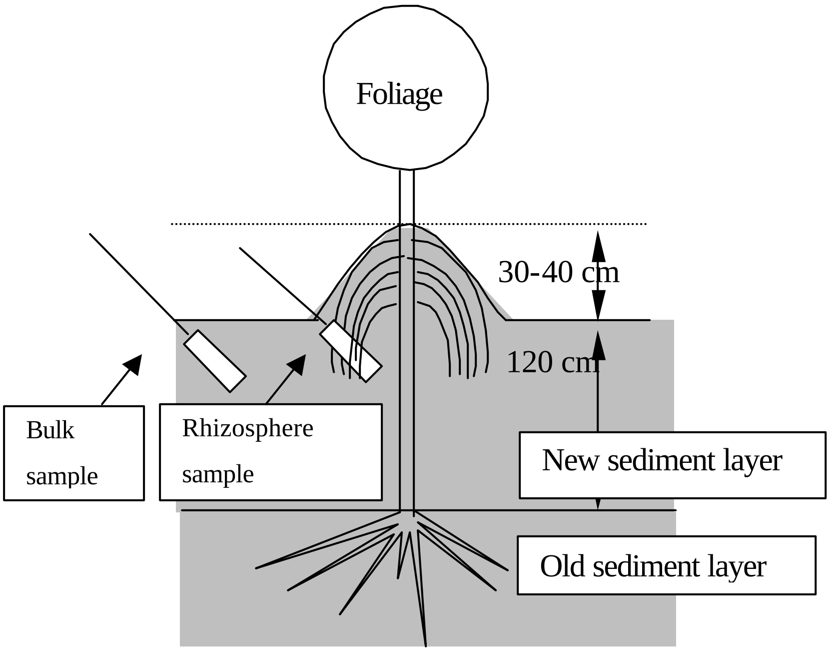


Figure 5–2: Sampling strategy in the adventitious root zone formed in the new sediment layer, which was applied to the *Salix triandra* 'Noir de Villaines' stand.

## 5.3 Results and Discussion

The sediment used in the rhizobox experiment was fine-textured material with high OM and carbonate content (Table 5–1). The redox potential (Eh) of the anoxic sediment was –220 mV indicating that the sediment was strongly reduced. The moisture content at the time of collection of the sediment was 50.2 ± 1.7%. Table 5–2 presents the metal concentrations on a dry weight basis of the six sample types that were extracted with deionized water, ammonium-acetate at pH 7, and ammonium-acetate-EDTA at pH 4.65. For further reference, these samples were labeled as follows: bulk, rhizosphere, wet control, dry control, dried, and anoxic. The parameters measured in the water extracts are represented in Table 5–3. Before describing the effects of the willow roots on metal availability, the changes in metal extractability as a result of forced air drying are presented.

### *5.3.1 Effect of forced air-drying on metal availability*

Forced air drying of the sediment resulted in major changes in the parameters measured in the water and acetate extracts. The pH dropped significantly from 7.68 to 6.54 while the electric conductivity more then doubled from 2181 µS/cm to 5846 µS/cm (Table 5–3). Metal solubility was low in the anoxic sediment, but increased significantly through the forced air drying. The effect of drying was most pronounced for Cd in the water extract: 23 times more Cd was extracted from the dried sediment compared to the anoxic sediment (Table 5–2). When ammonium-acetate at pH 7 was used as the extractant, the Zn concentration increased the most as a result of drying (23-fold). With ammonium-acetate-EDTA at pH 4.65 however, the increase was most significant for Cu (71-fold). The effect of drying was smallest on the solubility of Pb: The increase in Pb concentrations for each of the 3 extraction procedures was only three to four fold.

Generally, Cd, Zn, Pb, and Cu exhibit a low solubility in reduced sediment, which can be explained by their association with metal sulfides. These minerals tend to be very stable (insoluble) under reduced conditions because the metal-sulfide bonds tend to be highly covalent. (Hesterberg, 1998). The oxidation of these metal sulfides during aeration and oxidation results in the acidification of the sediment and the release of these previously immobilized metals (Satawathananont et al., 1991). The oxidation of sulfides in our trial resulted in an increase of soluble $SO_4^{2-}$ from 22 ± 4.8 mg/kg to 1206 ± 52.5 mg/kg and a release of heavy metals (Table 5–3). The oxidation of sulfides can have drastic effects on sediment pH if carbonates are not sufficiently present to provide buffering. For example, Brandon et al. (1993) reported a drop in pH from 7.6 to 3.2 as a result of drying and oxidation of sediment during a three year period. As a result of the high carbonate concentrations and subsequent buffering capacity of the sediment used in this trial, pH dropped by approximately one unit and remained neutral. Such a small shift can, however, strongly affect dissolved metal levels, as metal solubility increases strongly for Cd, Zn, Pb, and Zn in oxidized sediment as a function of decreasing pH (Tack et al., 1996).

Table 5–1: Characteristics of the sediment used in the rhizobox experiment.

| | |
|---|---|
| $pH\text{-}H_2O$ (1:2 solid:liquid suspension)[a] | 7.68 |
| OM (%)[b] | 6.1 ± 0.03 |
| Kjehldhal N (g/kg)[b] | 3.42 ± 0.025 |
| Carbonate content (%CaCO3)[b] | 8.2 ± 0.2 |
| Redox potential (mV vs. SHE)[c] | -220 |
| Cation exchange capacity (cmol $kg^{-1}$)[b] | 19.4 ± 0.5 |
| Particle size distribution | |
| Clay (0-2 µm) | 12% |
| Silt (2-50 µm) | 59% |
| Sand (50-2000) µm | 29% |
| Metal contents (mg/kg)[b] | |
| Cd | 3.8 ± 0.1 |
| Zn | 574.5 ± 7.9 |
| Cu | 77.4 ± 2.5 |
| Pb | 103.1 ± 4.3 |

[a]Measured on wet anoxic sediment.

[b]Means ± standard deviation of four replicates.

[c]Redox potential in mV versus standard hydrogen electrode (SHE)

Other processes can re-immobilize released metals after oxidation of the sediment, but perhaps not as effectively (Gambrell, 1994). It is well established that iron oxides effectively adsorb most trace and heavy metal cations (Jenne, 1968). Stephens et al. (2001) reported a decrease in metal leachability in oxidizing sediment after an initial seven week increase. The small increase in Pb concentration as a result of drying may be due to strong re-association with iron oxyhydroxides, which are formed during the oxidation of the sediment. Two of the common hydrous iron oxides, ferrihydrite and hematite, are known to preferentially adsorb Pb over other metals (Alloway, 1995). However, the latter is not expected to be present in our sediments. A sharp drop in pH after consumption of all carbonates would still result in desorption of Pb from hydrous oxides and clay minerals (Yong et al., 1990).

Drying of the sediment at 105°C to constant weight in a forced air oven increased the amount of dissolved organic carbon (DOC) in the water extracts by almost a factor four. This increase can be explained by the consumption of inorganic carbon (IC) and the release of previously bound organic carbon during oxidation.

### *5.3.2 Effect of root growth on metal availability in reduced sediment*

The extractability of Cd, Zn, and Cu for the three extraction procedures was higher in the rhizosphere compartment compared to the bulk and wet control sediments (Table 5–2). Water concentrations of Cd, Zn, and Cu in water extracts of the bulk and wet control were not significantly different; however, the ammonium-acetate at pH 7 extracts yielded significantly more Cd and Cu from the bulk compartment compared to the unplanted wet control. Results for Pb however were not that straightforward: The water and ammonium-acetate at pH 7 extraction showed higher available Pb concentrations in the bulk compartment compared to the rhizosphere compartment while with the ammonium-acetate-EDTA at pH 4.65 extraction exhibited only small differences between these compartments. The pH of the rhizosphere sediment was 0.4 and 0.2 units lower compared to the wet control and bulk treatment, respectively.

Table 5–2: Mean and standard deviations of metal concentrations (on dry weight basis), extracted with deionized water, ammonium-acetate at pH 7, and ammonium-acetate-EDTA at pH 4.65. Characters indicate homogenous sub-groups with no significant differences between means according to Tuckey's post hoc test ($\alpha = 0.05$).

| | Cd | | | Zn | | | Cu | | | Pb | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_2O$ (µg/kg) | | | | | | | | | | | | |
| Initial samples | | | | | | | | | | | | |
| Anoxic | 0.35 ± | 0.08 | a | 103± | 34 | a | 39.1± | 8.8 | a | 3.9± | 1.0 | a |
| Dried (105°C) | 8.07 ± | 0.83 | c | 682± | 81 | b | 324.9± | 47.4 | d | 11.7± | 1.4 | abc |
| Rhizobox samples | | | | | | | | | | | | |
| Bulk | 1.30 ± | 0.10 | a | 303± | 68 | a | 82.2± | 11.2 | a | 18.9± | 4.0 | c |
| Rhizosphere | 3.62 ± | 0.38 | b | 734± | 127 | b | 150.0± | 11.0 | bc | 7.0± | 1.0 | ab |
| Wet control | 0.79 ± | 0.08 | a | 226± | 16 | a | 91.3± | 23.8 | ab | 14.1± | 4.8 | bc |
| Dry control | 7.56 ± | 0.58 | c | 1009± | 125 | c | 177.8± | 18.8 | c | 20.1± | 6.7 | c |
| Ammonium-acetate pH 7 (mg/kg) | | | | | | | | | | | | |
| Anoxic | 0.04 ± | 0.02 | a | 0.8± | 0.1 | a | 0.24± | 0.01 | c | 0.08± | 0.01 | b |
| Dried (105°C) | 0.36 ± | 0.02 | c | 19.1± | 0.4 | b | 1.60± | 0.03 | f | 0.28± | 0.02 | d |
| Bulk | 0.25 ± | 0.01 | b | 20.0± | 1.1 | b | 0.16± | 0.02 | b | 0.41± | 0.01 | e |
| Rhizosphere | 0.47 ± | 0.02 | d | 25.0± | 0.9 | c | 0.61± | 0.01 | d | 0.17± | 0.03 | c |
| Wet control | 0.02 ± | 0.00 | a | 26.3± | 1.3 | a | 0.10± | 0.01 | a | 0.20± | 0.00 | a |
| Dry control | 0.48 ± | 0.01 | d | 23.1± | 0.7 | c | 0.75± | 0.01 | e | 0.48± | 0.01 | f |
| Ammonium-acetate-EDTA pH 4.65 (mg/kg) | | | | | | | | | | | | |
| Anoxic | 0.13 ± | 0.01 | a | 38± | 4 | a | 0.7± | 0.0 | a | 21.1± | 2.7 | a |
| Dried (105°C) | 1.83 ± | 0.01 | cd | 347± | 5 | cd | 46.8± | 0.4 | c | 84.9± | 2.1 | d |
| Bulk | 1.40 ± | 0.41 | b | 277± | 63 | bc | 7.2± | 0.8 | b | 65.4± | 4.4 | b |
| Rhizosphere | 2.14 ± | 0.04 | de | 351± | 5 | cd | 21.7± | 3.6 | c | 76.9± | 0.5 | cd |
| Wet control | 1.27 ± | 0.28 | bc | 260± | 35 | b | 10.2± | 0.6 | b | 68.2± | 0.8 | bc |
| Dry control | 2.45 ± | 0.19 | e | 397± | 35 | d | 39.0± | 3.8 | d | 80.2± | 6.8 | d |

Moisture contents at the time of sampling for the different compartments and control treatments were as follows: rhizosphere, 40.6%; bulk, 42.9%; wet control, 44.0%; and dry control, 24.7%. The redox potential measurements indicated that the sediment from all treatments was oxidized at the time of sampling. Readings were positive, but highly unstable, so no well defined redox potentials could be determined.

Table 5–3: Characteristics of the water extracts (mean ± standard deviation). Characters indicate homogenous sub-groups with no significant differences between means according to Tuckey's post hoc test ($\alpha$ = 0.05).

| | pH | | | EC (mS/cm) | | |
|---|---|---|---|---|---|---|
| Anoxic | 7.7± | 0.3 | c | 2.2± | 0.59 | a |
| Dried (105°C) | 6.5± | 0.1 | a | 5.8± | 0.58 | d |
| Bulk | 7.5± | 0.1 | bc | 4.1± | 0.98 | c |
| Rhizosphere | 7.3± | 0.1 | b | 6.8± | 0.12 | b |
| Wet control | 7.7± | 0.0 | c | 2.6± | 0.47 | e |
| Dry control | 6.7± | 0.2 | a | 5.9± | 0.86 | d |
| | $SO_4^{2-}$ (mg/kg) | | | $NO_3^-$ (mg/kg) | | |
| Anoxic | 22± | 5 | a | 4.0± | 1.3 | a |
| Dried (105°C) | 1206± | 53 | b | 67.5± | 2.1 | b |
| Bulk | 2317± | 63 | d | 175.3± | 41.9 | c |
| Rhizosphere | 2353± | 212 | d | 170.2± | 7.1 | c |
| Wet control | 2488± | 179 | d | 165.3± | 3.2 | c |
| Dry control | 1313± | 32 | c | 73.6± | 8.4 | b |
| | TC (mg/kg) | | | DOC (mg/kg) | | |
| Anoxic | 486.6± | 21.5 | d | 136.5± | 16.2 | b |
| Dried (105°C) | 508.8± | 11.0 | d | 508.1± | 5.6 | d |
| Bulk | 112.6± | 11.6 | a | 96.7± | 10.4 | a |
| Rhizosphere | 164.4± | 5.4 | b | 158.0± | 2.8 | b |
| Wet control | 119.4± | 8.9 | a | 101.7± | 8.0 | a |
| Dry control | 240.7± | 24.0 | c | 237.8± | 23.6 | c |

A common pattern of Cd, Zn, and Cu extractability was observed for the three types of extraction solutions used, ranging as follows: dry control > rhizosphere > bulk > wet control > anoxic sediment. Concentrations of these metals in the ammonium-acetate at pH seven extracts of the rhizosphere and dry control samples were most comparable. When focusing on the results of the water extracts, almost the same order was observed for the DOC concentration and the moisture content of the extracted samples; however, the DOC concentration of the bulk and anoxic treatments were inverted. The pH increased in the following order: dry (105°C) < dry control < rhizosphere < bulk < wet control anoxic. Pearson correlation coefficients for the 16 samples of the bulk, rhizosphere, wet, dry, and anoxic treatments extracted with water quantified this correlation (Table 5–4). Except for soluble Pb, the strong correlations indicated that the effects of plant growth on water extract characteristics are comparable to that of drying: i.e., pH and moisture content correlated well (r = 0.950), suggesting that the decrease in pH was associated with the increased aeration caused by plant growth. The good correlation between pH and the extractable Cd, Zn, and Cu concentrations indicated again the strong relationship between pH and metal mobility. These observations, together with the fact that this trend was also observed with the ammonium-acetate-EDTA extraction at pH 4.65, indicated that the increase in metal mobility was mainly due to an increased oxidation in the root zone.

Table 5–4: Pearson correlation coefficients between parameters measured in the water extracts and moisture content of the anoxic, wet and dry controls, bulk and rhizosphere sediments (n = 16).

| | Moisture % | EC | pH | Cd | Cu | Zn | Pb | DOC |
|---|---|---|---|---|---|---|---|---|
| Moisture % | 1 | -.698** | .950** | -.959** | -.870** | -.902** | -.623** | -.770** |
| EC | | 1 | -.713** | .781** | .870** | .881** | .268 | .587* |
| pH | | | 1 | -.976** | -.846** | -.892** | -.473 | -.870** |
| Cd | | | | 1 | .888** | .953** | .425 | .871** |
| Cu | | | | | 1 | .913** | .436 | .692** |
| Zn | | | | | | 1 | .364 | .754** |
| Pb | | | | | | | 1 | .222 |
| DOC | | | | | | | | 1 |

**: Correlation is significant at the 0.01 level
*: Correlation is significant at the 0.05 level

Generally, pH changes in the rhizosphere take place as a result of the differential uptake rates of cations and anions in plant roots (Nye, 1981). When a larger net influx of cations than anions occurs, protons are released to compensate for an excess of positive charges. Plants release hydroxyl or bicarbonate ions in the reverse case (Haynes, 1990). Results of our experiments indicated that the increased oxidation of the rhizosphere enhanced the oxidation of sulfides, resulting in a lower pH and the release of heavy metals. Root induced oxidation of $Fe^{2+}$ (and $Mn^{2+}$) is also associated with the production of $H^+$, which decreases rhizosphere pH (Begg et al., 1994). Carbonates are also known for their potential role in the immobilization of heavy metals in soil. Thus, the dissolution of carbonates also may have enhanced metal mobility in these experiments.

The solubility of Pb appeared to be less pH dependent and was controlled by other processes. The Pb concentrations in the water and ammonium-acetate extracts from rhizosphere sediments were lower than those from bulk sediments, but comparable to the concentrations found in extracts of the wet control. The formation of oxyhydroxides in the better-aerated rhizosphere compartment could explain this difference.

The repeated wetting of the dry sediment (105°C) in the dry control box for 2.5 months resulted in an increase of extractable Cd, Zn, and Pb. This coincided with a small pH increase from 6.5 to 6.7. However, Cu became less soluble in this period. As Cu can strongly complex with OM (Livens, 1991), it is likely that Cu, previously released as a result of forced air drying, reformed stable complexes with the OM present in the sediment.

OM and nitrogen concentrations measured at the end of the trial in bulk, rhizosphere, and wet and dry controls were not significantly different (Table 5–5). They were, however, significantly lower then the OM and N concentrations measured in the anoxic sediment. This indicated that OM decomposed in the 2.5 month period of the test. This decomposition was most pronounced in the dry control. The rhizosphere was slightly enriched with OM compared to the bulk sediment, but featured a lower N content.

Table 5–5: Organic metal and nitrogen content of the different sediment fractions (mean ± standard deviation). Characters indicate homogenous sub-groups with no significant differences between means according to Tuckey’s post hoc test ($\alpha = 0.05$).

| | OM (%) | | | N (mg/kg) | | |
|---|---|---|---|---|---|---|
| Initial samples | | | | | | |
| Dried (105°C) | 6.12± | 0.03 | b | 3422± | 25 | b |
| Rhizobox samples | | | | | | |
| Bulk | 5.66± | 0.15 | a | 3037± | 87 | a |
| Rhizosphere | 5.78± | 0.26 | ab | 3006± | 8 | a |
| Wet control | 5.91± | 0.09 | ab | 3083± | 33 | a |
| Dry control | 5.60± | 0.07 | a | 3021± | 37 | a |

Table 5–6 presents the metal concentrations measured in the different biomass compartments. The highest metal concentrations were found in the roots, but only Cd and Cu showed bio concentration factors (BCF) > 1. Metal accumulation in the above ground biomass compartments was low.

Table 5–6: Metal concentration (mg/kg) in biomass compartments of willows in the rhizobox experiment (n = 3) and field trial (n = 4) (mean ± standard deviation).

| | Cd | Cu | Pb | Zn |
|---|---|---|---|---|
| Rhizobox | | | | |
| Sediment | 3.8 ± 0.1 | 77 ± 2.5 | 103 ± 4.3 | 575 ± 7.9 |
| Root | 7.3 ± 0.3 | 94 ± 4.1 | 79 ± 3 | 429 ± 17 |
| Wood | 1.0 ± 0.04 | 4.9 ± 0.4 | 4.2 ± 0.2 | 65 ± 6.9 |
| Leaves | 0.9 ± 0.03 | 8.0 ± 0.6 | 2.1 ± 0.1 | 143 ± 8.2 |
| Field trial | | | | |
| Sediment | 3.7 ± 0.3 | 79 ± 3 | 279 ± 3 | 622 ± 8 |
| Root | 22 ± 1.1 | 67 ± 1.9 | 91 ± 1.1 | 419 ± 18 |
| Wood | 13 ± 0.5 | 6.7 ± 0.16 | 5.2 ± 0.2 | 316 ± 19 |
| Leaves | 18 ± 0.9 | 14 ± 0.5 | 7.8 ± 0.5 | 526 ± 22 |

The increase in Cd, Zn, and Cu extractability and decrease in pH after 2.5 months of willow growth can be attributed mostly to the indirect impact of increased oxidation as a result of aeration and evapotranspiration. Willow roots in anoxic substrates are known to meet their oxygen demand by generating a convective gas flow through pressurized ventilation (Grosse et al., 1996). Surplus oxygen is excreted and results in higher redox potentials in the rhizosphere, thereby protecting the root system from high concentrations of organic solutes and $Fe^{2+}$, $Mn^{2+}$, and $H_2S$ present in the bulk soil solution (Kozlowski, 1997). Adventitious roots, formed when the functions of the original root system weaken or cease, are also known to transport large quantities of $O_2$ to the rhizosphere resulting in oxidation (Hook, 1984). When lenticels, which channel $O_2$ to the adventitious roots, were blocked, the diffusion of $O_2$ into *Salix* roots is stopped, and the oxidation of the rhizosphere is halted. As the willow roots increased the oxidation of the rhizosphere in our experiment, this resulted in higher Cd, Zn, and Cu availability in the root zone. This increased oxidation can be attributed to i) a better aeration of the root zone through active $O_2$ transport in willow roots and ii) transpiration by the trees. This increased oxidation of the root zone masked the direct chemical and biological influence of the willow root as would be observed in oxic soils. It is, for example, unclear if the increase in DOC concentration in the rhizosphere observed in this trial was the result of the higher aeration of the sediment matrix or the production of labile organic carbon by the roots (root exudates). Results from the rhizobox with dried sediment would have provided a clearer picture on the direct impact of willow roots on metal extractability and other parameters, as oxidation was not a driving variable in that experiment.

Our results are consistent with those presented by Marseille et al. (2000), except for the extractability of Pb. They evaluated the impact of plant growth (maize, rape, and rye grass) on the leaching of heavy metals from dredged sediment in a pot experiment. Plant growth resulted in a better aeration and oxidation of the sediment in the root zone, and leachate conductivity and DOC concentrations were consistently higher in potted plants. Cadmium, Zn, Cu, and Pb concentrations were all higher in the leachates from the potted plants compared to control pots. However, they found no evolution of the sediment matrix pH over the course of the experiment. Only in the case of rape was a decrease in leachate pH observed, but this change had little effect on heavy metal mobility. In a subsequent investigation they included *Salix* in their plant set (Bert et al., 2002). Cd and Zn leaching was found to be largest under *Salix* compared to the other plant species. Leaching was lowest under *Agrostis, tenuis* and *Deschampsia cespitosa*, growing on sediment amended with basic slags. Greger (1999), on the other hand, found 30% less bio-available Cd after a 90 day pot trial with willow. Recently, Hammer and Keller (2002) described the metal extractability in the rhizosphere of willows grown in oxic Swiss soils. They reported a depletion of readily available Cd, Cu, and Zn ($NaNO_3$ extraction) in the rhizosphere, which was always lower than quantities taken up by the plant. They detected no changes in the DPTA and EDTA extractable pools as a result of 90 days of willow growth.

### 5.3.3 Field trial: long-term effects

Two years of willow root growth had significant effects on the chemical characteristics and metal contents of the sediments (Table 5–7). The rhizosphere sediment featured higher OM and nitrogen contents, a slightly higher pH, and lower salt content compared to the bulk sediment. The total Cd, Zn, Cu, and Pb concentrations were lower in the rhizosphere sediment. These differences were significant for Cd, Cu, and Pb. The concentrations of Cd and Zn in both the ammonium-acetate and ammonium-acetate-EDTA fractions of the rhizosphere sediment were also lower. This indicates that certain fractions, even from the more strongly bound ammonium-acetate-EDTA (pH 4.56) were lost despite the slightly higher pH in the root zone. Copper was more available in the rhizosphere for both ammonium-acetate extractions, which probably released Cu associated with OM. The same was observed for Pb with the ammonium-acetate (pH 7) extraction.

The root zone sediment was highly structured—featuring fine aggregates—and was very permeable. The bulk soil did not feature fine aggregates and was still compact and unstructured. These observations suggest that a fraction of all the investigated metals leached during the 2 years of root growth. The significantly lower salt content in the water extracts of the rhizosphere sediment supports this conclusion. Part of this lost fraction could also be incorporated in the above ground biomass, although metal concentrations in the wood were low. Metal concentrations in the water extracts were slightly higher in the rhizosphere compared to bulk sediment, except for Zn, indicating that more metals were directly available for leaching through the root zone. Metal concentrations in the biomass were highest in the adventitious root compartment (Table 5–6). Only Cd and Zn were further translocated to above ground compartments. Cadmium was the only element that truly accumulated in the whole plant (BCF > 1).

Table 5–7: Mean chemical characteristics and standard deviations (n = 4) of rhizosphere and bulk sediment samples from the field trial. * indicates significant differences between rhizosphere and bulk sediment concentrations (p = 0.05).

| | | | Rhizosphere Mean | Std. Dev. | Bulk Mean | Std. Dev. | Sign |
|---|---|---|---|---|---|---|---|
| pH | | | 7.9 | | 7.6 | | * |
| [1]EC | | µS/cm | 256± | 34 | 955± | 214 | * |
| [1]DOC | | mg/kg | 54± | 3 | 79± | 11 | * |
| OM | | % | 7.2± | 0.2 | 6.2± | 0.01 | * |
| N | | mg/kg | 3560± | 11 | 3160± | 17 | * |
| [1]$NO_3^-$ | | mg/kg | 30± | 3.5 | 37± | 7.1 | |
| [1]$SO_4^{2-}$ | | mg/kg | 19± | 2.1 | 7.2± | 1.8 | |
| Cd | Total | mg/kg | 3.12± | 0.23 | 3.65± | 0.29 | * |
| | $H_2O$ | µg/kg | 4.5± | 1.2 | 3.7± | 0.9 | |
| | $NH_4OAc$ pH7 | mg/kg | 0.38± | 0.06 | 0.53± | 0.07 | * |
| | $NH_4OAc$ EDTA pH4.65 | mg/kg | 1.66± | 0.09 | 2.04± | 0.2 | * |
| Zn | Total | mg/kg | 615± | 11 | 622± | 8 | |
| | $H_2O$ | µg/kg | 221± | 8 | 254± | 9 | |
| | $NH_4OAc$ pH7 | mg/kg | 10.8± | 0.3 | 14.4± | 2.1 | * |
| | $NH_4OAc$ EDTA pH4.65 | mg/kg | 191± | 9.17 | 202± | 8.59 | |
| Cu | Total | mg/kg | 74± | 2 | 79± | 3 | * |
| | $H_2O$ | µg/kg | 303± | 89 | 193± | 74 | |
| | $NH_4OAc$ pH7 | mg/kg | 0.77± | 0.04 | 0.6± | 0.04 | * |
| | $NH_4OAc$ EDTA pH4.65 | mg/kg | 4.88± | 0.07 | 5.57± | 0.15 | * |
| Pb | Total | mg/kg | 268± | 5 | 279± | 3 | * |
| | $H_2O$ | µg/kg | 37.6± | 8.4 | 17.9± | 9.2 | * |
| | $NH_4OAc$ pH7 | mg/kg | 1.99± | 0.09 | 1.01± | 0.03 | * |
| | $NH_4OAc$ EDTA pH4.65 | mg/kg | 16.2± | 1.9 | 16.9± | 0.1 | |

[1]: Measured in the water extract

The aim of phytostabilization techniques is to render heavy metals more immobile and reduce the chemical and physical risks to the environment. The trials investigating the short- and longer-term effects of willow root growth on metal availability suggest that planting willow crops on contaminated sediments can increase the risk of heavy metal leaching. Cadmium, Zn, and Cu became more available during ripening and oxidation of the sediment as a result of increased oxidation of the root zone. Subsequently, a fraction of the metals was lost due to leaching in the aggregated and permeable root zone.

However, it must be mentioned that the trial presented here can be considered a worst-case scenario: An extremely dense root zone was compared to completely unrooted and biologically inactive sediment. In addition, the presence of the roots altered the ripening sediment in such a manner that the physical characteristics became completely different from the unrooted sediment. Sediment in the root zone became better structured and aggregated and thus more permeable for downward water flow. With a normal root density, as found in contaminated oxic soils, the effects would be less profound.

When oxic soils are planted, the introduction of a root system does not dramatically change the physical characteristics of the root zone as observed in this trial. However, living and dying roots can create pathways of preferential flow for percolating water (Gish et al., 1998). In this case, water movement through the rooted sediment increased as a result of the improved sediment structure; however, it can be argued that in conventional plantings the high evapotranspiration of willow stands may result in a decreased downward water movement compared to unplanted soil. While measurements of heavy metal availability in the root zone are usually performed in pot experiments or during the growing season in field trials, the behavior of metals in the root zone during the dormant season may be crucial to assess the ecological risk of planting trees on contaminated sites. During winter roots are less active, evapotranspiration is minimal, and precipitation is high. Hence, care should be taken that metals mobilized during the growing season, but retained in the root zone through hydraulic control, are not leached during the winter season.

Field observations on the influence of tree growth on metal mobility are scarce, and findings are often contradictory. Eriksson and Ledin (1999) found that long-term cropping of *Salix* resulted in a 30-40% decrease in plant-available Cd, although the effects on concentrations of total Cd were negligible. Their data on exchangeable Cd also showed that uptake occurred throughout the soil profile and that the involved Cd pool was large. Pulford et al. (2002) showed that the concentrations of EDTA-extractable Cd, Cu, Ni, and Zn in sewage sludge-amended soil were higher under willows than in unplanted areas. Klassen et al. (2000) investigated the behavior of Pb in the root zone of birch planted on contaminated soil (3000 mg/kg) and mine tailings (13,000 mg/kg). As a result of Pb exclusion by birch, the rhizosphere became enriched with Pb in both treatments. Planting did not affect the leaching of Pb from the contaminated soil and there were indications that Pb became more immobilized, yet the amount of Pb leached from the highly contaminated mine tailings increased. Zhu et al. (1999), on the other hand, reported that the establishment of a grass cover could reduce Pb movement, but enhance short-term Cd and Zn leaching. Garten (1999) modeled the effect of a forest cover on $^{90}Sr$ leaching. Losses from the contaminated soil were reduced by 16% under forest compared to grass as a result of greater evapotranspiration. Furthermore, Schnoor (2000) reported that metal percolation under poplar trees was comparable to that under a clay cap. These findings suggest that when using plants to restore contaminated soils, increases in metal availability in the root zone with the increased risk of metal leaching must be considered.

## 5.4 Conclusions

Since the revegetation of contaminated sites has received increasing attention in recent years, more attention should be paid to the behavior of heavy metals in the root zone. The leaching of heavy metals under forested polluted sites is an important pathway for metals to disperse to the wider environment. The two trials presented in this chapter showed that the introduction of dense willow root systems could significantly alter the availability and the extractability of heavy metals in the root zone. Two and a half months of willow root growth increased extractability of Cd, Zn, and Cu after increased oxidation of the root zone in oxidizing sediment compared to bulk sediment. This increased oxidation was attributed to i) a better aeration of the root zone through active $O_2$ transport in willow roots and ii) transpiration by the trees. The direct chemical (exudates, pH changes) and biological (microorganisms) influences of the willow roots were masked by the willow-induced oxidation processes. Two years of willow root growth had significant effects on the chemical characteristics and metal content of the sediment. Metal concentrations were significantly lower in the root zone, suggesting that a fraction of the metals leached during the two years of root growth. The root zone sediment was well structured, featured fine aggregates, and was well permeated. The bulk soil, on the other hand, did not feature fine aggregates, was very compact, and was unstructured, thereby preventing percolation and metal leaching. The extractability of Cd, Cu, and Pb was greater in the rhizosphere compared to the bulk sediment, suggesting that more metals were becoming directly available for leaching through the root zone. These findings indicate that a tree-based strategy to restore sediments, especially anoxic sediments, may result in the dispersal of metals to unwanted compartments in the ecosystem. As such, possible metal losses to the environment must be closely monitored.

# 6 Fate of heavy metals during fixed bed downdraft gasification of willow wood harvested from contaminated sites

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**Abstract**

Growing energy crops can be an interesting land use option for the restoration and phytoremediation of large areas of contaminated land, but results in the production of large volumes of heavy metal enriched biomass. Small scale fixed bed downdraft gasifier installations (100 kWe - 1 MWe) can play an important role for the on site conversion of this biomass to electricity and heat. To asses the fate of heavy metals during the conversion of metal enriched willow wood, 3 subsequent gasification operations were conducted in a small scale 100 kW fixed bed downdraft gasifier. The gasification of about 100 kg of wood resulted in the production of 40 g of ashes, 1.2 kWh of electricity and 9 MJ of heat. The bottom, cyclone, fine fly ash and gasifier bed ash fractions were sampled, weighed and analyzed for Cd, Cu, Cr, Pb, Ni, and Zn. The concentrations of Cd, Pb, and Zn increased with decreasing ash particle size. For the other elements such increase was not observed. Cu was predominantly associated with the bottom ashes while most of the Zn was found to be in the filter fly ash. Only 7% of total Cd and Pb were recovered in the bottom ash fraction indicating that a large percentage of these metals were volatilized during gasification. The scrubber placed after the hot cyclone thus has an essential role in intercepting volatilized heavy metals before combustion of the gas. Although most Cd and Zn were volatilized during gasification, their concentrations in the bottom ashes still exceeded the Flemish threshold values for use of this fraction as fertilizer although by a small margin. Adjusting combustion temperatures and applying appropriate cyclone technologies could probably further reduce metal concentrations in the most voluminous ash fractions.

## 6.1 Introduction

Willow wood is a widely used biofuel in gasification installations for electricity and heat production (Senelwa and Sims, 1999). The production of willow biomass on metal contaminated sites can however result in the accumulation of metals in the different ash fractions and/or losses to the atmosphere. In recent years, much of attention was paid to the restoration and phytoremediation of contaminated land with trees, and especially willow based SRF systems (Pulford and Watson, 2003).

Willow trees are known to accumulate significant amounts of heavy metals, especially Cd, in their biomass compartments (Brieger, 1992; Ostman, 1994; Felix, 1997; Greger and Landberg, 1999). This characteristic, together with heavy metal tolerance was proven to be clone dependent (Landberg and Greger, 1999; Punshon and Dickinson, 1999). Willow clones characterized with a high heavy metal uptake and managed in SRF systems can thus be used to remove a fraction of the heavy metals from contaminated soils. Clones with low uptake can be used to revegetate, restore and stabilize contaminated and derelict sites without the risk of spreading heavy metals to the environment through leaf fall. In either case, wood enriched with heavy metals is produced. As phytoremediation is an emerging technology with still limited field scale applications, little attention has yet been paid on the use and conversion of the produced biomass. Only if the wood conversion and the produced metal enriched solid residues can be managed in an economically environmental sound manner, will biomass production in phytoremediation projects be a sustainable technology that contributes to a solution for contaminant land restoration.

The fuel conversion system used for conversion is key to the distribution and release of metals from biofuels. Bio-energy systems have the potential to be a significant source of metals to the geo- and atmosphere and appropriate technology must be employed to ensure that releases are not excessive (Riddel-Black and Fergusson, 2000). Small scale fixed bed downdraft gasifier installations (100 kWe - 1 MWe) can play an important role for the conversion of willow biomass produced in phytoremediation projects. They are highly mechanized remote controlled stand alone installations which require little follow up and maintenance. Larger scale plants could objects to using contaminated wood in their biomass supply chain. In addition, these installations can produce electricity and heat on the phytoremediation site thus shortening the supply chain and minimizing transport costs, which are regarded as a major cost in bio-energy production operations (Coelman et al., 1996). Gigler et al. (1999) compared the chain designs for small to large scale energy conversion and concluded that small scale is generally cheaper than large scale when costs are expressed in Euro/ton DM due to increased transport costs for large scale. However, when costs are expressed in Euro per kWh, large scale is cheaper than small scale, due to the higher energy conversion efficiencies.

With the gasification of contaminated wood it is important to understand which ash fractions are formed and how heavy metals will behave during this process. This is especially true with the subsequent handling of the produced ash fractions in mind. Biofuel ashes are generally returned to agricultural fields or forests to maintain a closed and sustainable nutrient cycle. Ideally, by concentrating the bulk of heavy metals in a small volume of fly ashes it should be possible to the major part of the ash produced, the so called ‘usable ash’. Although Hansen et al. (1998) reported low Cd leachability from fly ashes the long-term effects and accumulation of cadmium through the recycling of fly ashes could pose a problem.

The trial presented in this chapter investigated the fate of heavy metals present in willow wood during the conversion to electricity and heat in a small scale 100 kW fixed bed downdraft gasifier. The wood was harvested from a contaminated dredged sediment disposal site planted with a high density willow stand. The distribution of the different ash fractions and associated heavy metals was assessed in 3 subsequent gasification operations.

## 6.2 Methods and Materials

### *6.2.1 Wood properties*

In 2000, a willow stand (*Salix viminalis* L., clone 86133) was harvested from an afforested dredged sediment disposal site in Menen (Belgium, 50°48' N, 3°08' E). The harvested stand was planted 5 years before in March 1995. Wood was left one month on site for drying and subsequently chipped to 30–50 mm pieces in a traditional forestry chipper. Chips were further air dried to a moisture content of 10% prior to the tests. The bulk of the chipped wood was sub-sampled 10 times for heavy metal analysis. The sub-samples were dried at 70°C in a forced air oven and milled. A pressurized microwave decomposition procedure with a $HNO_3$/HCl/HF mixture was used to destruct the samples. Extracts were subsequently measured on an ICP-AES (Varian Vista-axial, Varian, Palo Alto, CA) for Cd, Zn, Pb, Cu, Ni, and Cr concentrations. The analytical quality of the measurements was checked by including a method-blank and laboratory controls sample every 10 samples. The moisture content was determined by drying the wood in a forced air oven at 105°C to constant weight. Ash content was measured after ashing at 550°C. Sediments at the harvested site were sampled in a 5 x 5 m grid to a depth of 30 cm, resulting in a total of 10 samples. These were dried at 105°C, milled and extracted for heavy metal analysis.

### *6.2.2 Test installation*

The measurements were carried out in 100 kW fixed bed downdraft gasifier. This setup was the pilot scale version of the since 2002 commercially available 150 kW Xylowatt downdraft gasifier. The installation was batch fed with about 90-105 kg of contaminated wood (moisture content 10%) for each test. The commercial variant is equipped with a conveyor belt and inlet for continuous feeding. The tree subsequent gasification tests were performed in the same week. Figure 6–1 presents the installation and its components. The main components of the producer gas CO, $CO_2$, $CH_4$, and $H_2$ were measured continuously during gasification by a non-dispersive infrared (NDIR) analyzer (Beckman URAS 10) for CO, $CO_2$, and $CH_4$ analysis and by Catharometry (Thermados) for $H_2$ determination. The analysis equipment was calibrated before each test. Values were acquired and stored on PC. Temperatures in the boiler, the hot cyclone and of the gas before entering the condensation unit were recorded. The airflow was measured by the pressure drop across an orifice and the pressure gauge signal was logged on PC. In addition, the exhaust gas temperature was measured. The pressure drop created by the furnace was continuously measured by a pressure gauge (0-10,000 Pa). A hot cyclone was used for the removal of fly ashes. The installation was equipped with a water scrubber which acted as a cooling tower to remove smaller ash fractions. Scrubber effluent was cleaned on active coal. The produced gas can be fed to a 20 kWe Dual fuel engine for conversion to electricity and heat.

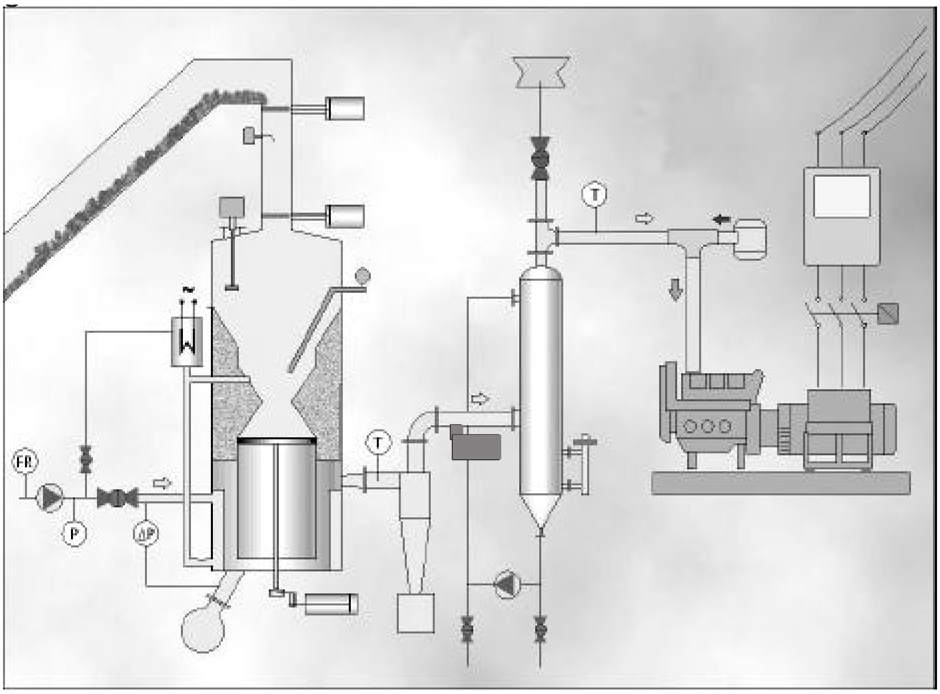

Figure 6–1: Scheme of the fixed bed downdraft gasifier used in the tests with the locations of sampling the different ash fractions: 1) gasifier boiler, 2) gasifier bed ashes, 3) bottom ashes, 4) cyclone ashes, 5) filter fly ash sampled in condensation unit, 6) scrubber, 7) cogeneration unit.

### 6.2.3 *Sampling of the ash fractions*

The different ash fractions distinguished in this trial were: i) bottom ash: the ash fraction formed in the combustion chamber which was collected in an ashtray under the combustion chamber, ii) cyclone fly ash: the inorganic ash particles carried with the flue gas. Fly ashes were collected in a cyclone placed behind the combustion unit, iii) filter fly ash: finer fly ash fraction precipitated on filters as a condensable phase in a condensation unit. The filter fly ash in this installation is normally intercepted by the scrubber, iv) gasifier bed ashes: the ashes left in the combustion unit after the three tests. Flue dust or the finest fly ash fraction which is normally not precipitated was not sampled and measured in these tests.

After each test the bottom and cyclone ash samples fractions were collected, weighed, mixed and sampled. The sample used for the heavy metal analysis consisted of at least five sub-samples from the bulk ashes which were previously throughoutly mixed. The gasifier bed ashes were collected, weighed and sampled after the three trials when the gasifier was emptied. All ash samples were ground manually with mortar and pestle, and sieved on a 1 mm mesh. The filter fly ash was sampled using a dilution and cold filter tunnel placed behind the hot cyclone. A known amount of flue gas was sampled in a, smooth and polished line at 200°C to avoid tars condensing and deposit development. The gas was subsequently cooled by dilution in dry and clean air at 20°C. As a result the tars present in the gas condensed. The obtained diluted gaseous mix was passed through a glass fiber filter (pore diameter 0.45 µm) to intercept the formed solid particles and tars. The mass of the filters was measured before and after the sampling to quantify the weight of adsorbed materials. This procedure was repeated at least 12 times during each test. Filters from each test (12-16) were pooled in groups of four to six prior to analysis. Sub-samples of the pooled filters were subsequently digested in an $HNO_3$/HCl/HF mixture during a pressurized microwave decomposition procedure (CEM, MDS 2000). Extracts were subsequently analyzed for the investigated heavy metals on ICP-AES (Varian Vista-axial, Varian, Palo Alto, CA). The analytical quality of the measurements was checked by including a method-blank and laboratory controls sample every 10 samples. Moisture and ash contents of the different ash fractions were determined as described above.

## 6.3 Results and discussion

### *6.3.1 Wood properties*

The heavy metal concentration of the wood used in these trials is presented in Table 6–1. The concentrations of Pb and Cd in this study were elevated compared with the background values of metals in plants: 0.1–2.4mg Cd/kg, 1–400 mg Zn/kg, 0.2–2.0 mg Pb/kg, and 5–20mg Cu/kg (Kabata Pendias and Pendias, 1992). The wood was thus enriched in heavy metals but only Cd was truly accumulated (BCF > 1) when compared with soil concentrations. The Cd, Cu, and Zn concentrations were comparable with measurements in a *Salix viminalis* 'Orm' stand grown on contaminated dredged sediment (Vervaeke et al., 2003), but Pb concentration were lower in the present study. Compared to the metal concentrations of the *Salix triandra* and *fragilis* clones presented in Chapter 4, the harvested *Salix viminalis* clone can thus be considered as a poor metal accumulator.

Table 6–1: Mean metal concentrations (mg/kg) in wood and sediment ± standard deviation with their BCF (BCF = wood metal concentration/substrate metal concentration).

| | Wood (mg/kg) | | | | Sediment (mg/kg) | | | | BCF |
|---|---|---|---|---|---|---|---|---|---|
| Cd | 3.82 | ± | 0.26 | mg/kg | 2.6 | ± | 0.22 | mg/kg | 1.49 |
| Cr | 4.13 | ± | 0.79 | mg/kg | 125.9 | ± | 13.2 | mg/kg | 0.03 |
| Cu | 6.56 | ± | 0.61 | mg/kg | 57.4 | ± | 3.8 | mg/kg | 0.11 |
| Ni | 2.18 | ± | 0.14 | mg/kg | 39.9 | ± | 3.1 | mg/kg | 0.05 |
| Pb | 3.49 | ± | 0.42 | mg/kg | 93.1 | ± | 5.4 | mg/kg | 0.04 |
| Zn | 150 | ± | 28 | mg/kg | 399 | ± | 19 | mg/kg | 0.38 |

### 6.3.2 Gasification specifications

Wood consumption during the tree test was approximately 31 kg/h. Each test lasted approximately 3 hours. The average composition of the produced gas was comparable to that obtained from the gasification of clean wood: CO = 23%, $H_2$ = 15%, $CO_2$ = 10%, and $CH_4$ = 2-3%. The lower heating value of the gas was stable during the tests with an upper level of about 5000 kJ/Nm³. The thermal power of the gas was round 100-120 $kW_{th}$. The 3 tests produced respectively 215, 218, and 173 $Nm^3$ of gas. The combustion of this gas in a 20 $kW_e$ Dual fuel engine resulted in the production of 1.2 kWh of electricity and 9 MJ of heat for each kg of gasified wood.

### 6.3.3 Weights of the ash fractions

The gasification of the total 269 kg DM of willow wood resulted in the production of 8.3 kg bottom ashes (3.1%), 1.9 kg cyclone ashes (0.7%), 0.7 kg filter ashes (0.2%), and 4.8 kg of gasifier bed ashes (1.8%). The latter is normally burned in an uninterrupted process. About 6% of the weight of the processed wood is thus recovered as ashes. Bottom ash makes up 75% of the total ash amount. The percentages for cyclone ash and fine filter ash are respectively 18 and 7%. These percentages are consistent with percentages obtained for a range of biomass plants reported by Obernberger et al. (1997). The bottom and cyclone ash production was fairly constant over the 3 trials (Table 3). However, in the first trail a significantly higher production of filter fly ash was observed compared to the other trials. This was probably due higher tar and fly ash production during start up of the installation. The concentration of fine fly ash particles in the gas measured after the cyclone for the subsequent trials were respectively 2062 mg/$Nm^3$, 824 mg/$Nm^3$, and 589 mg/$Nm^3$. The changes in filter fly ash concentrations over the 3 tests is presented in Figure 6–2. It can be expected that this filter fly ash fraction will be largely removed in the scrubber. The scrubber used in the experimental setup and commercial installations reduces the amount of particles and tars from 500-5000 mg/Nm³ to 10 mg/$Nm^3$ (Navez, unpublished data).

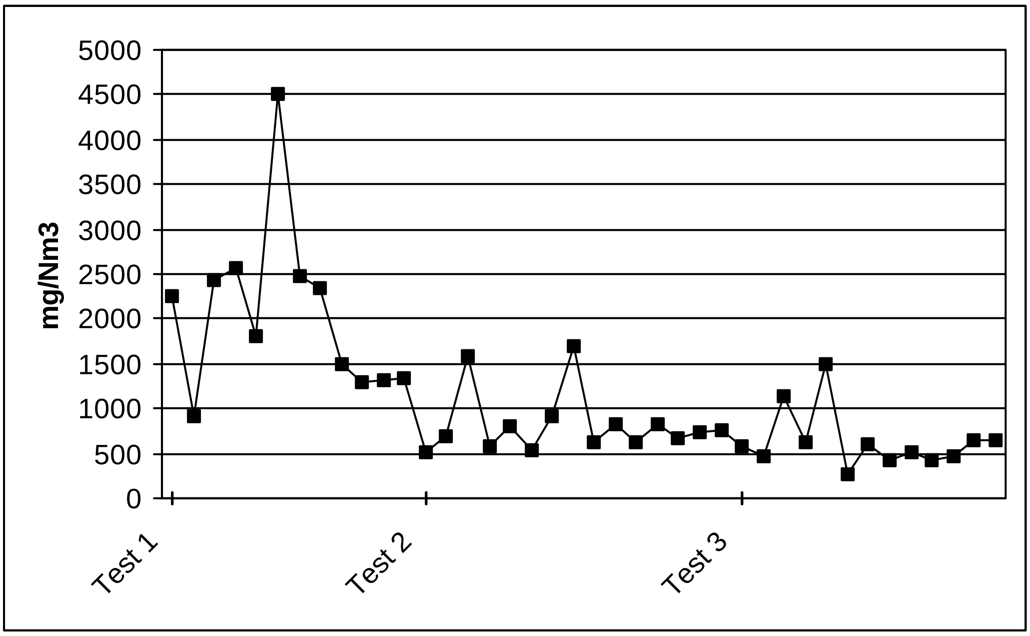


Figure 6–2: The changes in filter fly ash concentrations (mg/Nm$^3$) over the 3 tests.

*6.3.4 Heavy metals in the ash fractions*

Heavy metals present in the wood were distributed across the different ash fractions as a result of gasification. An enrichment of Cd, Zn and Pb in the fly ashes compared to the bottom ashes was observed (Table 6–2). The Zn and Pb concentrations were respectively 56 and 43 times higher in the filter fly ash compared to the bottom ash. For Cd this factor is 14. Zn, Pb and Cd are known to sublimate and form gaseous compounds during gasification. When the flue gas is cooled they form aerosols and condense on fly ash particles. Cd, Pb and Zn concentrations thus increase significantly with decreasing temperatures of precipitation and decreasing ash particle size (Obernberger et al., 1997). No increase in concentrations was observed for the other investigated metals; the concentration of Cu and Ni were in the same order of magnitude for all the ash fractions. The same was true for Ni in the bottom ash and cyclone ashes. However, no Cr was found in the filter fly ashes. Concentrations in the bottom and the gasifier bed ashes were comparable for all elements.

Table 6–2: Concentrations and mineral masses of heavy metals in the different ash fractions from 3 gasification tests.

| | TEST 1 | | | | | TEST 2 | | | | | TEST 3 | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Weight of wood** | 95.2 | kg DM | | | | 94.3 | kg DM | | | | 80.0 | kg DM | | | |
| **Bottom ashes** | 2.7 | kg DM | | | | 3.1 | kg DM | | | | 2.5 | kg DM | | | |
| | Concentration | | Mineral mass | | % | Concentration | | Mineral mass | | % | Concentration | | Mineral mass | | % |
| Cd | 10.1 | mg/kg | 27.0 | mg | 7% | 7.8 | mg/kg | 24.0 | mg | 7% | 9.5 | mg/kg | 24.0 | mg | 8% |
| Cr | 22.1 | mg/kg | 59.1 | mg | 15% | 17.3 | mg/kg | 53.5 | mg | 14% | 19.3 | mg/kg | 48.7 | mg | 15% |
| Cu | 122.0 | mg/kg | 326.1 | mg | 52% | 76.2 | mg/kg | 235.3 | mg | 38% | 95.4 | mg/kg | 240.6 | mg | 46% |
| Ni | 16.9 | mg/kg | 45.2 | mg | 22% | 12.6 | mg/kg | 38.8 | mg | 19% | 18.2 | mg/kg | 45.9 | mg | 26% |
| Pb | 7.7 | mg/kg | 20.6 | mg | 6% | 7.4 | mg/kg | 22.9 | mg | 7% | 8.13 | mg/kg | 20.5 | mg | 7% |
| Zn | 0.88 | g/kg | 2.4 | g | 16% | 0.7 | g/kg | 2.2 | g | 16% | 0.88 | g/kg | 2.2 | g | 19% |
| **Cyclone ashes** | 0.6 | kg DM | | | | 0.7 | kg DM | | | | 0.7 | kg DM | | | |
| | Concentration | | Mineral mass | | % | Concentration | | Mineral mass | | % | Concentration | | Mineral mass | | % |
| Cd | 62.2 | mg/kg | 36.2 | mg | 10% | 61.2 | mg/kg | 40.5 | mg | 11% | 41.1 | mg/kg | 26.30 | mg | 9% |
| Cr | 13.9 | mg/kg | 8.1 | mg | 2% | 22.9 | mg/kg | 15.1 | mg | 4% | 13.4 | mg/kg | 8.59 | mg | 3% |
| Cu | 109 | mg/kg | 63.4 | mg | 10% | 96.8 | mg/kg | 64.0 | mg | 10% | 59.9 | mg/kg | 38.27 | mg | 7% |
| Ni | 13.9 | mg/kg | 8.1 | mg | 4% | 14.4 | mg/kg | 9.5 | mg | 5% | 28.2 | mg/kg | 18.05 | mg | 10% |
| Pb | 22.2 | mg/kg | 12.9 | mg | 4% | 24.7 | mg/kg | 16.3 | mg | 5% | 24.0 | mg/kg | 15.32 | mg | 5% |
| Zn | 1.41 | g/kg | 0.8 | g | 6% | 1.57 | g/kg | 1.0 | g | 7% | 1.3 | g/kg | 0.83 | g | 7% |
| **Filter fly ash** | 0.44 | kg DM | | | | 0.18 | kg DM | | | | 0.10 | kg DM | | | |
| | Concentration | | Mineral mass | | % | Concentration | | Mineral mass | | % | Concentration | | Mineral mass | | % |
| Cd | 71.9 | mg/kg | 31.9 | mg | 9% | 170.6 | mg/kg | 30.6 | mg | 9% | 136.4 | mg/kg | 14.0 | mg | 5% |
| Cr | 0.0 | mg/kg | 0.0 | mg | 0% | 0.0 | mg/kg | 0.0 | mg | 0% | 0.0 | mg/kg | 0.0 | mg | 0% |
| Cu | 78.6 | mg/kg | 34.9 | mg | 6% | 74.2 | mg/kg | 13.3 | mg | 2% | 126.4 | mg/kg | 12.9 | mg | 2% |
| Ni | 12.2 | mg/kg | 5.4 | mg | 3% | 12.8 | mg/kg | 2.3 | mg | 1% | 14.7 | mg/kg | 1.5 | mg | 1% |
| Pb | 225.8 | mg/kg | 100.1 | mg | 30% | 457.8 | mg/kg | 82.2 | mg | 25% | 305.3 | mg/kg | 31.2 | mg | 11% |
| Zn | 17.9 | g/kg | 7.9 | g | 56% | 70.3 | g/kg | 12.6 | g | 89% | 50.9 | g/kg | 5.2 | g | 43% |

Table 6–3: Concentrations and mineral masses of heavy metals in the gasifier bed ash fraction after the three gasification tests

| Gasifier bed ash | 4.8 | Kg DM | | | |
|---|---|---|---|---|---|
| | Concentration | | Mineral mass | | % |
| Cd | 12.1 | mg/kg | 59 | mg | 6% |
| Cr | 16.5 | mg/kg | 80 | mg | 7% |
| Cu | 110.8 | mg/kg | 536 | mg | 30% |
| Ni | 15.6 | mg/kg | 75 | mg | 13% |
| Pb | 7.9 | mg/kg | 38 | mg | 4% |
| Zn | 1.1 | g/kg | 5 | g | 13% |

The heavy metal material balance for the 3 tests is presented in Figure 6–3. Low recoveries (between 30 to 40%) of Cd, Cr, Ni, and Pb were observed throughout all the tests. Recoveries for Cu and Zn were between 80 and 100%. Cu was predominantly associated with the bottom ashes while most of the Zn was found to be in the filter fly ash. The weights of the bottom and cyclone ashes and their metal concentrations were straightforward to measure and consistent for the three tests. This would indicate that our measurements underestimated the mass and/or heavy metal concentrations of particulates and condensates in the produced syngas after the hot cyclone. The observed discrepancies may have originated from incomplete sampling of the filter fly ash after the cyclone and the high margin of error due to the small mass of metals measured in the installation. For example for Cd, only 4 g had to be accounted for in each test. Continuous operation of the gasification installation combined with continuous measurements would result in more robust measurements.

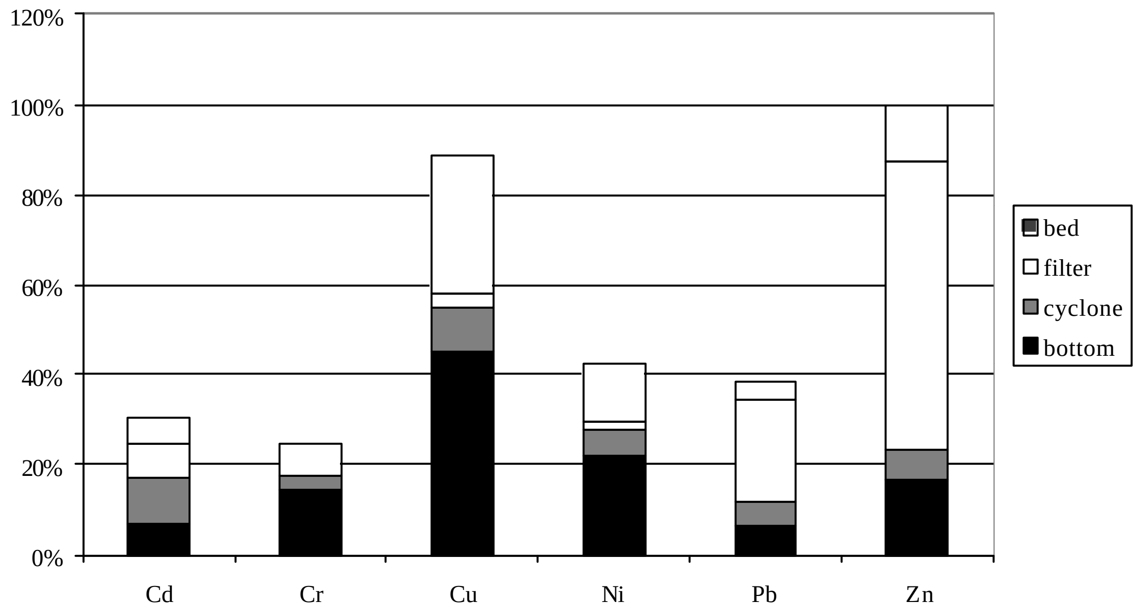


Figure 6–3: Heavy metal material balance (100%: metal input from willow wood)

However, the fact that 7% of Cd, was found in the bottom ash fraction indicates that the large percentage of the metals is volatilized during the combustion. The same percentage was observed for Pb. About 50% of the Cu was however retained in the bottom ashes. The small scale of the investigated installation results in high temperatures throughout the system. The temperature in the boiler section of the installation is between 1000 and 1200°C. The high temperature (600–800°C) in the cyclone limited the amount of metals which precipitated and which could be recovered in the cyclone fly ash fraction. A large fraction of the metals would thus still be in volatilized form after the hot cyclone. As already mentioned, this fraction was not fully accounted for during the gas sampling. Assuming that the unaccounted metal fraction is associated with the filter fly ash and flue gas, the largest amounts of metals, except for Cu, would have to be intercepted by the scrubber to ensure clean syngas. The gas temperature in the scrubber drops from 600 to 80°C and generally the scrubber reduces the particles load of the gas to only 10 mg/Nm$^3$. It can be expected that majority of the associated metals will be intercepted and removed from the gas. Water and coal used in the scrubber will thus eventually get enriched with heavy metals and will have to be handled and disposed of in the proper way. Possibilities of recovering heavy metals from the charcoal through leaching can then be considered.

Heavy metal concentrations in the bottom and cyclone fly ash fraction can be compared to legislation threshold for their use as fertilizer. Figure 6–4 compares the metal concentrations to the threshold values for the reuse of the ashes according to the Flemish legislation (VLAREA, sub-attachment 4.2.1.a). For the bottom ashes only the Cd threshold value is exceeded, although only by a slight margin. Cd and Zn are in excess concentrations in the cyclone ashes. According to Flemish law, none of the examined ash fractions can be used as fertilizer and have to be landfilled in proper facilities. New technological designs in biomass gasification were developed to limit this problem. Narodoslawsky and Obernberger (1996) and Ljung and Nordin (1997) describe technological ways to concentrate Cd and other volatile metals in a small ash fraction so that the largest part of the ash and nutrients can be safely recycled to the soil. Such technologies can be of great importance for the conversion of willow wood grown on contaminated substrates in phytoremediation projects.

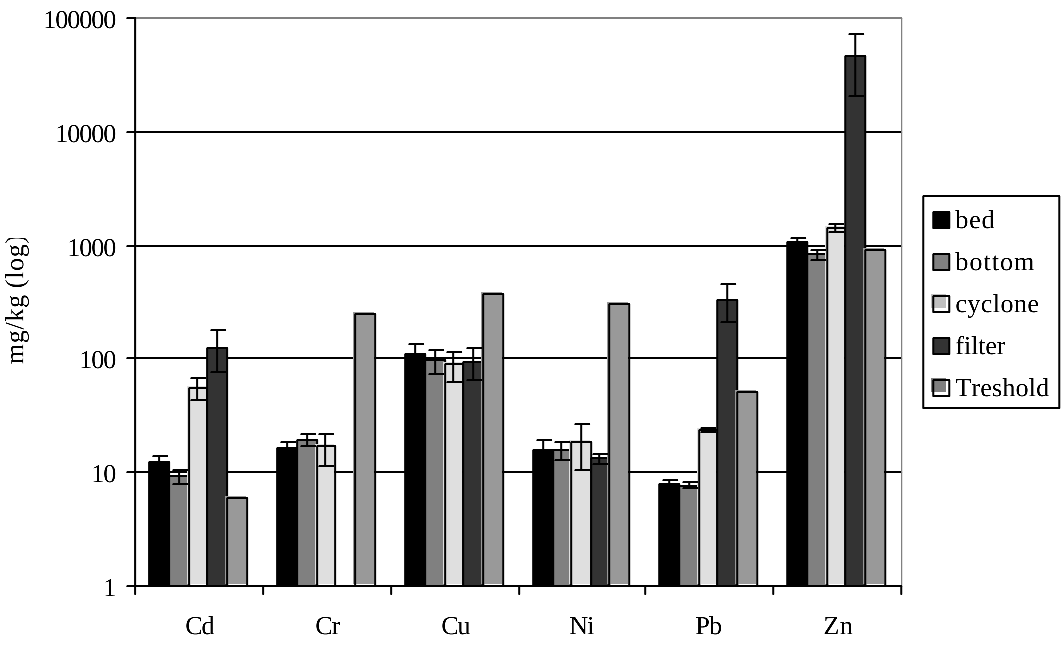


Figure 6–4: Average metal concentrations (mg/kg) of different ash fractions compared to the VLAREA threshold concentrations for fertilizer.

## 6.4 Conclusions

Every land restoration project with SRF produces heavy metal enriched willow wood. The on-site gasification of this biomass in small scale installation can be a promising way to valorize produced biomass to electricity and heat. Although we were unable to account for the mass and heavy metal concentration of the finest filter ash fraction, measurements of the course bottom and cyclone ash fraction indicate that a large amount of the metals present in the wood is volatilized during gasification. This is the result of the high combustion temperatures and the use of a hot cyclone. The concentration of most of the heavy metals in a small fraction is preferable as it allows the recycling of more voluminous ash fractions and reduces disposal costs. In addition the recovery of heavy metals can then be considered. While the gasification tests resulted in low metal contents in the bottom and cyclone ash fractions, Cd and Zn concentration still exceeded Flemish legislation threshold for the use of these ash fractions as fertilizer. Differences between the measured concentrations and the threshold values were however small. Adjusting combustion temperatures and applying appropriate cyclone technologies could thus probably further reduce metal concentrations in the largest ash fractions.

# 7 Multi-layered dredged sediment disposal in afforested disposal sites

Vervaeke[1], P., De Vos[2], B., Lust[3], N. 2004. Multi-layered sediment disposal in afforested disposal sites. Environmental Engineering. Submitted.

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**Abstract**

The storage of dredged sediments in afforested disposal sites results in larger volumes of sediment can be stored in the same area, while creating an ecosystem, stabilizing the substrate, and rendering the site more esthetically attractive. This chapter presents the findings of a pilot scale trial on multi-storey sediment disposal in afforested disposal sites. The effect of introducing a new sediment layer on the willow stand was determined and the environmental impact of the establishment of such a disposal site was assessed.

The results from the stand measurements before and after sediment application indicated that tree survival was dependent on the formation of a new adventitious root system in the new sediment layer. After sediment application, a large proportion of the trees (66%) in the clay part of the site died, while 22% showed symptoms of stress, as a result of the absence of adventitious roots in the new sediment layer. These roots failed to form, as was observed with the most developed trees, or lost contact with the sediment layer as a result of the sediment inclination. On the sand part were trees were stabilized against wind action and were little inclination occurred tree survival was excellent. Several option should be considered to ensure a successful outcome of the technique: i) willow with high adventitious rooting capability should be selected, ii) the sand fractions should be distributed over the whole area of the disposal site, and iii) coarser sediments should be applied last during hydraulic raising. Results indicate that *Salix* trees with a well developed root system in the sediment layer can increase the dewatering speed and ripening.

When willows are used to stabilize and revegetate contaminated substrates, as is the case in this eco-technique, it is advisable to use species which are characterized with a limited uptake of heavy metals. This is necessary to reduce the risk of spreading heavy metals to the environment through leaf fall. However, as a result of the lower metal concentrations and leaf biomass production after the sediment application, smaller amounts of heavy metals reached the stands surface with leave fall.

## 7.1 Introduction

Each year, large volumes of sediment are dredged worldwide. A large percentage of this dredged sediment is disposed in confined disposal sites, as more technical treatment techniques are often not economically feasible (Mulligan et al., 2001). When sediment disposal is combined with other land use functions, as for example nature and ecosystem development, the social and ecological impact of such an operation is generally more acceptable. However, when ecosystem development is considered an option for the restoration of land disposed dredged sediment, care must be taken to reduce environmental risks. This chapter presents a pilot scale trial to investigate a new eco-technique for the disposal of dredged sediments, based on the introduction of a forest ecosystem on dredged sediments. The technique involves a multi-layered dredged sediment disposal on previously afforested disposal sites.

Previous research (De Vos, 1994; Vervaeke et al., 2001) showed that hydraulically raised sediment disposal sites can be easily planted with willow species using the SALIMAT technique. This results in the establishment of a dense willow stand on the dredged sediment surface with the advantages of creating an ecosystem, stabilizing the substrate and rendering the site more esthetically attractive. Moreover, if multiple layers of sediment can be brought in the same afforested disposal site, larger volumes of sediment can be stored in the same area, while the previously beneficial properties of the stand are retained.

Multi-layered dredged sediment disposal is already practiced in traditional dredged sediment disposal sites. A new layer of sediment is brought into the site after the previous layer was sufficiently dewatered and ripened. Applying this technique in afforested sediment disposal sites could result in shortening the time between sediment applications, as it can be hypothesized that the presence of willow stems and the formation of a new root system in the new sediment layer could increase the speed of sediment dewatering and consolidation. Consequently, sediments could be repeatedly disposed in a shorter time frame and upland storage capacity could be optimized.

The multi-layered disposal technique can be described in the following four phases (Figure 7–1). In a first phase (A) a disposal site is constructed and is hydraulically raised with new dredged sediment. Immediately after raising the sediment SALIMAT is applied to plant the willow stand. The willow stand develops in a second phase and the sediment consolidates gradually (B). After 4 to 7 growing seasons, a second layer of sediment is brought into the disposal site (C). The willow trees form new adventitious roots in the fresh sediment layer. The process of hydraulically filling the disposal site can be repeated until the desired height is reached. When the embankments are planted with long living tree species (Ash, Oak, Elder), the natural propagation of these new species in the disposal site will eventually result in the replacement of the willow pioneer vegetation by a stable mixed deciduous forest (D).

The first objective of this trial was to study the technical feasibility of multi-layered sediment disposal in afforested disposal sites. The hypothesis that the multi-layered disposal of sediments in afforested disposal sites has several advantages over traditional on land disposal of sediments was investigated. Concurrently, the effect of introducing a new sediment layer on the willow stand characteristics was determined. In addition, the environmental impact of the establishment of such a disposal site was assessed. Therefore the following research activities were undertaken. i) The hypothesis of the repeated hydraulic raising of sediments was assessed in an on field pilot scale trial. A new sediment layer was brought into two sediment disposal sites covered with willow stands of different stand ages, i.e. in their third and seventh growing season. ii) A monitoring program was set up to describe the sediment dynamics after introduction into the stands. Parameters describing ripening, oxidation and inclination were recorded on a monthly basis during two growing seasons following the application. The dynamics of the sediment were compared to the behavior of sediments in traditional disposal facilities. iii) The impact of applying a sediment layer in a willow stand on the stand characteristics was assessed by measuring stand characteristics and development in the growing seasons before and after the sediment application. iv) The dispersal of heavy metals to the different compartments of the system through leaf fall, leaching and water recirculation was determined.

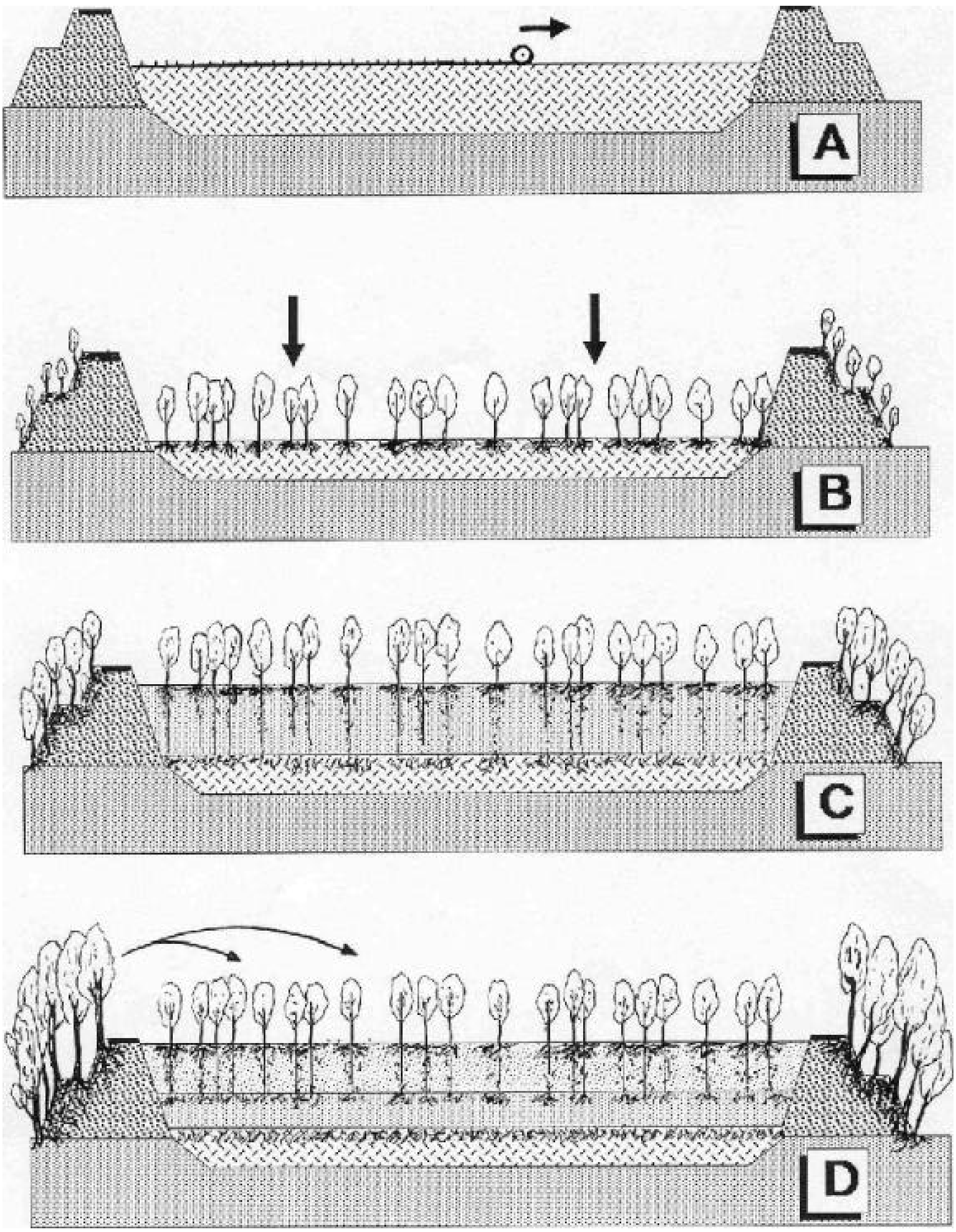


Figure 7–1: The technique of multi-layered dredged sediment disposal in afforested disposal sites in four steps.

## 7.2 Methods and Materials

### *7.2.1 Site description*

The dredged sediment disposal site selected for the trial is situated at the experimental site in Menen, Belgium (50°48' N, 3°08' E). The main disposal site, labeled A in the rest of this chapter, measures 20 x 150 m and is situated in the south west corner of the site (Figure 7–2). The site was hydraulically raised in 1993 and subsequently planted with willow using the SALIMAT technique (Vervaeke et al., 2001). Two willow clones were equally included in each SALIMAT: *Salix fragilis* 'Belgisch Rood' and *Salix triandra* 'Noir de Villaines'. Six years after planting the *Salix triandra* trees almost completely disappeared from the stand as a result of competition (Chapter 3, this work). Sections A to E of the disposal site were covered by a 6 year old homogenous *Salix fragilis* stand with some remaining *Salix triandra* trees on the edges. A small patch of *Salix triandra* trees remained in section F of the disposal site which was characterized with a coarser texture (Figure 7–3). Section G was not planted and only vegetated by grasses. At the moment of the introduction of the new sediment layer in May 1999 trees were in their seventh growing season. A smaller adjacent site B (20 x 20 m), covered by a 2 year old stand was added to the experimental setup. This site was planted in 1997 with *Salix fragilis* 'Belgisch Rood' and *Salix triandra* 'Noir de Villaines' in five 4 x 5 m blocs for each species using 20 cm cuttings. Trees in this disposal site were in their third growing season at the moment of the raising of the new sediment layer. A grid was laid out on disposal site A to monitor sediment and stand dynamics. A total of 17 permanent grid points were established (Figure 7–3). The grid points were marked at 3 m height so they could be examined again after the application of the sediment.

Both disposal sites were ringed with new embankment covered with HDPE liner in March 1999 (Figure 7–2) to hold the new volume of sediment. The inlet through which the sediment was brought into the disposal sites was situated in the SW corner of the embankment, while an overflow collector was constructed at the opposite site. Water from this collector was led to an adjacent disposal site which acted as a sedimentation basin. Water exiting from this basin was subsequently brought back to the river Leie in a ditch. Disposal site A was equipped with nine beacons positioned in 15 m intervals along the length of the disposal site. Two such beacons were placed in disposal site B. These beacons were used to asses the new sediment layer thickness and to monitor the inclination of the sediment during dewatering and ripening.

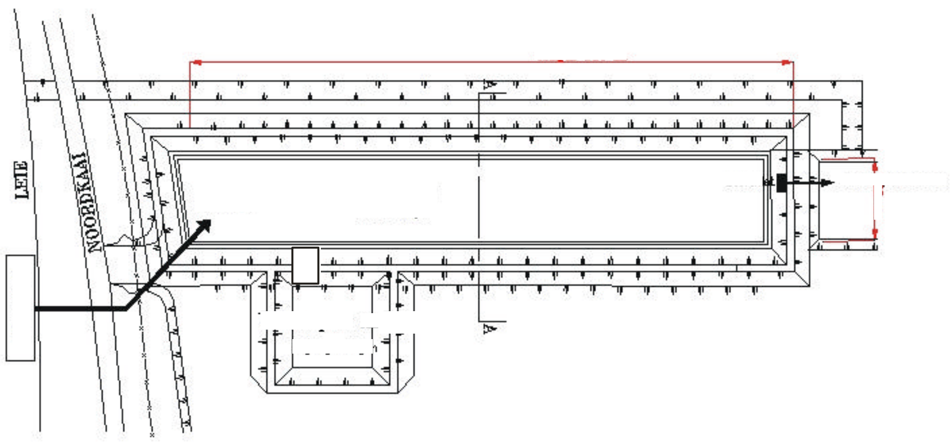


Figure 7–2: Diagram of disposal sites A and B with their new embankment.

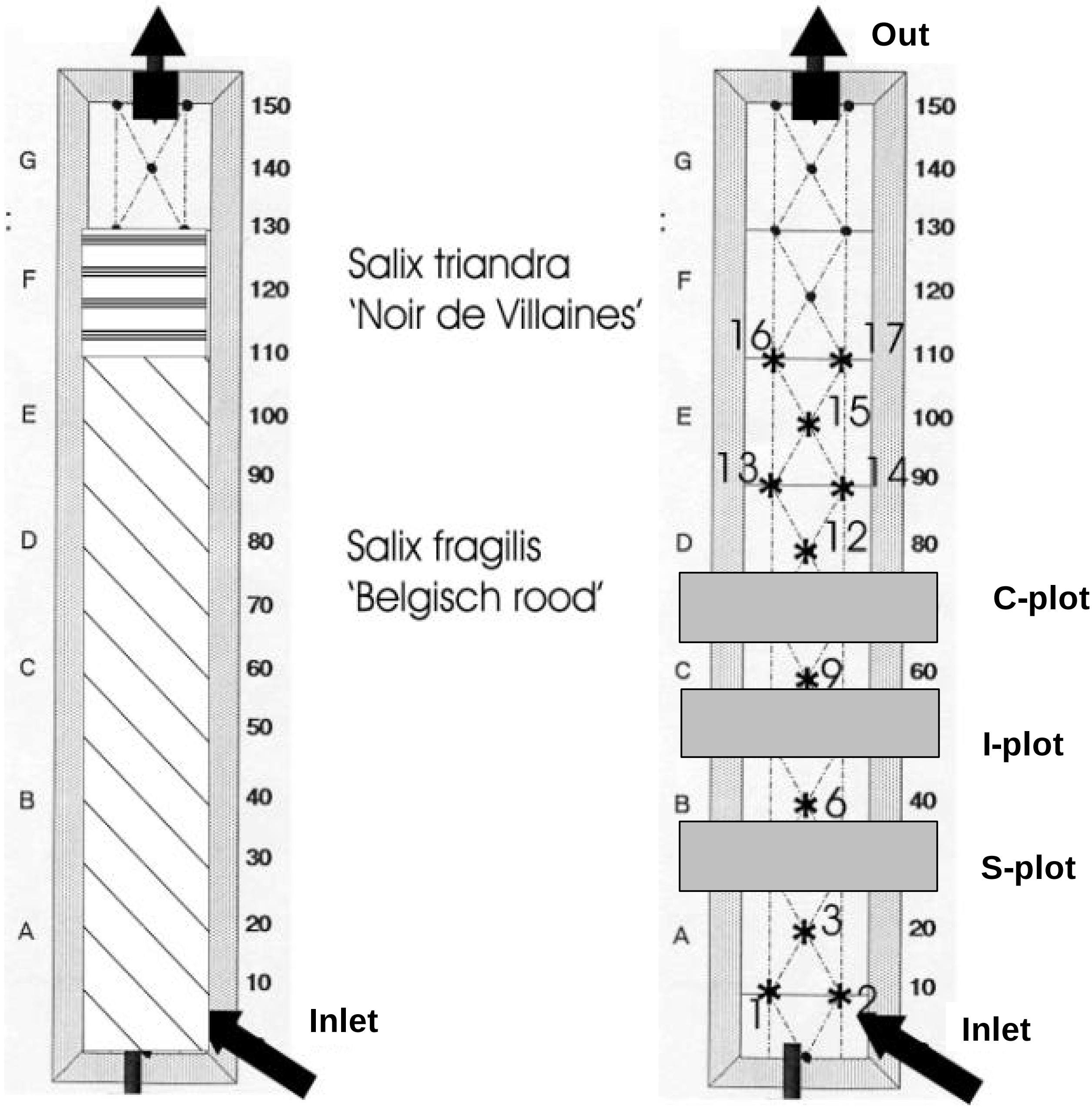


Figure 7–3: Left: Distribution of *Salix fragilis* 'Belgisch Rood' and *Salix triandra* 'Noir de Villaines' in disposal site A. Right: The location of the 17 grid points and the S, I and C plots in disposal site A

### 7.2.2 *Dredging and sediment characteristics*

All sediments used in this trial were dredged from the river Leie in the vicinity of the experimental site using a hydraulic crane on a barge. Dredging operations and filling of the disposal site lasted one week in May 1999. Tree zones of the Leie were dredged in succession: the turning point, the bridge, and the lock. The sediment was transported in 160 $m^3$ barges to the experimental site, mixed with Leie water and pumped into the disposal sites through a tube system by a pump boat. In total 63 barges were used to fill the A and B disposal sites, which amounted to a total volume of about 10,000 $m^3$. This was sufficient to fill both disposal sites with a 2 m sediment layer. Excessive pumping water was continuously removed through the overflow collector.

The sediment in every barge was sampled at least five times immediately after dredging. The samples of all barges arriving at the site in one day were subsequently pooled and the main physical and chemical parameters of the sediment were determined. Part of the sediment samples was dried at 105°C until constant weight, grinded and sieved through a 2 mm mesh. Moisture content of the samples was determined gravimetrically. The carbon content was measured using the Walkley and Black method (Nelson and Sommers, 1996). The pH in a 1:5 sediment:deionized water mixture after 2 hours of shaking. Total nitrogen content was measured using the modified Kjehldahl method. Samples were extracted in a $HNO_3$/HCl/HF mixture during microwave digestion (CEM, MDS 2000). Extracts were subsequently analyzed for the investigated heavy metals on ICP-AES (Varian Vista-axial, Varian, Palo Alto, CA). The analytical quality of the measurements was checked by including a method-blank and laboratory control samples every 10 samples. The particle size distribution of the samples was determined according to the pipette method of Gee and Bauder (1986). Sediment at the inlet was regularly sampled (n = 38) during the week of sediment raising. The moisture content of these samples was determined gravimetrically at 105°C.

### *7.2.3 Sediment dynamics*

After pumping the sediment into the two stands in May 1999 the new sediment layer in both disposal sites was impassable for sampling for the rest of the growing season. This was the result of stagnating water on the sediment surface and the subsequent plasticity and low bearing capacity of the new sediment layer. Only the sandiest parts at the inlet tube of disposal site A were passable from July 1999. Stagnating water covered the rest of the disposal site until October 1999. Pontoons were constructed to allow the grid points 9, 12, and 15 to be reached. From December 1999 regular samplings were performed to characterize the sediment in the disposal site and describe it dynamics during ripening. Eleven of the 17 grid points 1-9, 12, and 15 were sampled in December 1999. Sampling in 2000 was performed on a monthly basis from March to November at the 17 grid points. Disposal site B was not sampled for reasons to be explained later. At each grid point samples from 3 depths (0-20, 60-80 en 130-150 cm) were collected with an auger. Samples from the first sampling campaign in December were used to characterize the particle size distribution of the sediment in the disposal site. In addition the EC, pH, density, water content and redox potential were determined. The samples collected in 2000 were analyzed for water content, redox potential and pH. The depth of the interface between oxic and anoxic sediment was recorded at each grid point with every sampling. The thickness of the sediment layer was measured monthly using the nine beacons. The measurements at the different grid points were interpolated between the grid points with the inverse power to the distance equation according to Franke and Nielson (1980) (Equation 7–1).

$$Z = \frac{\sum_{i=1}^{n} \frac{Z_i}{h_{ij}^{\,b}}}{\sum_{i=1}^{n} \frac{1}{h_{ij}^{\,b}}}$$

Equation 7–1

In which:

$Z$ the interpolated value,

$Z_i$ the value measured at the neighboring grid point,

$h_{ij}$ the distance between the interpolated point and the grid point

$b$ the weighed power (= 2)

### 7.2.4 Stand characteristics and dynamics

The structure, growth and vitality of the *Salix fragilis* stand were recorded before and after the raising of the sediment to assess the impact of the new sediment layer on these characteristics. Woody biomass on disposal sites A and B was measured before sediment application in January 1999. In disposal site A, all biomass in 17 one m radius plots in the vicinity of the 17 grid points was cut and weighed (Figure 7–3). The trees were separated in two pieces at 2 m height to distinguish between biomass that would be covered by the new sediment layer and biomass that would remain above the new surface. A distinction was made between dead and living wood. Sub-samples were used to gravimetrically determine the dry weight of the collected wood. The height, diameter and the density of living and dead trees were measured and the grid points were marked at 3 m height so they could be examined again after the application of the sediment. The same procedure was applied in disposal site B.

The biomass above the new sediment layer was measured in February 2000 by cutting five 1 m radius plots from the stand in the vicinity of grid points 3, 6, 9, 12, and 15. Diameters of the trees were determined at a height of 0,5 m above the surface. The allometric relationship between tree diameter and weight was determined based on measurements from 21 trees (Tahvanainen, 1996).

In September 2000, a throughout description of the stand structure and vitality was performed. Three 5 x 15 m plots were established in different zones of the disposal site according to the texture. Plot S was located on the sand part of the disposal site and encompassed grid points 4 and 5. Plot I lies in the intermediate zone between the clay and sand part. Plot C is located in an area with high clay content and contains grid points 10 and 11 (Figure 7–3). The diameter, height, status of the roots and tree health of each tree in the three plots was recorded. Tree height was divided in five classes: 0-2 m, 2-4 m, 4-6 m, 6-8 m, and larger then 8 m. To evaluate the rooting status tree classes were used: i) no formation of a new adventitious root system, ii) formation of an adventitious root system which is still in contact with the new sediment layer, and iii) formation of an adventitious root system which has lost contact with the new sediment layer as a result of sediment consolidation. Diagrams of the two latter classes are presented in Figure 7–4. Roots were studied in more detail by digging three profile pits next to three trees at grid point 6. Tree vitality was classified as follows: i) living trees with no indications of stress, i.e. leave discoloration and early leaf fall, ii) stressed trees, i.e. leaves are discoloring or falling, and iii) dead trees. The diameter of all trees in the three plots was measured at 0.5 m height. Above ground stem biomass was calculated using the previously determined allometric relationship between tree weight and diameter.

The small patch of *Salix triandra* trees in section F of the disposal site was not investigated in as much detail as the main *Salix fragilis* stand. However visual observations were recorded in the two growing seasons following the sediment application.

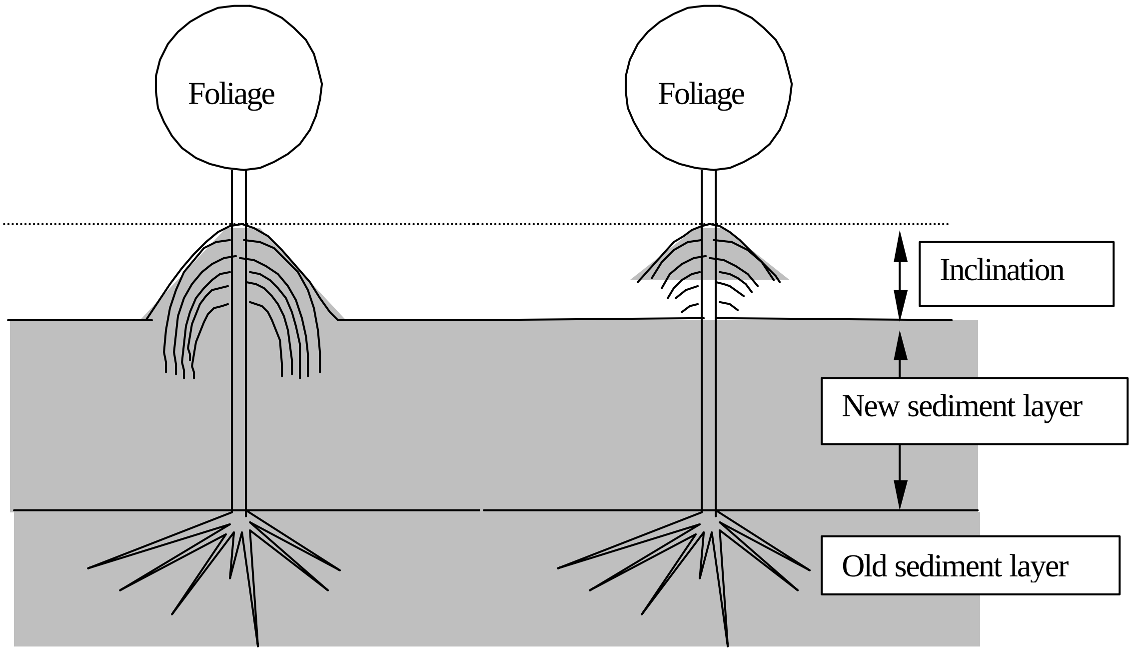


Figure 7–4: Left: trees with adventitious root systems still in contact with the new sediment layer. Right: trees of which the adventitious root systems lost contact with the sediment layer.

### *7.2.5 Nutrient and heavy metal uptake*

Foliar and wood samples were collected in August 1998, 1999 and 2000 from the different grid points. In 1998 and 2000 sampling was performed at all 17 grid points, while in 1999 grid points 1-9, 12, and 15 were sampled. At least two trees were cut at a distance of 1.5 m of every grid point with each sampling. All leaves were collected from each tree, mixed and sub-sampled. In 1998 and 2000 the leaf biomass was measured through the collection of leaf litter in a funnel (diameter 0.5 m) at each of the grid points. In 1999 grid points 1-9, 12 and 15 were reachable and sampled. Leaves in the funnels were collected monthly from August to December, dried at 105°C and then weighed. Leave, wood, and litter samples were milled and digested in an $HNO_3$/HCl/HF mixture during microwave digestion (CEM, MDS 2000). Extracts were subsequently analyzed for the investigated heavy metals on ICP-AES (Varian Vista-axial, Varian, Palo Alto, CA). The analytical quality of the measurements was checked by including a method-blank and laboratory controls sample every 10 samples (BCR 60).

### 7.2.6 Effects on surface and ground water

Excess water on the sediment disposal site was removed through the overflow collector. This water was led through an adjacent 20 x 150 m disposal site which acted as a sedimentation basin. Water exiting from this basin was subsequently brought back to the river Leie in a ditch. This cycle of excess pumping water was sampled at three locations during the disposal of the sediment: i) at the overflow collector ($W_{in}$), ii) after passing through the sedimentation basin ($W_{out}$), and iii) before entering the Leie ($W_{Leie}$). Sampling continued two weeks after the end of the dredging operations until no more water passed through the overflow collector. The pH and EC of the water samples were measured on site after which samples were split. Two percent $HNO_3$ was added to one part, while both parts were kept at 4°C prior to analysis. Acidified samples were used for element analysis on an ICP-AES. Suspended solids and N were measured on the other part. Samples were passed through a 0.45 µm filter to intercept suspended solids. Nitrogen was measured with the Kjeldahl method.

The effect of the sediment application on groundwater quality was assessed using 10 ground water sampling tubes which were placed around the disposal sites A and B to a depth of 4 m. The ground water table was located at a depth of 3 m. Ground water samples were collected monthly from August 1998 to October 2000. Sample preparation and analysis were conducted as described above.

## 7.3 Results

### *7.3.1 Sediment characteristics and dynamics*

A week of pumping of the sediment and Leie water mixture into the stand resulted in filling of the disposal site up to a height of 3.5 m. In total 64 barges were emptied which amounted to a sediment volume of 10,000 $m^3$. As the measured density of the sediment was 1.38 $g/cm^3$ this corresponds with approximately 14,000 ton of sediment. The mean dry matter content of the sediment in the barges was 46.5%. The dredged sediment thus consisted of approximately 6500 ton dry matter and 7500 ton water. The dry matter content at the inlet of the disposal site, thus after mixing the sediment with Leie water, was reduced to 14%. This means that the 6500 ton dry matter was suspended in 41,500 ton water of which 7500 ton was originally associated with the dredged sediment. Thus about 34,000 ton of Leie water was used to pump the sediment in the disposal sites.

The physical and chemical characteristics of the sediments from the three dredging zones are presented in Table 7–1. Sediments dredged from the lock were different from the sediments from the two other zones, as they were characterized with a higher sand content, lower OM content, and lower concentrations of heavy metals.

After pumping the suspension, the disposal site was filled to a height of 3.5 m. Excessive pumping water was continuously removed through the overflow collector at the end of the site. After the sediment settled, the water on top of the new sediment layer slowly receded during the rest of the growing season. In July the area closest to the inlet became passable. Water covered the rest of the disposal site until October 1999. The thickness of the sediment layer was 230-250 cm at the inlet and 170-180 cm at the overflow collector.

Table 7–1: Chemical and physical characteristics of the sediment used in the trial (mean ± standard deviation)

| Parameters | | Turning point (n=7) | | Bridge (n=6) | | Lock (n=4) | |
|---|---|---|---|---|---|---|---|
| pH-$H_2O$ | | 7.6 | ± 0.06 | 7.6 | ± 0.14 | 7.7 | ± 0.03 |
| redoxpot. | mV | -199 | ± 18.53 | -212 | ± 24.65 | -217 | ± 38.96 |
| EC | µS/cm | 1027 | ± 85.58 | 998 | ± 237.29 | 652 | ± 150.49 |
| C | % | 5.2 | ± 0.35 | 4.6 | ± 0.85 | 2.6 | ± 1.33 |
| Moisture content | % | 41.1 | ± 2.62 | 45.2 | ± 6.44 | 57.9 | ± 9.23 |
| > 50 µm | % | 15 | ± 5.60 | 10 | ± 5.07 | 35 | ± 20.81 |
| 20-50 µm | % | 62 | ± 12.02 | 48 | ± 4.20 | 53 | ± 4.51 |
| 10-20 µm | % | 7 | ± 2.68 | 11 | ± 3.56 | 2 | ± 3.18 |
| 2-10 µm | % | 10 | ± 1.49 | 22 | ± 3.68 | 3 | ± 3.60 |
| <2 µm | % | 7 | ± 2.39 | 9 | ± 2.98 | 8 | ± 1.88 |
| N (tot) | g/kg DS | 4.0 | ± 0.39 | 3.2 | ± 0.65 | 1.8 | ± 0.09 |
| P | g/kg DS | 3.1 | ± 0.25 | 2.5 | ± 0.51 | 1.6 | ± 0.60 |
| S | g/kg DS | 3.8 | ± 0.60 | 3.3 | ± 1.10 | 2.3 | ± 0.54 |
| Ca | g/kg DS | 11.8 | ± 2.49 | 11.8 | ± 3.92 | 15.4 | ± 3.88 |
| K | g/kg DS | 9.3 | ± 0.34 | 8.7 | ± 0.43 | 8.2 | ± 0.22 |
| Na | g/kg DS | 5.0 | ± 0.66 | 4.6 | ± 0.83 | 4.3 | ± 0.48 |
| Mg | g/kg DS | 0.5 | ± 0.12 | 0.4 | ± 0.22 | 0.6 | ± 0.26 |
| As | mg/kg DS | 15.2 | ± 1.42 | 16.7 | ± 2.39 | 11.1 | ± 2.11 |
| Cd | mg/kg DS | 8.6 | ± 0.47 | 7.4 | ± 0.75 | 4.4 | ± 2.03 |
| Cr | mg/kg DS | 141.0 | ± 8.97 | 120.6 | ± 24.02 | 76.7 | ± 24.77 |
| Cu | mg/kg DS | 114.4 | ± 6.17 | 89.6 | ± 17.24 | 49.6 | ± 19.46 |
| Pb | mg/kg DS | 233.2 | ± 25.27 | 166.4 | ± 82.58 | 134.4 | ± 61.67 |
| Ni | mg/kg DS | 33.5 | ± 2.96 | 41.7 | ± 8.21 | 26.4 | ± 8.54 |
| Zn | mg/kg DS | 802.7 | ± 101.78 | 720.7 | ± 217.79 | 394.7 | ± 158.00 |

Figure 7–5 visually presents the distribution of the sand fraction over disposal site A. The hydraulic raising of the sediment resulted in the establishment of a texture gradient in the new sediment layer. The heavier sand fractions settled close to the inlet while the smaller silt and clay fractions remained in suspension and were transported further into the disposal site. This resulted in the establishment of two easily distinguishable zones in the disposal site: an area close to the inlet (section A: 0-30 m) which was characterized with a high sand fraction and the rest of the disposal site (sections B to G: 30-150 m) which was filled with the finer clay and silt fractions. A sharp transition between the sand and clay parts was observed. While the 0-20 cm samples of grid points 4 and 5 were characterized with a sand fraction of 69 and 78%, respectively, the sand fraction at grid point 6 was only 34%. The sand content decrease with depth in the sand part of the site: at the surface sand contents range from 69 to 89% while at a depth of 1.5 m sand content is 17 to 37%. This was attributed to the different sand contents at the three dredging zones. Sediment with low sand content from the bridge and the turning point were pumped first into the disposal site to be followed by the sediment from the lock which was characterized with a high sand content. The results describing the dynamics of the sediment will be discussed separately for the sand and clay part of the disposal site.

The $pH_{H20}$ of the sediment varied only to a small extent (between 7.3 and 7.5). The EC increased with increasing clay content from 505 to 1044 µS/cm. The opposite was true for the density and the DM content. Only the 0-20 cm samples from the gridpoints closest to the inlet were characterized with positive redox potentials.

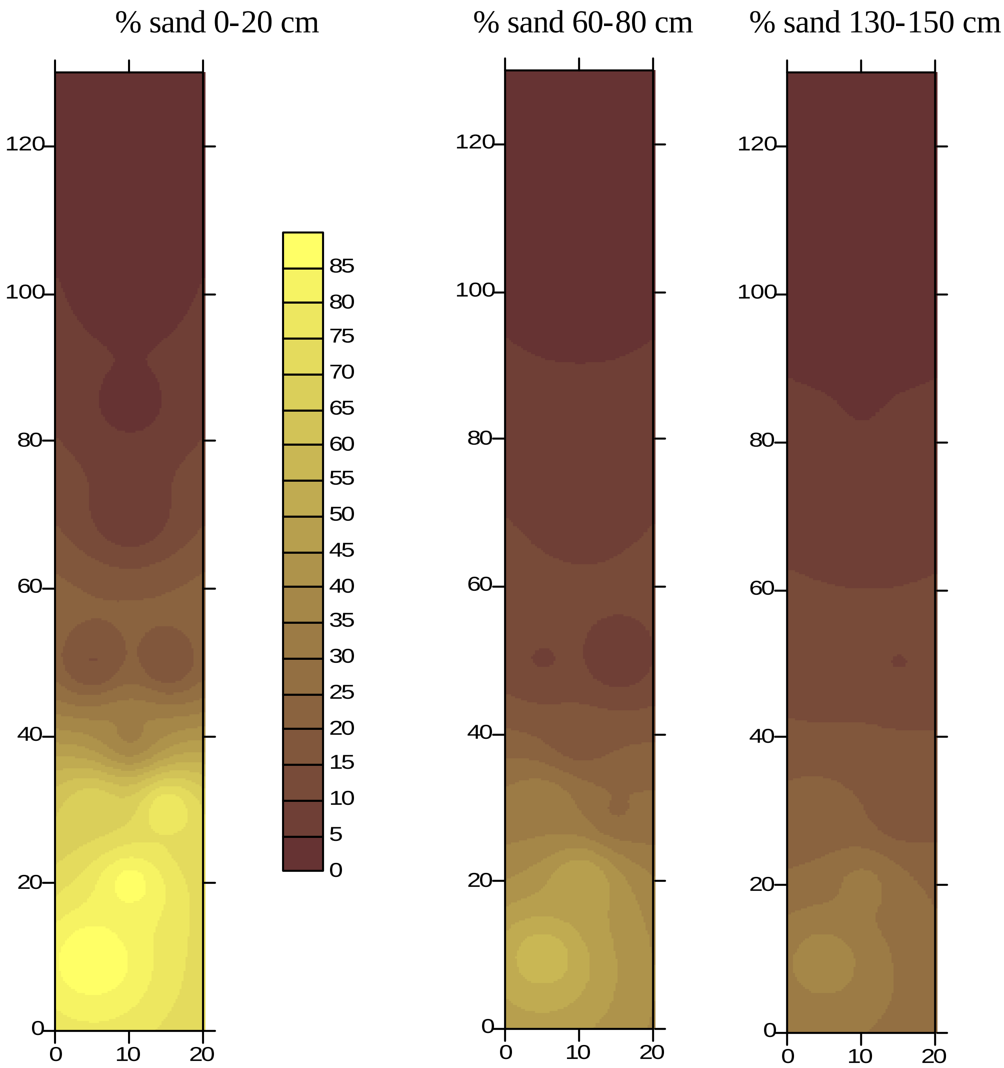


Figure 7–5: Sand content (%) at 3 depths (0-20 cm, 60-80 cm, and 130-150 cm) of the new sediment layer

Figure 7–6, Figure 7–7, and Figure 7–8 present the changes in redox potential during the 2000 growing season in the 0-20 cm, 60-80 cm, and 130-150 cm sediment layers, respectively. The evolution of the ripening depth during the 2000 growing season is shown in Figure 7–9. Equation 7–1 was used to interpolate values between the grid points. Figure 7–10 shows the depth of the sediment layer at the nine beacons measured during the growing season of 2000. The percentage of sediment consolidation for each beacon is presented in Figure 7–11.

In December 1999 the surface of the sand part was completely oxidized. The redox potentials of the 0-20 cm were all positive and dry matter contents varied between 80 and 90%. At grid points 1 and 3 the depth of sediment ripening reached 50-60 cm. Further from the inlet at grid points 4 and 5 the depth of sediment ripening at that time was 30 cm. Between December 1999 and March 2000, few changes in sediment dynamics were observed. From March 2000 on, the depth of sediment ripening in the sand part increased with 5 to 10 cm. The first positive redox potentials in the 60-80 cm samples were measured in April 2000. Sediment ripening strongly increased in July and August 2000. The depth of sediment ripening in August 2000 varied between 80 and 100 cm. At the end of the 2000 growing season the depth of ripening was 120 cm.

The volume reduction as a result of sediment ripening in the sand part was limited as a result of the high sand content. A consolidation of 10 cm was measured on beacon 1 close to the inlet in October 2000. For beacon 2 this figure was 15 cm. With increasing distance from the inlet and decreasing sand content the amount of consolidation increased. As a result, the consolidation in the clay part of the site was much more pronounced. From July 1999 to October 2000 the surface of the sediment lowered by 40 to 50 cm. The speed of ripening was however much slower. Until March 2000 the surface of sections B-G were still saturated with water. Only at grid points 6 and 7 the first signs of oxidation were noticed in the upper 5 cm. From June 2000 the depth of ripening at these points was between 10 and 20 cm. At the other grid points only the first 2 cm below the surface became oxidized. In September 2000 the first positive redox potential readings were recorded in the intermediate zone (section B) and in the area close to the overflow collector (Sections E and F). However, the bulk of the sediment volume remained in reduced conditions until December 2000.

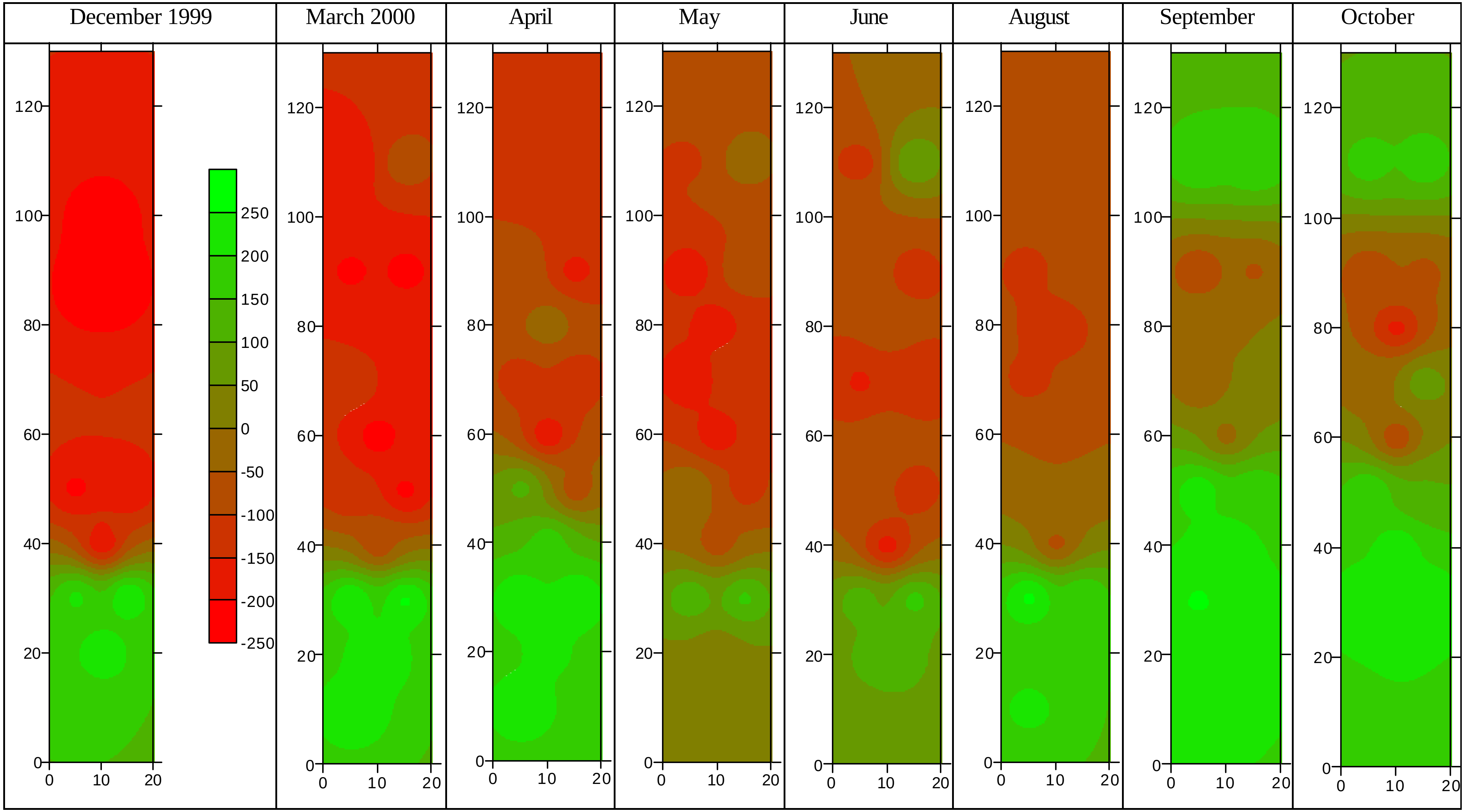


Figure 7–6: Change in redox potential (mV) in the 0-20 cm sediment layer during the 2000 growing season

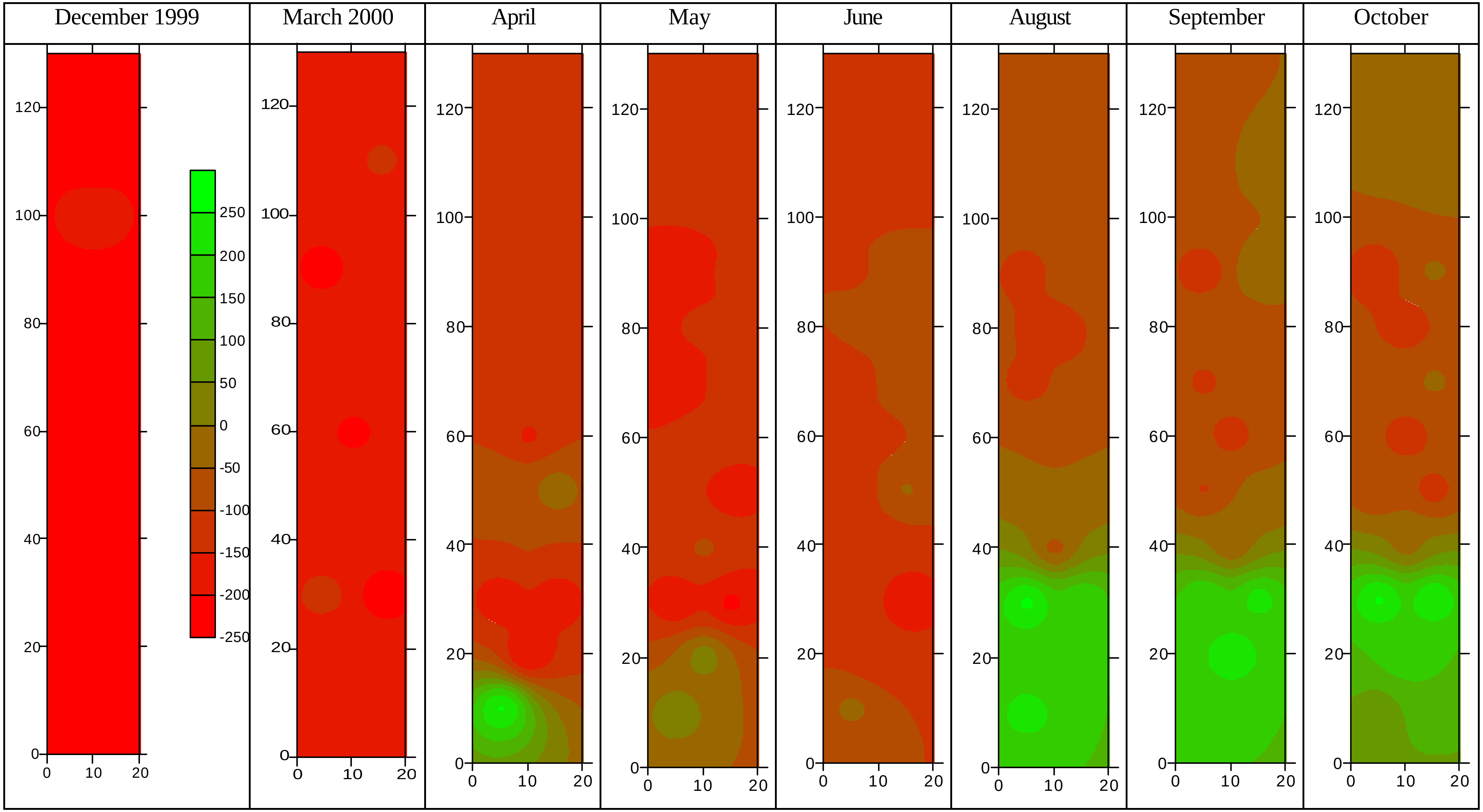


Figure 7–7: Change in redox potential (mV) in the 60-80 cm sediment layer during the 2000 growing

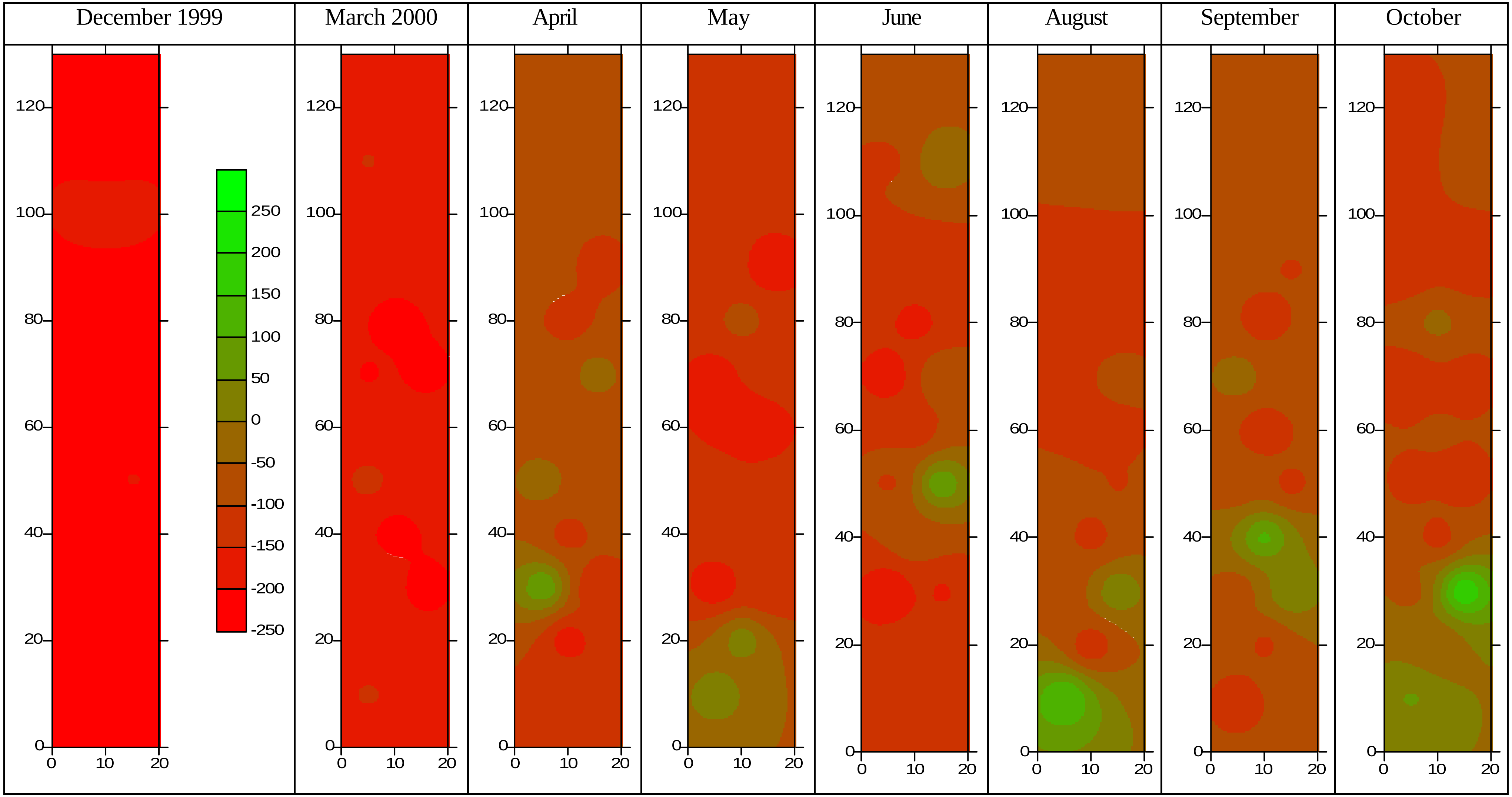


Figure 7–8: Change in redox potential (mV) in the 130-150 cm sediment layer during the 2000 growing season

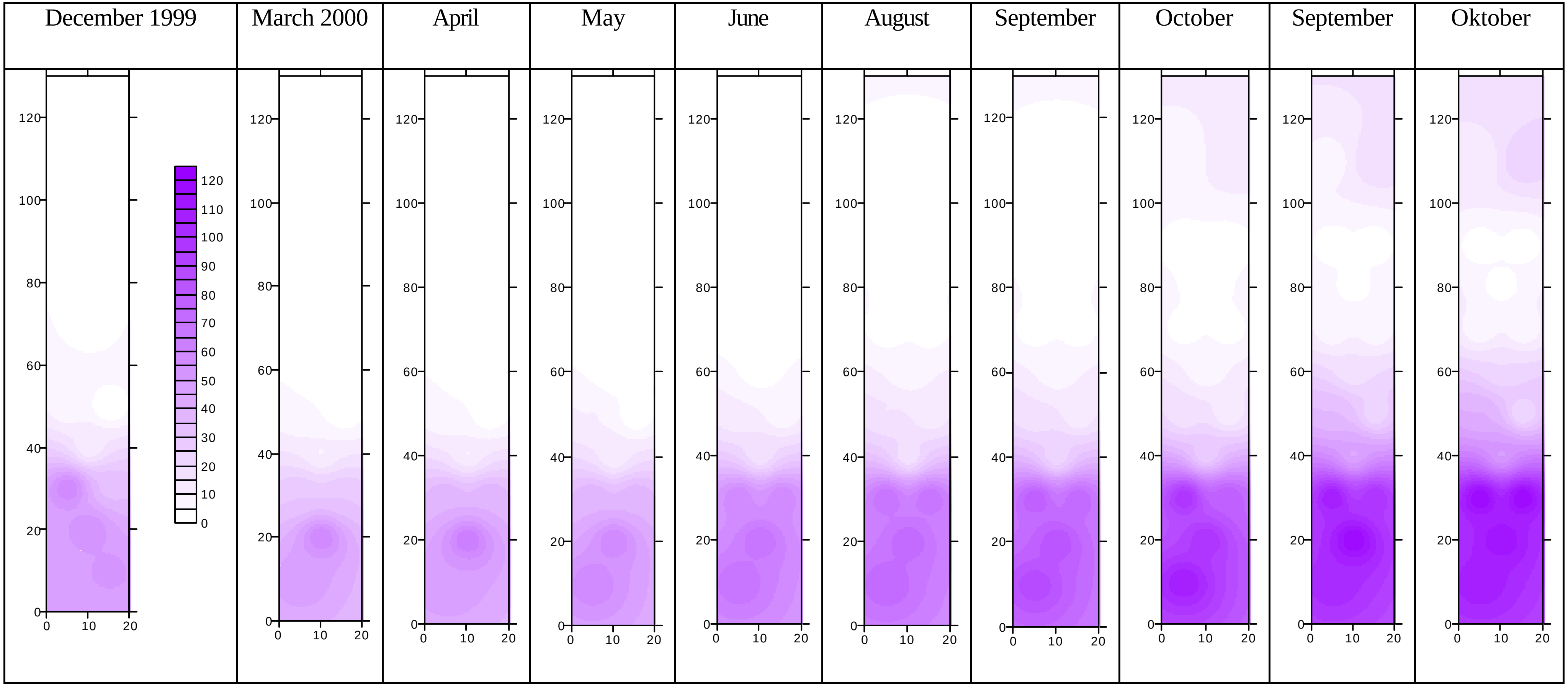


Figure 7–9: Change in ripening depth during the 2000 growing season (cm)

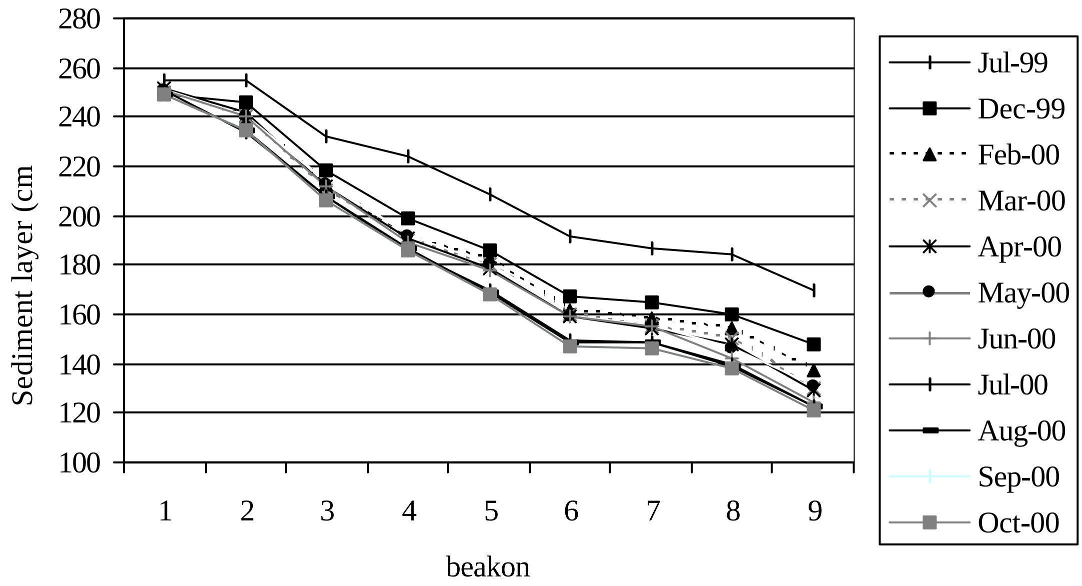


Figure 7–10: Depth of the sediment layer at the nine beacons measured during the growing season of 2000 (cm)

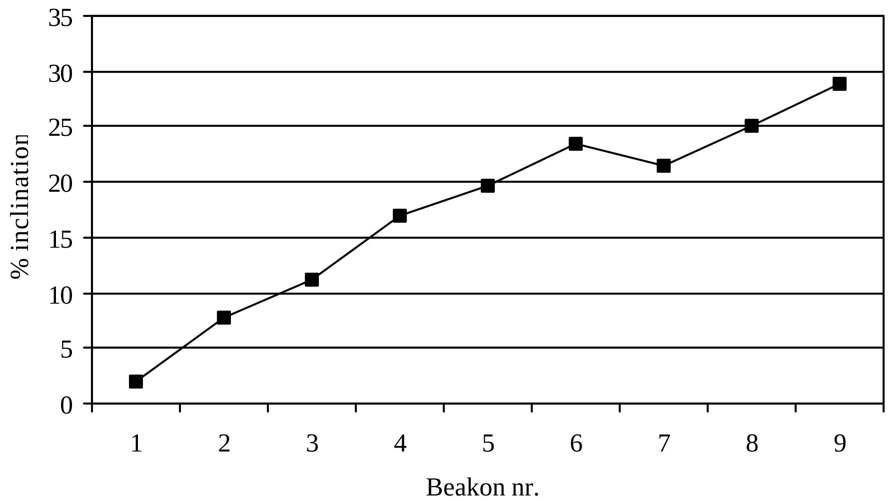


Figure 7–11: Percentage inclinations compared to the original sediment thickness for each of the beacons in October 2000

### *7.3.2 Stand characteristics and dynamics*

The total woody biomass of the *Salix fragilis* stand in January 1999, thus before the sediment application, was 76.4 ± 4.5 ton DM/ha. The biomass was distributed equally over the whole stand surface. The amount of living biomass that would be covered by the new sediment was 27 ton DM/ha if a 2 m layer was applied. Almost an equal quantity or 29.4 ton DM/ha of living biomass would stay above the raised surface. The amount of dead biomass was about 19 ton, most of which consisted of dead trees smaller then 2 m. As mentioned in the previous paragraph, the thickness of the new layer was not exactly 2 m but varied between 2.5 at the inlet and 1.7 m at the overflow collector. The stem number of the *Salix fragilis* stand was 135,000 stems/ha. Only 31% or 32,000 trees/ha were still living. The large amount of small dead stems was the result of intensive competition which occurred in the high density stand in the previous growing seasons. The first year after planting in 1993, the density was 400,000 living shoots/ha. After 3 years about 110,000 living trees were counted, almost the same number as the dead trees. The diameter distribution of the trees measured in January 1999 in the *Salix fragilis* stand is presented in Figure 7–12. The dead biomass predominantly consisted of dead trees with a diameter smaller then 30 mm. These trees died as a result of competition with their better developed neighbors. The mean height of living trees in the *Salix fragilis* stand at the time of sampling was 8.35 ± 0.59 m.

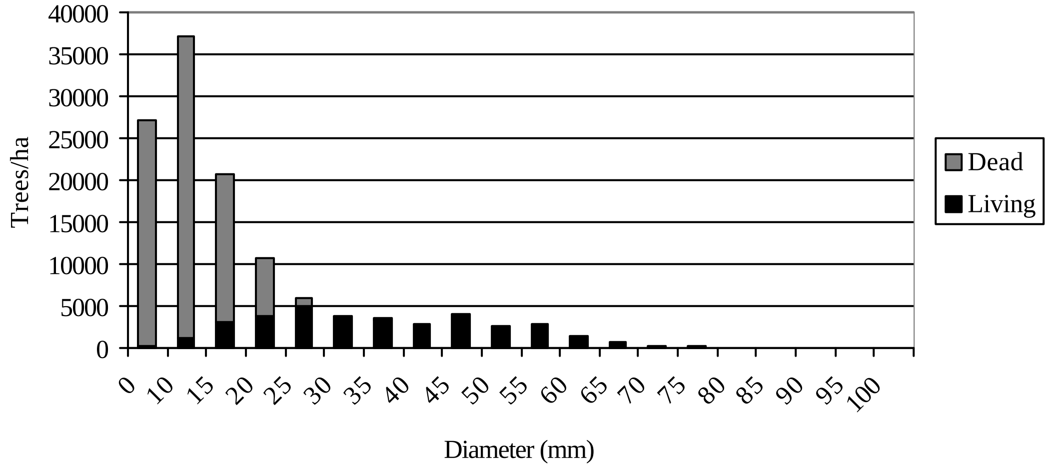


Figure 7–12: Stem number of dead and living *Salix fragilis* trees in disposal site A before sediment application.

The stem number in disposal site B was 69,000 *Salix fragilis* and 60,000 *Salix triandra* shoots/ha. The woody biomass in the fragilis and triandra plots was 18 and 16 ton/ha respectively, while the mean tree height was 2.15 and 1.98 m. With the application of the sediment this two year old stand became almost completely submerged. The new layer was 1.9 m thick resulting in only small portions of the trees remaining above the raised surface. After 3 weeks the trees died.

The woody biomass of the *Salix fragilis* stand measured in February 2000 was 32 ± 1.2 ton DM/ha. The biomass was distributed equally over the stand surface. In January 1999, it was estimated that about 29 ton DM would remain above the new surface. The increment in the 1999 growing season yielded thus only about 3 ton, which is considerable less then the mean annual production of 12.7 ton DM/ha.year which was measured in the previous growing seasons. The relationship between dry weight and diameter was: dry weight = 0.0283 x diameter$^{2,7446}$ with $R^2$ = 0.973 (Figure 7–13). The stem number at that time was about 13,000 trees/ha of which 92% were living trees. Dead trees were equally distributed over the whole stand surface. None of the trees with an original diameter smaller then 35 mm were recovered after the sediment application as their maximum height before the treatment was 4 m. The 0-2 m trees were completely covered by the new sediment layer.

The crowns of trees with a height between 2 and 4 m were submerged for several weeks in the 3.5 m mixture of sediment and pumping water. After the water was removed from the sediment surface these trees died, making up the 8% of the total amount of stems sticking above the new sediment surface. Sediment application thus removed all the existing dead trees which made up the bulk of the 0-35 mm trees, and reduced the amount of living trees from 32,000 to 13,000 stems/ha. This reduction was mostly attributed to the loss of 17,000 living trees per ha with heights smaller than 4 m and diameters smaller than 35 mm.

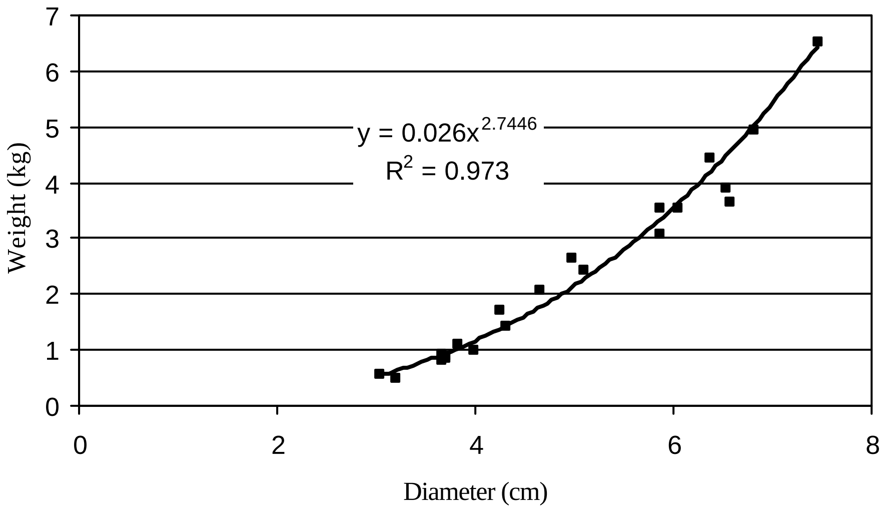


Figure 7–13: Allometric relation between *Salix fragilis* tree diameter and dry weight measured in February 2000.

Leaves in the whole of the *Salix fragilis* stand showed a slight yellowing in July and August 1999. This was most pronounced in the clay part of the disposal site. This discoloration was not observed in the *Salix triandra* plot. Early leaf fall was observed in the *Salix fragilis* stand in the beginning of September 1999. Leaf fall in other stands at the experimental site only started in October. A total litter production of 2.67 ton DM/ha was measured, which was lower then the litter production in previous growing season (3.12 ton DM/ha).

The next growing season after sediment application started in March 2000. This was simultaneously with the other willow stands at the experimental site. In the first half of May, the leaves of many fragilis trees in the clay part of the stand started yellowing, after which they wilted and fell. These trees subsequently died. This early leaf fall was not observed for trees growing on the sandy part of the site nor for the *Salix triandra* stand.

In June 2000, symptoms of several diseases were observed in the *Salix fragilis* stand. Trees on the sandy part of the site developed cancerous cracks in their bark from which a dark crystallized fluid escaped. These symptoms were attributed to the non lethal Brown Spot Disease, which mostly occurs when trees suffer from strong fluctuations in water availability. This disease proved to be non-lethal as no wilting of infected trees was observed. Trees in the clay part of the site developed the same symptoms one month later. In June 2000, leaves of trees in the clay part of the site dried and turned brown. These symptoms were also observed on new shoots which had developed on stressed trees. Microscopic investigation revealed spores of the *Venturia chlorospora* fungus. Shortly after, the infected trees died. This process continued in the clay part of the stand until the end of the growing season. Leaf fall in the sand part of the stand started normally at the end of September.

Table 7–2 presents the biomass, total number of stems, and the amount of living, stressed and dead trees measured in the three plots at the end of September 2000. The mean stocking density of 13,100 trees/ha for the three plots was comparable to the density measured in February 2000. However, several changes in the stand development were observed over the 2000 growing season. While before sediment application in February 1999 the woody biomass was equally distributed over the surface, the stand developed differently in the three examined plots in the 2000 growing season. In the sandy part woody biomass increased with 5 ton/ha compared to the February 2000 measurements. The production measured in the clay and intermediate parts were significantly less then the production on the sand part and even slightly lower compared with the February 2000 biomass measurements.

This indicates the complete stop of biomass production in these parts of the site as a result of sediment application. During the 2000 growing season, a large proportion of the trees (66%) in the clay part of the site died, while 22% showed symptoms of stress. In the intermediate zone of the sediment this dieback was less outspoken. The part of the stand on the sand part of the site remained healthy with only 8% dead trees. Several of the dead trees in the intermediate and clay parts of the stand fell during storms in August 2000.

Table 7–2: Woody biomass, stocking density, and tree vitality in the 3.125 $m^2$ plots measured in September 2000.

| | Biomass (ton DS/ha) | Number of stems (trees/plot) | (trees/ha) | | Number of stems (trees/plot) | (%) |
|---|---|---|---|---|---|---|
| Plot S (sand) | 37 | 98 | 13,000 | Living | 85 | 87 |
| | | | | Stressed | 5 | 5 |
| | | | | Dead | 8 | 8 |
| Plot I (intermediate) | 28 | 96 | 12,800 | Living | 70 | 73 |
| | | | | Stressed | 4 | 4 |
| | | | | Dead | 22 | 23 |
| Plot C (clay) | 30 | 104 | 13,800 | Living | 21 | 20 |
| | | | | Stressed | 22 | 21 |
| | | | | Dead | 61 | 59 |
| Total stand | 32 | | 13,200 | Living | 176 | 59 |
| | | | | Stressed | 31 | 10 |
| | | | | Dead | 91 | 31 |

Figure 7–14 depicts the combined diameter distribution of the dead, stressed and living trees for the three plots. Most of the dead trees are found in the larger diameter classes, while the amount of living trees decreases with decreasing diameter. As already mentioned most of the dead trees were found in the clay part of the sediment. From Figure 7–15, which shows the diameter distribution of trees on the clay part of the site, it becomes clear that the best developed trees growing on this clay part suffered most from the sediment

application. The majority of the dead trees were found in the larger then 45 mm diameter classes. The majority of the surviving trees were found in the 30 to 45 mm range. This indicates that the best developed trees in the clay part of the site were most vulnerable to the sediment application.

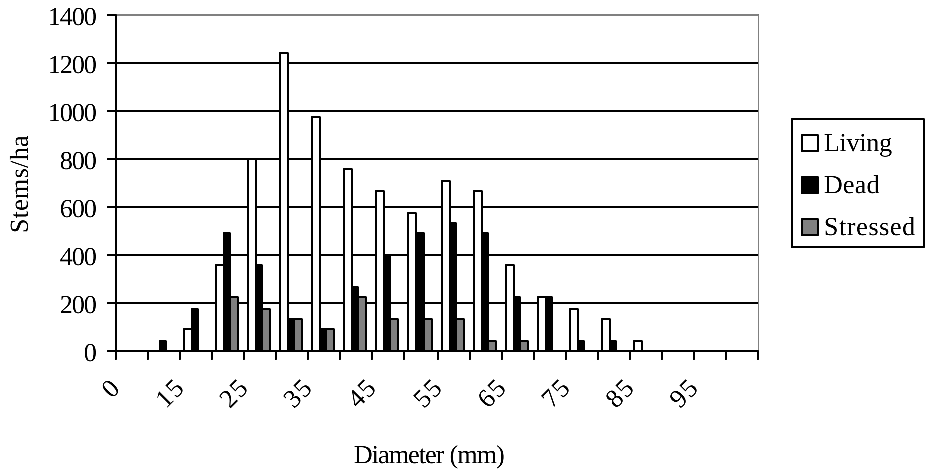


Figure 7–14: Diameter distribution of living, dead, and stressed *Salix fragilis* trees combined for the S, I, and C plots.

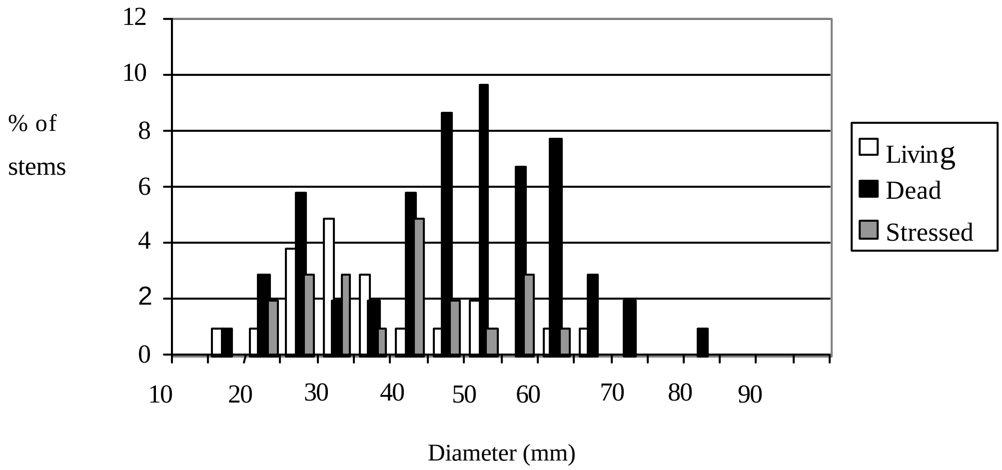


Figure 7–15: Diameter distribution of living, dead, and stressed *Salix fragilis* trees in the C plot.

This is also supported by the measured tree heights in the 3 plots (Table 7–3). In the sand part, about 72% of the living trees are characterized with a height larger then 6 m. All the dead and stressed trees were smaller then 6 m. The opposite was observed in the clay part. Here, only 5% of the total amount of trees was alive and characterized with heights larger then 6 m, while 69% of the dead trees were found in the larger than 6 m classes. As the stand was made up for 92% of living trees in February 2000, it becomes evident that the majority of trees in the 6-8 m and > 8 m classes died during the 2000 growing season. The same was observed in the intermediate transect: the largest part of the trees that died were found in the height classes > 6 m.

Table 7–3: Distribution (% of total and % of vitality class) of *Salix fragilis* trees over the different height classes in the 3 plots in September 2000.

| | | Height (% total) | | | | Height (% vitality class) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 2-4 m | 4-6 m | 6-8 m | > 8m | 2-4 m | 4-6 m | 6-8 m | > 8m |
| Plot S | Living | 10 | 14 | 24 | 38 | 12 | 16 | 28 | 44 |
| | Stressed | 3 | 2 | 0 | 0 | 60 | 40 | 0 | 0 |
| | Dead | 5 | 3 | 0 | 0 | 63 | 38 | 0 | 0 |
| Plot I | Living | 23 | 31 | 15 | 2 | 33 | 43 | 21 | 3 |
| | Stressed | 0 | 2 | 2 | 0 | 0 | 50 | 50 | 0 |
| | Dead | 7 | 1 | 12 | 2 | 32 | 5 | 55 | 9 |
| Plot C | Living | 8 | 8 | 5 | 0 | 38 | 38 | 24 | 0 |
| | Stressed | 5 | 10 | 7 | 1 | 23 | 45 | 32 | 5 |
| | Dead | 13 | 6 | 40 | 3 | 21 | 10 | 64 | 5 |
| Stand | Living | 14 | 17 | 15 | 13 | 23 | 30 | 25 | 22 |
| | Stressed | 3 | 5 | 3 | 0 | 26 | 45 | 29 | 3 |
| | Dead | 8 | 3 | 17 | 2 | 27 | 11 | 56 | 5 |

The adventitious root formation study in the tree plots showed that all living trees were characterized by an adventitious root system in the new sediment layer (Table 7–4). Most of the trees (92%) in the sand part of the site were characterized with adventitious roots. Except for 5% of them which showed stress symptoms, all these trees were found to be in healthy condition. The 8% of trees which failed to form adventitious roots were found to be dead. On the clay part on the other hand, 45% of the trees failed to form roots in the new sediment layer and most of these trees subsequently died. The other half of the trees did initially form adventitious roots but this did not ensure survival. More then half of the trees with root formation were stressed or dead as a result of the root system losing contact with the sediment layer as a result of sediment inclination, which amounted up to 40 cm in the clay part. In general, about 80% of the trees which originally formed roots which kept contact with the sediment layer were in good health. The other 20% were stressed or dead. The formation of adventitious roots which kept contact with new sediment layer was thus essential to ensure tree survival.

Table 7–4: Distribution (% of total and % of vitality class) of *Salix fragilis* trees over the different root classes in the three plots in September 2000.

| | | Root formation (% total) | | | Root formation (% vitality class) | | |
|---|---|---|---|---|---|---|---|
| | | Roots + contact | Roots - contact | No roots | Roots + contact | Roots - contact | No roots |
| Plot S | Living | 87 | 0 | 0 | 100 | 0 | 0 |
| | Stressed | 5 | 0 | 0 | 100 | 0 | 0 |
| | Dead | 0 | 0 | 8 | 0 | 0 | 100 |
| Plot I | Living | 70 | 0 | 3 | 96 | 0 | 4 |
| | Stressed | 1 | 3 | 0 | 25 | 75 | 0 |
| | Dead | 2 | 1 | 20 | 9 | 5 | 86 |
| Plot C | Living | 20 | 0 | 0 | 100 | 0 | 0 |
| | Stressed | 5 | 13 | 4 | 23 | 59 | 18 |
| | Dead | 1 | 16 | 41 | 2 | 28 | 70 |
| Stand | Living | 58 | 0 | 1 | 98 | 0 | 2 |
| | Stressed | 4 | 5 | 1 | 35 | 52 | 13 |
| | Dead | 1 | 6 | 23 | 3 | 20 | 77 |

Two of the three trees which were excavated at grid point 6 in September 2000 formed an adventitious root system in the new sediment layer. All roots originated from a 15 cm zone of the stem just below the new sediment surface. Two types of roots were observed: i) a very dense and compact root system concentrated around the stem. The length of the primary roots of this type was 40– 50 cm. and ii) up to 4 m long lateral roots which grew horizontally just below the sediment surface. Secondary roots grew 10 cm downwards into the sediment from the horizontal primary roots. The bark below the new root system of both trees was showing signs of decay at 1.5 m of depth. Bark could easily be removed from the stem which also showed signs of rot. This indicates that this section of the stem and the original root system lost their functions. The functions of the original root system were taken over by the newly formed adventitious roots. If no adventitious roots were formed trees died as a result of a lack of nutrients and water. This was observed for the third excavated tree.

From the height and diameter measurements of the trees in the clay part it already became apparent that the best developed trees were characterized with a high mortality. Figure 7–16 shows that with increasing tree diameter the adventitious root formation decreased. About 73% of trees with diameters > 45 mm did not form adventitious roots and 94% of these trees subsequently died. These findings corroborate the results from Figure 7–15 which showed that the majority of trees with a diameter > 45 mm died in the second year after sediment application.

The mean litter production collected from August to December 2000 for the whole stand was 900 kg DM/ha. This was considerably less than the productions measured in the previous growing seasons. In the clay part this production was only 233 kg DM/ha as the majority of the trees died during the 2000 growing season. On the sand part the productions was 2010 kg DM/ha which was in the same order of magnitude as the 1999 production.

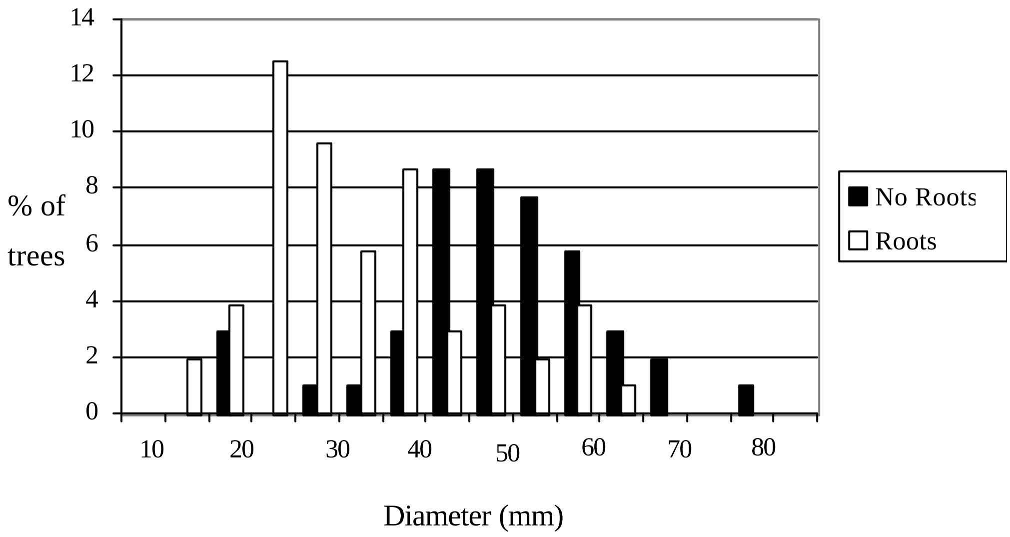


Figure 7–16: Diameter distribution of adventitious rooted and unrooted *Salix fragilis* trees in the C plot.

The small *Salix triandra* plot at the end of the disposal site was not studied in as much detail as the main *Salix fragilis* stand. However, visual observations showed that no dieback of the trees occurred. Every *Salix triandra* tree formed an extensive and dense adventitious root system at the base of its stem. This root system withstood the effect of the declining sediment surface and kept contact with the new sediment layer. This resulted in the formation of small root mounds at the base of the trees (Figure 5–2). No discoloring of the leaves was observed and leaf fall started simultaneously with other *Salix triandra* trees on the experimental site. This indicated that the *Salix triandra* trees were more tolerant to the sediment application compared to the adjacent *Salix fragilis* trees, were adventitious roots failed to form or lost contact with the new sediment layer.

### 7.3.3 Nutrient and heavy metal uptake

Table 7–5 presents the mean nutrient and heavy metals concentrations in leaves, wood and litter of *Salix fragilis* trees at the 17 grid points of disposal site A. The results for the nutrient concentrations in the leaves allow an evaluation of the nutrient status of the investigated stand. Threshold values for sufficient and optimal nutrient concentrations in willow leaves are given in Table 3–3 (van den Burg, 1990). All nutrients are sufficiently present in the 3 examined growing seasons. However, the introduction of the new sediment layer resulted in significant changes in nutrient concentrations. Both the N and P concentrations are higher after the sediment application. On the other hand, the S, Ca, Mg, Mn, Al, and Fe concentrations are all lower in 1999 compared to the 1998 values although they are still sufficiently present according to van den Burg (1990). The concentrations of these elements reached the 1998 levels again in 2000. The increase in N and P concentrations are also observed for the wood, although differences were not significant. The wood concentrations of S, Ca, Mg, Mn, Al, and Fe are lower in 1999, but subsequently increase in the 2000 growing season.

Heavy metal concentrations in leaves were all significantly lower in the year of sediment application. The difference was most outspoken for Cd and Zn. The same trend was observed for the litter: the litter collected in 1999 was characterized with lower Cd, Zn, Ni, Pb, and Zn concentrations compared to the 1998 samples. In 1998 significantly higher Cd and Zn concentration were found in the litter compared to the leaves sampled in August. This difference was however not observed in the 1999 growing season. Table 7–6 depicts the mineral mass of heavy metals recycled to the surface with leaf fall before and after the sediment application.

Table 7–5: Nutrient and metal concentrations in leaf, wood and litter compartments of the *Salix fragilis* stand.

| | | Leaf | | | | | | | Wood | | | | | | | Litter | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1998 | | 1999 | | 2000 | | sign | 1998 | | 1999 | | 2000 | | sign | 1998 | 1999 | sign |
| N tot | mg/kg | 23,932 | a | 25,898 | ab | 28,175 | b | * | 4028 | a | 4985 | a | 5049 | a | | 18,984 | 21,876 | * |
| P | mg/kg | 1943 | a | 2266 | ab | 2450 | b | * | 626 | a | 789 | a | 725 | a | | 1551 | 1540 | |
| K | mg/kg | 23,755 | a | 19,806 | b | 15,096 | c | * | 1586 | a | 2037 | ab | 2385 | b | * | 4928 | 10,891 | * |
| S | mg/kg | 10,321 | a | 5180 | b | 9486 | a | * | 811 | a | 712 | a | 1160 | b | * | 6953 | 6210 | |
| Ca | mg/kg | 28,530 | a | 22,365 | a | 28,640 | a | | 8928 | a | 8122 | a | 12,057 | b | * | 36,470 | 26,567 | * |
| Mg | mg/kg | 3463 | a | 2132 | b | 2448 | b | * | 681 | a | 641 | a | 928 | b | * | 2075 | 1870 | |
| Mn | mg/kg | 574 | a | 459 | a | 606 | a | | 42.7 | a | 50.2 | a | 86.9 | b | * | 1025 | 673 | * |
| Al | mg/kg | 185 | a | 181 | a | 60.0 | b | * | 59.6 | a | 266 | b | 113 | a | * | 199 | 191 | |
| Fe | mg/kg | 292 | a | 253 | a | 241 | a | | 61.7 | a | 174 | b | 156 | b | * | 422 | 292 | * |
| Na | mg/kg | 282 | a | 290 | a | 823 | b | * | 89.6 | | 110 | | 304 | | | 448 | 583 | * |
| Cd | mg/kg | 21.6 | a | 11.5 | b | 9.5 | b | * | 5.7 | a | 3.3 | b | 4.6 | ab | * | 38.3 | 11.4 | * |
| Cr | mg/kg | 1.5 | a | 0.7 | b | 1.7 | a | * | 1.7 | a | 1.9 | a | 6.3 | b | * | 1.5 | 1.74 | |
| Cu | mg/kg | 18.1 | a | 10.6 | b | 11.1 | b | * | 2.4 | a | 2.6 | a | 4.9 | b | * | 17.7 | 9.4 | * |
| Ni | mg/kg | 6.1 | a | 1.9 | b | 3.4 | b | * | 1.0 | a | 0.9 | a | 5.0 | b | * | 5.1 | 0.6 | * |
| Pb | mg/kg | 10.2 | a | 7.2 | b | 4.0 | c | * | 1.3 | a | 1.7 | ab | 2.8 | b | * | 14.5 | 10.2 | * |
| Zn | mg/kg | 1206 | a | 321 | b | 759 | ab | * | 116 | a | 92.8 | a | 176 | b | * | 1952 | 504 | * |

Table 7–6: Mineral mass of heavy metals recycled to the surface with leaf fall before and after the sediment application.

| | 1998 | | | 1999 | | |
|---|---|---|---|---|---|---|
| | Concentration mg/kg | Litter production kg/ha.year | Mineral mass g/ha.year | Concentration mg/kg | Litter production kg/ha.year | Mineral mass g/ha.year |
| Cd | 38.3 | 3120 | 119.5 | 11.4 | 2670 | 30 |
| Cr | 1.5 | 3120 | 4.7 | 1.74 | 2670 | 4.6 |
| Cu | 17.7 | 3120 | 55.2 | 9.4 | 2670 | 25 |
| Ni | 5.1 | 3120 | 15.9 | 0.6 | 2670 | 1.6 |
| Pb | 14.5 | 3120 | 45.2 | 10.2 | 2670 | 27.2 |
| Zn | 1952.5 | 3120 | 6091.8 | 504.9 | 2670 | 1348 |

### *7.3.4 Effects on surface and ground water*

When excess pumping water is brought back to the river Leie, it is highly enriched with salts and N. Only Zn exceeds the basic surface water quality threshold values (Vlarem II, appendix 2.3.1) for heavy metals, although with a slight margin. The sedimentation basin and the ditch intercepted a large percentage of the metals and suspended solids.

Measurements from the ground water samples showed that an As contamination has occurred at the site in the past. Up to 98 µg/l As was found in groundwater samples prior to sampling. This As contamination could possibly be attributed to the nearby paint factory. The continued monitoring of the groundwater up to two years after the operations showed that the groundwater did not get enriched with heavy metals.

Table 7–7: Mean chemical characteristics of water sampled at three locations of the excess pumping water cycle compared to the basic surface water quality threshold values (Vlarem II, appendix 2.3.1). Colored values exceed threshold.

| Parameter | | $W_{in}$ | $W_{out}$ | $W_{leie}$ | Threshold |
|---|---|---|---|---|---|
| pH | | 7,47 | 7,48 | 7,51 | 6,5<pH<8,5 |
| EC | µS/cm | 1563 | 1566 | 1649 | 1000 |
| SS | mg/l | 40 | 31 | 22 | 50 |
| Ntot | mg/l | 44,8 | 43,7 | 40,0 | 6 |
| P | mg/l | 2,7 | 1,6 | 1,1 | 1 |
| S | mg/l | 38,6 | 39,8 | 67,2 | 250 |
| As | µg/l | 13,8 | 8,0 | 7,9 | 30 |
| Cd | µg/l | 2,3 | 1,3 | 1,5 | |
| Cr | µg/l | 48,1 | 28,3 | 19,2 | 50 |
| Cu | µg/l | 50,7 | 55,1 | 32,7 | 50 |
| Pb | µg/l | 90,6 | 57,0 | 40,3 | 50 |
| Ni | µg/l | 17,3 | 11,2 | 13,7 | 50 |
| Zn | µg/l | 320 | 196 | 209 | 200 |

## 7.4 Discussion

Multi-layered dredged sediment disposal in afforested disposal sites could be an interesting technique to store dredged sediments while creating an ecosystem, stabilizing the substrate, increasing dewatering and rendering the site more esthetically attractive. The introduction of a new sediment layer into a tree stand is comparable with a prolonged flooding of the stand. In the first several months the stand was flooded by a mixture of water and sediment. As the sediment settled and excess water was gradually removed, the stand was covered by a reduced sediment layer which slowly riped and oxidized. Willows are known to be very tolerant to flooding, and are suitable tree species to be used in this eco-technique. Hosner (1960) compared the relative tolerance of 14 tree species to flooding and found that *Salix* species were the most tolerant. In addition, Good et al. (1992) concluded that there exists a substantial intraspecific variability in the tolerance to flooding between different *Salix* species and clones. One of the prime adaptations of willow to flooding is the formation of adventitious roots (Kozlowski, 1997). However, the pilot scale experiment described in this chapter showed that applying a new layer of sediment in an afforested disposal site resulted in widespread die back of *Salix fragilis* trees in large parts of the disposal site, but that trees can withstand a new sediment layer application if certain conditions are met. The results from the stand measurements before and after sediment application indicated that tree survival was dependent on the formation of a new adventitious root system in the new sediment layer. The formation of adventitious roots was shown to be depending of tree species, on the trees location on the site, and on tree characteristics.

In general, the tolerance of trees to flooding is highly correlated to the ability of trees to form adventitious roots (Clemens et al., 1978). Adventitious roots are formed when the original root system ceases to fulfill its function and the newly formed roots subsequently take over nutrient and water uptake to ensure sufficient supply to the above ground parts. Additional functions are the oxidation of the rhizosphere to detoxify harmful compounds in reduced soils and the increased supply of gibberellins and cytokinine to the leaves (Reid and Bradford, 1984).

Adventitious roots are often thicker and are characterized with more intercellular space than roots growing in well aerated soils. They can transport large amounts of oxygen into the reduced substrate (Hook et al., 1970). *Salix* trees are known to be very tolerant to flooding (Hosner, 1960) and rapidly form adventitious roots under flooded conditions. However, this characteristic is highly species and clone dependent (Good et al., 1992). This was also shown in our trial where adventitious root development of *Salix triandra* trees was much more vigorous compared to *Salix fragilis* trees. As a result, all *Salix triandra* trees survived the new sediment application while most of the *Salix fragilis* trees on the clay part of the disposal site died.

The survival of the *Salix fragilis* trees was highly dependent on their location in the disposal sites. Fragilis trees situated near the inlet mostly survived the treatment while trees situated in the rest of the disposal site almost all died as a result of the sediment application. The hydraulic raising of the disposal site from a single fixed inlet resulted in the formation of a strong texture gradient. The heavier sand fractions settled close to the inlet while the smaller silt and clay fractions remained in suspension and were transported further into the disposal site. This resulted in the establishment of two easily distinguishable zones in the disposal site: an area close to the inlet which was characterized with a high sand fraction and the rest of the disposal site which was filled with the finer clay and silt fractions. *Salix fragilis* trees in the well drained sandy part of the disposal site almost all formed an adventitious root system in the new sediment layer and survived. However, in the ill drained clay part of the disposal site, a large percentage of *fragilis* trees failed to form adventitious roots in the new layer. These trees subsequently died. It was shown that the best developed trees were most likely to lack an adventitious root system and that with increasing tree diameter the adventitious root formation decreased. Observations in the months after sediment application suggested that the absence of adventitious roots was the result of the movement of these large trees as a result of the wind. Due to this movement, large trees formed a void between the stem and the sediment which prevented close contact necessary for the formation of adventitious roots.

Smaller trees were less susceptible to wind action and were positioned more stable in the new sediment layer. These trees formed adventitious roots in the layers and initially survived. However, initial adventitious root formation was no guarantee for further survival in the growing season after the sediment application. As a result of dewatering and ripening the sediment surface in the clay part of the disposal site dropped up to 40 cm. This resulted in exposing the newly formed adventitious root systems above the surface after which nutrient and water supply to the tree was interrupted. Only trees which formed an extensive adventitious root system which could keep contact with the sediment were able to survive. As already mentioned, contrary to *Salix fragilis* trees, *Salix triandra* trees formed extensive root systems which kept contact with the new sediment layer. The formation of adventitious roots in close contact with new raised sediment was thus essential to ensure tree survival.

In this experiment a single inlet was used for the hydraulic raising of the sediment which resulted in the concentration of the clay and silt fraction in the largest part of the disposal site. This lead to a high degree of inclination of the sediment as it consolidated. The use of a mobile inlet would result in a more homogeneous distribution of the particle fractions across the disposal site. If the sediment applied in this trial would be homogeneously mixed, the following particle size distribution would be found in the whole disposal site: >50 µm: 18%, 20–50 µm: 55%, 10-20 µm: 7%, 2-10 µm: 13 %, and < 2 µm: 8%. The >20 µm fraction of the whole disposal (73%) site would then be comparable to the >20 µm fraction found at the sand part of the site when a single inlet is used (60 to 87%). This would reduce the inclination, increase drainage and dewatering speed, and increase the possibility of adventitious root formation and hence tree survival. Another option which can increase the survival chances of the trees is to ensure that they are well stabilized in the new sediment layer. This can be accomplished by hydraulically raising the sandiest sediments in the latest stages of the filling of the disposal site. As a result, trees will be less susceptible to wind action and will have a greater chance to form adventitious roots in the new sediment layer.

Trees tolerant to flooding such as *Salix* can survive prolonged periods of flooding. However, they rapidly wilt once parts of the canopy become submerged, as it results in the immediate loss of leaves and the decay of growth shoots. This was reported for a range of *Salix* species of which parts of the canopy became submerged as a result of flooding (Good et al., 1992). The 6 year old *Salix fragilis* trees with a maximum height of 4 m at the time of sediment application died after a large part of their canopy was submerged immediately after pumping the sediment and water mixture up to a height of 3.5 m. The 2 year old trees in disposal site B were completely submerged by the new sediment layer.

As a result of the extensive dieback of *Salix fragilis* trees in sections B to E, no positive effects of the trees on sediment dewatering and ripening could be observed in these sections. In general, the sediment in the disposal site, except for the zone close to the inlet, dewatered very slowly. Two growing seasons after the sediment application large volumes of sediment were still in reduced conditions, especially in the deeper layers. However, the sediment layer in the *Salix triandra* stand oxidized at a faster rate then the adjacent sediment between the stressed and dead *Salix fragilis* trees. This indicates that *Salix* trees with a well developed root system in the sediment layer can increase the dewatering speed and ripening.

Foliar nutrient analysis's showed that trees over the whole of the sediment disposal site were well supplied with nutrients. Both N and P concentrations in leaves and wood increased in the two growing seasons after the sediment application. This increase in N and P concentrations results from the introduction of readily available N and P with the new sediment, which were easily taken up by the new adventitious root system. This increase was also reported in flooded willow trees (Hosner, 1960). Leaf heavy metal concentrations all significantly decreased in both samplings after the sediment application. This can be attributed to the low bio-availability of heavy metals in the reduced sediment (Tack et al., 1998). This decrease was not observed in the wood samples. On the contrary, wood heavy metal concentrations increased in the second growing season after the sediment application, as metals became more available with the oxidation of the new sediment layer. This trend was not observed for the leave samples. The *Salix fragilis* 'Belgisch Rood' used in this trial clone is characterized with a high uptake of heavy metals. When willows are used to stabilize and revegetate contaminated substrates, as is the case in this eco-technique, it is advisable to use species which are characterized with a limited uptake of heavy metals. This is necessary to reduce the risk of spreading heavy metals to the environment through leaf fall. However, as a result of the lower metal concentrations and leaf biomass production after the sediment application, smaller amounts of heavy metals reached the stands surface with leave fall.

## 7.5 Conclusions

The multi-layered disposal of dredged sediments in disposal sites previously planted with a willow stand proved to be a successful technique if certain conditions are met. To minimize damage to the stand, trees on the disposal site should form a new adventitious root system in the raised sediment layer and roots should keep contact with the new sediment during and after inclination of the sediment layer. It is therefore important to use willow species which are characterized by a vigorous formation of extensive adventitious root systems as for example *Salix triandra*. *Salix fragilis* trees proved less capable of forming adventitious roots which were able to keep contact with the new substrate. To reduce the impact of sediment inclination it is important not to concentrate clay and silt fractions in parts of the disposal site but to ensure a homogeneous distribution of the sand particle fractions over the entire site. This can be established using a mobile sediment inlet. Another option which can increase the survival chances of the trees is to ensure that they are well stabilized in the new sediment layer. This can be accomplished by hydraulically raising the sandiest sediments in the latest stages of the filling of the disposal site. As a result, trees will be less susceptible to wind action and will have a greater chance to form adventitious roots in the new sediment layer.

When willows are used to stabilize and revegetate contaminated substrates, as is the case in this eco-technique, it is advisable to use species which are characterized with a limited uptake of heavy metals. This is necessary to reduce the risk of spreading heavy metals to the environment through leaf fall. However, as a result of the lower metal concentrations and leaf biomass production after the sediment application, smaller amounts of heavy metals reached the stands surface.

# 8 General discussion and conclusions

## 8.1 General discussion

This work showed that the combination of on land contaminated dredged sediment disposal and biomass production with willow cultures is a feasible land use option to integrate both land uses into the environment. Land disposed contaminated dredged sediments proved to be a suitable and fertile substrate for the growth of *Salix* trees. Both the annual increments and leaf nutrient status indicated that growing conditions are optimal for the development of willow stands on dredged sediments. The SALIMAT planting technique proved to be successful for the rapid introduction of a dense willow stand on hydraulically raised dredged sediment. When the willow wood is harvested at regular intervals, these contaminated dredged sediment sites with little other beneficial use can be made useful through the production of biomass for energy purposes. If planted in rows, willows grown on contaminated dredged sediments can be operated as in traditional SRF systems. The pilot scale production of willow biomass on land disposed dredged sediments contaminated with organic contaminants for renewable energy purposes has recently started in the Netherlands (Breteler et al., 2001). However, findings from this work indicated suggest that any tree-based strategy to restore land disposed heavy metal contaminated sediments, whether it is for phytostabilisation or extraction, may result in the dispersal of heavy metals to unwanted compartments in the ecosystem, through leaf fall, root activity, and biomass conversion. As such, possible metal losses to the environment must be closely monitored.

Some remarks can be made from a management point of view. In traditional SRF for example, cuttings are planted in rows to allow mechanical harvesting (Willebrand and Ledin, 1995). Using the SALIMAT technique to introduce the trees results in a dense stand; which is difficult to access with machinery. A new SALISTRIP system was recently developed to allow planting cuttings in rows on unpassable substrates. Another concern may be the low bearing capacity of the dredged sediments. Applying heavy machinery for harvest may result in damage to roots and soil structure.

The successful establishment of willow stands on dredged sediments provides the opportunity to apply these stands for the phytoremediation of the sediments. However, the potential of actively cleaning contaminated dredged sediments from heavy metals through repeated harvest appears to be limited. Metal uptake rates by the investigated willow species were insufficient to ensure the phytoextraction of all metals in an appropriate time scale. Hence, the use of willow cultures for phytoextraction purposes on contaminated dredged sediments is only an option if only Cd is in slight excess of threshold values for reuse of the sediment. Both *Salix fragilis* 'Belgisch Rood' and *Salix triandra* 'Noir de Villaines' proved to be good Cd accumulators and are thus well suited for Cd phytoextraction purposes. The other metals (Cr, Cu, Ni, Pb, and Zn) are accumulated in too small quantities to result in significant exports of these metals from the site. This is a serious drawback to the feasibility of a phytoextraction system based on willow as dredged sediment is most often contaminated with a range of heavy metals. Finding presented in this work and reports in literature (Hasselgren, 1999; Klang-Wetsin and Perttu, 2003) suggests that the potential to remove metals from contaminated site declines with tree age. Several factors such as dilution, metal availability in the root zone, and root activity can have an influence on this trend. Identifying these factors is a most needed task in further research.

In general, phytoextraction of heavy metals is only feasible for Cd in low concentrations as for example in agricultural land enriched with Cd through the application of fertilizer. Another use can be for remediation projects where the Cd dose to the stand can be controlled, as for example in sludge applications in SRF stands. Unless metal accumulation in willow biomass or the biomass production itself can be drastically increased, the prospect of willow based phytoextraction systems becoming an interesting option for the remediation of contaminated sediments is small.

Another drawback when metal accumulating willow clones are selected for the phytoremediation of dredged sediments are the large stocks of metals in leaf fall, which can result in unwanted fluxes of Cd and Zn to the environment. This fact is often overlooked in literature dealing with willow as a phytoextraction crop for heavy metals. Up to half of the accumulated amount of Cd in the aboveground biomass is recycled to the stand surface with leaf fall, resulting in increased risks of food chain accumulation and dispersal. For Zn as much four times of the element is recycled through leaf fall as is exported through the harvest of the stems. To ensure maximal Cd export and to minimize the risk of spreading Cd to higher trophic levels, leaves should be harvested in combination with the wood. However, this may endanger the biomass production over successive harvests, and hence the sustainability of the SRF system. In addition, a combined harvest of stems and leaves can complicate stand management. Sampling of biomass compartments should be performed close to the harvest and leaf senescence in order to correctly assess the potential amount of exportable heavy metals and the recycling of metals with leaf fall. The sampling and analysis of wood and bark should be done separately as they are characterized with different metal concentrations.

This study only considered the compartmentalization and fate of metals in tree biomass and closely associated abiotic compartments but did not investigate metal transfer to higher trophic levels. In general, the main route for mobile metals to food chains is via soil and litter feeding animals, from example from earthworm to bird. The direct transfer from contaminated tree biomass to for example phloem and leaf feeders appears to be limited (Crawford et al., 1996a and b). Especially the behaviour of Cd should be closely monitored. Mertens et al. (2001) found only elevated Cd levels in small mammals in three willow stands on sediment disposal sites compared to the background levels. However, calculations using the BIOMAG model indicated that the Cd pollution in the soil caused low risk for predators. This pathway can be of critical concern and merits further investigation.

The more extensive use of willow stands in a combined SRF and sediment disposal land use system for phytostabilization and revegetation is a more promising option. For this purpose, non accumulating willow clones, for example *Salix viminalis* clones 'Orm' and '86133', should be selected to reduce the risk of spreading heavy metals with leaf fall. The introduction of SALIMATS resulted in an effective 'green capping' of the polluted dredged sediment disposal site through the development of a high density fast growing stand with a long growing season. As a result, metals are stabilized against dust blowing, water erosion, and food chain accumulation through the development of a high density, perennial root system and the accumulation of OM and litter on the sediment surface. Previously derelict disposal sites can thus be safely valorized for the production of willow biomass for renewable energy purposes.

The on-site gasification of harvested biomass in a small scale fixed bed downdraft gasification installation proved to be a promising technology to produced electricity and heat in combined land uses of SRF and dredged sediment disposal. However, as a result of the high combustion temperatures and the limited temperature gradients in such small systems large amount of the metals, especially Cd and Zn, present in the wood are volatilized during gasification. On the other hand, Cu was mostly retained in the coarser ash fractions. An efficient flu gas cleaning system should thus be incorporated in the system to minimize losses of metals to the environment from the gasification system. The recovered ash fractions are enriched with heavy metals, as a result of which ashes can not be recycled to the stand for fertilization but have to be handled and stored with proper care.

In addition to the use of *Salix* for phytostabilisation and extraction purposes it can be expected that there are possibilities for its use in the phytodegradation of organic contaminants. However, research on this topic is still very limited. Vervaeke et al. (2003) indicated that the introduction of a willow stand resulted in an increased degradation of mineral oil, while a slower PAH dissipation was observed in the planted sediment. However, this study was not able to target the specific factors responsible for the differences in degradation of PAHs and mineral oil in fallow sediments and sediments planted with willow. As it was expected that the introduction of a dense root system would stimulate microbial activity and PAH degradation, further investigation on laboratory and glasshouse scale is needed to provide more insight.

While it was shown that the selective metal uptake limits the prospects for phytoextraction of metals from dredged sediment the metal removal by willow would be of value if it depletes the fractions of bio-available or environmentally active metals in the substrate. However, it should be considered in any phytoremediation application with willow that metals become more available in the willow root zone. This can lead to increased leaching of metals to deeper layers of the profile. Higher Cd, Cu and Zn availability in the root zone of willow were attributed to the increased oxidation in the vicinity of the roots in oxidizing sediment. This increased oxidation was attributed to i) a better aeration of the root zone through active $O_2$ transport in willow roots and ii) transpiration by the trees. In addition, longer-term effects of willow roots on sediment structure were observed which resulted in leaching of a fraction of the available metals. The willow root zone sediment was well structured, featured fine aggregates, and was well permeated. The unrooted bulk soil, on the other hand, was very compact, and was unstructured, thereby preventing percolation and metal leaching. Further investigation should indicate if metals are stabilized against leaching in the root zone of willow stands planted on already oxidized substrates through hydraulic control and interception, as was suggested for poplar by Schnoor (2000). To completely immobilize heavy metal in the sediments and thus prevent metal uptake by the trees, the top layer of sediments could be mixed with amendments.

The multi-layered disposal of dredged sediments in disposal sites previously planted with a willow stand proved to be a successful technique if certain conditions are met. However, as a result of the large scale dieback of trees in this study no effects of the presence of the trees on sediment dynamics could be identified. To minimize damage to the stand, trees on the disposal site should form a new adventitious root system in the raised sediment layer and roots should keep contact with the new sediment during and after inclination of the sediment layer. It is therefore important to use willow species which are characterized by a vigorous formation of extensive adventitious root systems as for example *Salix triandra*. *Salix fragilis* trees proved less capable of forming adventitious roots which were able to keep contact with the new substrate. To reduce the impact of sediment inclination it is important not to concentrate clay and silt fractions in parts of the disposal site but to ensure a homogeneous distribution of the sand particle fractions over the entire site. Another option which can increase the survival chances of the trees is to ensure that they are well stabilized in the new sediment layer. This can be accomplished by hydraulically raising the sandiest sediments in the latest stages of the filling of the disposal site. As a result, trees will be less susceptible to wind action and will have a greater chance to form adventitious roots in the new sediment layer. As multi-layered sediment disposal is a phytostabilization technique, non metal accumulating willow clones should be selected.

## 8.2 General conclusions

This work showed that the combined disposal of contaminated dredged sediments and biomass production of willow biomass is a feasible land use option to integrate both land uses in the landscape. Land disposed contaminated dredged sediments proved to be a suitable and fertile substrate for the growth of *Salix* trees. The introduction of dense willow stands managed in SRF systems can thus be regarded as a phytostabilization step in the remediation and restoration of dredged sediment disposal sites. The possibilities of actively cleaning sediments through the export of heavy metals with repeated harvests are limited. Only dredged sediments which only feature slightly elevated Cd concentrations compared to threshold values are eligible for remediation with metal accumulating willow clones. Other metals are not accumulated in sufficient quantities to result in a timely remediation of the sediment.

If the aim of the project is only to stabilize the sediments without biomass production large volumes of dredged sediment can be stored on the same afforested area in multi-layered afforested disposal sites. Steps should however be taken that conditions are favorable for adventitious root growth, which is essential for tree survival.

In every phytostabilization use of willow it is essential that non metal accumulating willow clones are selected to prevent large amount of especially Cd and Zn reaching the stand surface with leaf fall. Willow root activity on the other hand can result in an increased availability and higher risk of leaching. As such, possible metal losses to the environment must be closely monitored in every phytoremediation strategy based on willow.

The regularly harvested willow wood from both phytoextraction and stabilization applications with willow can be safely conversed to heat and electricity in small scale downdraft fixed bed gasification units if the necessary precautions for flu gas cleaning are taken. Previously derelict dredged sediment disposal sites can thus be valorized for the production of willow biomass for renewable energy purposes.

# Dutch summary

Fytoremediatie is een nieuwe bodemsaneringstechniek waarbij vervuilde substraten gestabiliseerd en of gereinigd worden met behulp van planten. Sinds enkele jaren kan het gebruik van *Salix* soorten rekenen op een toenemende belangstelling in deze context. Als een gevolg van historische pollutie van onze waterlopen is baggerspecie aangereikt met verschillende zware metalen. De behandeling van deze vervuilde baggerspecie stelt sinds verschillende jaren een technologische en economische uitdaging. Als gevolg hiervan worden grote volumes vervuilde baggerspecie geborgen op land, wat resulteert in aanzienlijke vervuilde oppervlaktes langsheen waterlopen. Het gecombineerde landgebruik van korte rotatie bosbouw (KRB) met de berging van vervuilde baggerspecie kan een optie zijn om deze landgebruiktypes te integreren in het Vlaamse landschap. Daarenboven bestaat de mogelijkheid dat de vervuilde specie biologisch gereinigd kan worden door middel van fytoremediatie met behulp van wilgen.

Deze studie had als centrale doelstelling de mogelijkheden en beperkingen van fytoremediatie van vervuilde baggerspecie met behulp van bebossingstechnieken te onderzoeken. Twee concepten werden hierbij onderzocht: de fytoremediatie van landgeborgen specie met behulp van korte rotatie bosbouw systemen en het etagebouwconcept, waarbij verschillende lagen baggerspecie in een reeds bebost depot worden gebracht. Bij het fytoremediatieonderzoek werd het gedrag van zware metalen in dergelijke systemen als centraal onderzoeksthema genomen. Hierbij werden verschillende mogelijke verspreidingswegen van zware metalen, zoals bladval, uitspoeling en hun gedrag bij vergassing onderzocht. Verder werd aandacht besteed aan de verschillende aspecten van deze technologieën: zoals de aanplanting, de bestandsontwikkeling, het beheer en de conversie van de geproduceerde biomassa. Het onderzoek van het etagebouwconcept richtte zich op de bepaling van de praktische haalbaarheid van deze technologie op pilootschaal.

Verontreinigde baggerspecie is een geschikt substraat voor de groei van wilgen. Dit bleek uit de nutriëntengehalten in de bladeren en de jaarlijks geproduceerde biomassa die opliep tot 17 ton DS/ha.jaar, wat hoger is dan in traditionele KRB systemen. Met behulp van de SALIMAT planttechniek kon hydraulisch opgespoten baggerspecie snel en efficiënt beplant worden met een dicht wilgenbestand (tot 440,000 scheuten/ha). De aanleg van dergelijke bestanden kan bijgevolg als een fytostabilisatiemaatregel beschouwd worden. Door regelmatige oogst van de geproduceerde biomassa kunnen opslagplaatsen voor baggerspecie, die voorheen geen bijkomende landgebruiksfunctie hadden, worden aangewend voor de productie van hernieuwbare energie.

Het potentieel om vervuilde baggerspecie actief te reinigen door herhaalde oogsten van met zware metalen aangerijkte biomassa is beperkt. Enkel voor specie waarvan alleen de Cd concentratie de drempelwaarde voor hergebruik als bodem overschrijdt zijn er vooruitzichten om fytoextractie met wilgen toe te passen. Te hoge Cd concentraties resulteren echter in onaanvaardbaar lange remediatieperiodes: om de Cd concentraties van de in dit werk onderzochte baggerspecie terug te brengen naar zijn drempelwaarden waren minstens 40 tot 60 jaar nodig, afhankelijk of bladeren al dan niet samen met het hout worden geoogst. De twee onderzochte wilgenklonen *Salix fragilis* 'Belgisch Rood' en *Salix triandra* 'Noir de Villaines' bleken goede accumulators van Cd te zijn en zijn geschikt voor gebruik in fytoextractietoepassingen voor Cd. In het hout en de bladeren werden Cd concentraties tot respectievelijk 26.4 mg/kg en74 mg/kg gemeten. De overige zware metalen (Cr, Cu, Ni, Pb, en Zn) worden in te kleine mate geaccumuleerd in de bovengrondse biomassa van wilg om voldoende export ervan mogelijk te maken.

Wanneer metaalaccumulerende wilgenklonen worden aangeplant op met Cd verontreinigde specie bereiken aanzienlijke hoeveelheden Cd het bestandsoppervlak met de bladval. Tot de helft van de totale hoeveelheid Cd in de bovengrondse delen wordt op deze wijze gerecycleerd. De mineraalmassa van Zn in de bladeren is zelfs 4 maal meer dan deze in het hout. Dit resulteert in de verhoging van het risico voor opname in de voedselketen en verspreiding van de bladerennaar aanpalende niet vervuilde percelen. Om een maximale Cd export te behalen en het risico op verspreiding van zware metalen te beperken dienen bladeren samen met het hout geoogst en afgevoerd te worden. Dit kan echter de duurzaamheid van de biomassaproductie over verschillende oogsten in gevaar brengen. Daarenboven bemoeilijkt deze operatie het beheer van het KRB systeem. De concentraties van zware metalen vertonen aanzienlijke seizoenale veranderingen over een groeiseizoen in alle onderzochte biomassacompartimenten van wilg. Bemonsteringen van deze compartimenten dienen zo kort mogelijk bij de oogst of de bladval te gebeuren om mineraalmassa's die geëxporteerd kunnen worden met oogst en bladval te berekenen. De bemonstering en analyse van hout en schors dient afzonderlijk te gebeuren daar deze compartimenten gekenmerkt worden door sterk verschillende metaalconcentraties.

Omwille van de beperkte en selectieve metaalaccumulatie en het risico op verspreiding van zware metalen is fytostabilisatie een interessantere optie voor de valorisatie van vervuilde baggerspecie. Voor dit doel dienen niet accumulerende wilgenklonen, zoals *Salix viminalis* 'Orm' en '86133' geselecteerd te worden. Het aanplanten met behulp van SALIMAT resulteert in een effectieve 'groene' afdekking van het vervuild oppervlak door de aanleg van een snelgroeiend dicht bestand met een lang groeiseizoen. De ontwikkeling van een dicht meerjaars wortelsysteem en de accumulatie van niet met zware metalen aangerijkt strooisel en organische stof resulteert in de stabilisatie van zware metalen tegen water erosie, verspreiding door de wind, en opname in de voedselketen.

De op verontreinigd sediment geproduceerde biomassa kan vervolgens ter plaatse gevaloriseerd worden in kleinschalige vergassingsinstallaties. Omwille van de hoge verbrandingstemperaturen en het beperkte temperatuursverval worden een groot percentage van de in het hout aanwezige zware metalen, vooral Cd en Zn, gevolarizeerd tijdens de vergassing. Cu werd echter vooral teruggevonden in de grotere asfracties. Installaties voor de verwerking van met zware metalen aangrijkt hout dienen dus uitgerust te worden met een efficiënt gasreinigssysteem om verspreiding van zware metalen naar de omgeving te beperken.

In elke fytoremediatietoepassing met wilgen dient rekening gehouden te worden met een hogere beschikbaarheid van zware metalen in de wortelzone van het bestand. De verhoogde beschikbaarheid van Cd, Cu en Zn werd toegeschreven aan een versnelde oxidatie van het sediment in de wortelzone. Deze was het resultaat van i) een betere doorluchting van de wortelzone door actief transport van $O_2$ door de wortels en ii) de verhoogde evoptranspiratie. Op langere termijn vertoonde de aanwezigheid van wortels een duidelijke invloed op de sedimentstructuur, die in een verhoogde uitspoeling van zware metalen resulteerde. De wortelzone van wilgen was goed gestructureerd en geaggregeerd terwijl onbeworteld sediment zeer compact en ongestructureerd bleef. Verder onderzoek moet aantonen of zware metalen in reeds geoxideerd substraat gestabiliseerd kunnen worden tegen uitspoeling als een gevolg van hydraulische controle en interceptie.

De praktische uitvoering van het etagebouwconcept bleek haalbaar indien aan verschillende voorwaarden voldaan werd. Om schade aan het bestand te beperken is het noodzakelijk dat de bomen een nieuw adventief wortelsysteem ontwikkelen in de nieuwe specielaag. Daarenboven dient dit wortelsysteem het contact met de specie te behouden terwijl deze uitrijpt en inklinkt. Wilgensoorten die gekenmerkt worden door de vorming van een uitgebreid en snel ontwikkelend adventief wortelsysteem dienen derhalve geselecteerd te worden. Uit het onderzoek bleek dat dit laatste het geval was voor *Salix triandra*, terwijl *Salix fragilis* slechts beperkte anventiefwortelsystemen ontwikkelde. Om de impact van inklinking op het nieuwe bestand te minimalizeren is het belangrijk een goede menging van zand en klei fracties over het volledige oppervlak van het bestand te verkrijgen. Dit kan bekomen worden door gebruik te maken van een mobiele spuitmond bij het opspuiten van de nieuwe sedimentlaag. Verder kunnen bomen beter gestabiliseerd worden in de nieuwe specielaag indien het meest zandige sediment als laatste wordt aangebracht. Als een gevolg van een uitgebreide sterfte konden geen effecten van het bestand op de baggerspecieuitrijping vastgesteld worden. Zoals aangewezen in elke fytostabilisatietechniek dienen niet accumulerende wilgenklonen geselecteerd te worden om de verspreiding van zware metalen naar de omgeving te beperken.

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# Curriculum Vitae

Pieter Vervaeke (°1973) graduated in 1997 as Bio Engineer at the Katholieke Universiteit Leuven with a specialization in Soil Science. In 1998 he started working on the IWT project 'Ecotechnological treatment and design of dredged sediment disposal sites with afforestation techniques' at the Laboratory of Forestry of the Ghent University in cooperation with the dredging company Jan de Nul N.V. After completion of this project in 2001, he continued his research during the FWO project 'Establishment of willow stands on contaminated sediment: vegetation effects on speciation, mobility and bio availability of heavy metals' at the Laboratory of Analytical Chemistry and Applied Ecochemistry (UGent), in cooperation with the Laboratory of Forestry. Meanwhile, he prepared and finished his Ph.D study program. During his research he participated in the Biomass Platform Flanders, in the SEDNET WG3 'Remediation and Disposal of Sediments', in the COST Action 837 'Phytoremediation' WG 4 'Cultivation and Utilization of Plants', and attended a range of national and international congresses. He is currently employed as project engineer at the in-situ soil remediation department of Envisan Environmental Technologies. Pieter Vervaeke is the author or coauthor of the following publications in international journals:

- Vervaeke, P., Mertens, J., Lust, N., Tack, F.M.G. 2004. Seasonal changes of heavy metals in biomass compartments of *Salix* stands growing on contaminated dredged sediment: potentials and limitations for phytoremediation. Environmental Science and Technology, submitted.

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