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Seasonal Changes of Metals in Willow (*Salix* sp.) Stands for Phytoremediation on Dredged Sediment

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Fast growing biomass plants such as *Salix* species are promising for use in phytoremediation of contaminated land. This study assessed the seasonal variations and changes with stand age in metal concentrations of *S. fragilis* L. and *S. triandra* L. grown in field conditions on contaminated dredged sediment substrates with comparable properties. A lesser proportion of total soil Cd was extractable by ammonium-acetate in the 6-year-old stand (6%) compared to the 1-year-old stand (17%). This suggests that the potential to remove metals from the site declines with tree age. Metal concentrations in willow biomass compartments decreased with stand age. Concentrations of Cd and Zn in leaves, wood, and bark increased toward the end of the growing season, irrespective of the species. Only Cd behavior offered limited prospects for targeting effective removal of the metal from the sediment through repeated harvest. The most efficient removal of Cd would require the combined harvest of stems and leaves; at the same time the risk of spreading Cd and Zn to the surroundings with leaf fall would be avoided.

Introduction

Phytoremediation is an emerging technology to restore, stabilize, and clean large areas of moderately contaminated substrates. It applies living green plants for in situ risk reduction and remediation of contaminated soils, sludges, sediments, and groundwater bodies, through the removal, degradation, or containment of the contamination (*1*−*4*). Trees have been suggested as a low cost, sustainable, and ecologically sound solution for phytoremediation of trace metal contaminated land (*5*). The use of energy crops such as willow and poplar species in phytoremediation is promising (*6*). Willow trees accumulate Cd and Zn in their above ground biomass compartments. These can be regularly harvested. In addition, willows are easy to propagate, fast growing, metal tolerant, perennial crops, with an extensive root system and high evapotranspiration that can stabilize pollutants (*7*, *8*). In recent years willows were planted for the stabilization of radiocesium contaminated soils in Belarus (*9*), in post-mining landscapes (*10*), and on sanitary landfills (*11*). Nevertheless, studies that deal with the phytoremediation potential under field conditions remain limited (*12*).

Vervaeke et al. (*13*) showed that hydraulically raised dredged sediment can be successfully planted with *Salix* species. Dredged sediment is well suited as a substrate to produce willow wood. The combined use of land for dredged sediment disposal and biomass production for energy purposes, with the potential for phytoextraction or stabilization, could constitute an economically and ecologically sound option for the management of sediment disposal sites (*14*). Such management would provide a realistic alternative to an effective cleanup of total metal contents to acceptable levels. It requires that metal cycles are well-known and controlled to prevent metal transfer to other compartments of the ecosystem.

Optimizing rotation length and harvest time, for example, can increase the efficiency of the phytoextraction process. In this context, seasonal variations of trace metal concentrations in the different aboveground biomass compartments can be important parameters to correctly measure metal fluxes in the ecosystem (*15*) and to ensure either maximal metal export with harvest in phytoextraction, or control of metal pathways in phytostabilization applications. An important concern with planting trees on metal contaminated soils is the potential effects 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 via uptake to foliage (*16*).

This study aims to evaluate phytoremediation potential of willow trees growing on contaminated sediments under field conditions. The seasonal changes of metal concentrations in different biomass compartments were measured to identify management options to increase the efficiency of such a phytoremediation system and to limit the associated risk of spreading metals.

Materials and Methods

Experimental Site and Design. The field experiment was performed at an experimental dredged sediment disposal site in Menen (Belgium, 50°48′ N, 3°08′ E), along the river Leie. Four disposal sites that were raised and planted over the course of 6 years were selected. The sites were planted by the SALIMAT technique, i.e., willow rods of a length of 2 m were laid horizontally in the mud at distances of 20 cm (*13*). The oldest sites, DS4 and DS6, had been planted with *S. fragilis* (clone 'Belgisch Rood') and the trees were, respectively, in their fourth and sixth growing seasons at the time of sampling. The youngest sites, DS1 and DS2, were divided into 16 subplots; 8 subplots had been randomly selected and planted with *S. fragilis* (Belgisch Rood), and the other 8 subplots were planted with *S. triandra* (Noir de Villaines). Trees of DS1 and DS2 were in their first and second growing season, respectively. From each of the four disposal sites an adequate, representative plot was selected for sampling. An overview of the sample design is presented in Table 1.

Sampling and Analysis. Soil samples were taken in March 1998, equally spread over the plot, with an auger to a depth of 30 cm. Sixteen samples were taken on DS1 and 12 samples were taken on DS2. The plots DS4 and DS6 were smaller and, respectively, 4 and 5 samples were taken. All soil samples were dried at 40 °C, ground to pass over a 2 mm mesh, and mixed. The pH of the samples was measured in a 1:5 sediment/deionized water suspension (*17*). Total nitrogen was determined using the modified Kjehldahl method (*18*).

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TABLE 1. Overview of the Sampled Disposal Sites and Plots

disposal site	area	raised	planted	species	plot area
DS6	150 × 20 m	1992	end 1992	*S. fragilis*	10 × 20 m
DS4	100 × 20 m	1994	end 1994	*S. fragilis*	10 × 20 m
DS2	50 × 20 m	1995	start 1997	*S. fragilis; S. triandra*	20 × 20 m with 8 25-m^2 subplots of each species
DS1	100 × 20 m	1995	start 1998	*S. fragilis; S. triandra*	40 × 20 m with 8 50-m^2 subplots of each species

The Walkley and Black method (*19*) was used to assess the amount of organic carbon in each sample.

Other element concentrations (K, P, S, Cd, Cr, Cu, Ni, Pb, and Zn) were determined after extraction using a HNO_3/HCl/HF mixture during microwave digestion (CEM, MDS 2000). Extracts were subsequently analyzed 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 sample every 10 samples.

Estimation of a mobile pool of trace metals was made using an extraction with ammonium-acetate at pH 7 (*20*). Samples from DS1 were pooled (groups of 4 adjacent samples) and mixed throughout to obtain 4 composite samples before this procedure. The same was done with the 12 samples from DS2 (groups of 3 samples). For each of the replicates, 10 g of the fresh sediment was extracted after 2 h of reciprocal shaking of a 1:5 sediment/extractant suspension and filtered. The metal concentrations in the extracts were subsequently analyzed on a graphite furnace atomic absorption spectrophotometer (Varian AA-1475 with GTA-95, Palo Alto, CA) or a flame atomic absorption spectrophotometer (Varian SpectrAA-10, Varian, Palo Alto, CA), 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 pipet method (*21*).

Leaves, wood, and bark from each of the plots were sampled monthly from April to November 1998. Four replicates of each biomass compartment (wood, bark, leaves) were sampled in all the plots.

In DS1 and DS2, at least 3 complete trees were cut from 4 of the 8 subplots. The bark and leaves were removed immediately after sampling, and the weights of the wood, bark, and leaves were determined for each tree. In the 1-year-old stands, bark was only removed from the third month of sampling. The 3 wood samples originating from the same subplot were subsequently pooled together. The same procedure was followed for the bark and leaf samples. In the 4- and 6-year-old stands, 4 complete trees were cut with every sampling. The size of the trees in these stands made subsampling 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. Leaf samples were collected from at least 10 locations in the crown and pooled together for each tree. Leaves were rinsed at least 3 times in deionized water before analysis (*22*).

All wood, bark, and leaf samples were dried at 70 °C to constant weight and subsequently milled. The metals Cd, Cr, Cu, Ni, Pb, and Zn were extracted 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 standards every 10 samples.

Biomass Production. The biomass production was measured or estimated to calculate metal stocks and fluxes. Wood and bark biomass productions in the first- and second-year stands were 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 = $a \times \text{diameter}^b$, where a and b are empirical constants (*23*). The August measurements were used for the determination of the leaf biomass in these plots. Biomass productions reported in Vervaeke et al. (*13*) were used for the calculation of metal stocks 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 (*24*).

Statistical Analysis. The disposal site characteristics were compared with ANOVA using Tukey's post hoc test to identify differences between means. The same procedure was applied to compare ammonium-acetate-extractable metal fractions in the sampled sediments. Seasonal changes in metal concentrations were evaluated for the factors "month" and "stand" with ANOVA. Multiple comparison of means was performed according to Tukey's post hoc test. Statistical calculations were performed using the SPSS 11 software package.

Results

Dredged Sediment Characteristics. The chemical and textural characteristics of the sediments in the four investigated sites were comparable, except that DS6 showed 2−3 times higher Cd concentrations and 2 times lower Cr and Ni concentrations than the other sites (Table 2). That site tended to have the lowest ammonium-acetate-extractable metal contents (Table 3). Overall, the substrates were comparable, such that differences between plots can be largely attributed to either willow growth and/or age of the stand. Flemish legislation limits (*25*) for reuse of the sediment as soil were exceeded for Cd in every disposal site, for Cr in DS1, DS2, and DS4, and for Zn in DS1, DS4, and DS6.

The percentage of the total concentration that is extractable with ammonium-acetate was for most elements quite constant over the sites. Only for Cd did this rate show relevant changes. On the youngest sites about 18% of the total Cd concentration was extractable compared to 6% on the 6-year-old stand.

Wood Metal Concentrations. The youngest plantations accumulated the highest Cd levels in the wood. In addition, Cd concentrations from these stands increased strongly over the growing season (Figure 1). Cd concentrations for the stand in the first growing season increased from 6.8 ± 1.8 to 15.8 ± 1.9 mg kg^{-1} for *S. fragilis* and from 8.4 ± 2.4 to 25.2 ± 1.7 mg kg^{-1} for *S. triandra*. In contrast, Cd concentrations in the 4- and 6-year-old wood were fairly constant over the growing season, averaging 5.6 ± 0.7 mg kg^{-1} for the 4-year-old stand and 6.6 ± 1.9 mg kg^{-1} for the 6-year-old stand.

Zn concentrations of the youngest stands also slightly increased. The trend of Cu in the 1-year-old willow wood was opposite that of Cd and Zn; Cu concentrations decreased over the growing season from 17.4 ± 0.9 to 5.8 ± 0.5 mg kg^{-1} for *S. triandra* and from 15.6 ± 1.2 to 5.6 ± 0.3 mg kg^{-1} for *S. fragilis*. This decrease was not observed for the older stands.

Measurements for Cr and Ni were almost all below the detection limits (0.1 mg Cr kg^{-1}, 0.2 mg Ni kg^{-1}). For Cr, only 14% of the 192 samples were above the detection limit and most of these measurements were made in September, when

TABLE 2. Particle Size Distribution and Chemical Characteristics of the Sediments in the Four Disposal Sites (0−30 cm)[a]

depot	N	>50 μm (%)	<2 μm (%)	C (%)	pH (H_2O)	N (mg kg^{-1})	P (mg kg^{-1})
DS1	5	42 a	12 a	5.0 a	7.1 a	2130 a	1870 a
DS2	5	31 ab	13 a	3.7 b	7.0 a	1530 a	1460 a
DS4	4	36 ab	16 ab	4.0 b	7.1 a	2000 a	1560 a
DS6	5	22 b	19 b	3.7 b	6.9 a	3180 b	7490 b

	N	Cd (mg kg^{-1})	Cr (mg kg^{-1})	Cu (mg kg^{-1})	Ni (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
DS1	12	4.6 a	127 a	78.3 a	53.3 a	91 a	475 a
DS2	16	3.5 a	136 b	57.7 a	44.8 b	74 a	361 a
DS4	4	5.0 a	138 b	69.9 a	42.3 b	102 a	457 a
DS6	5	9.4 b	67.4 c	74.5 a	20.7 c	117 a	475 a
thresholds		1.6	118	85	65	138	385

[a] Total metal concentrations are compared against the Flemish legislative thresholds for reuse of the sediments as soil (*25*). Values for the same element followed by the same letter do not differ ($p < 0.05$) according to a Tukey's test.

TABLE 3. Ammonium-Acetate-Extractable Metal Concentrations (Mean ± Standard Deviation) (mg kg^{-1})[a]

	Cd	Cr	Cu	Ni	Pb	Zn
DS1	0.77 ± 0.06 a	0.54 ± 0.19 a	0.712 ± 0.10 a	1.31 ± 0.15 a	0.77 ± 0.04 ab	61.95 ± 10.82 a
DS2	0.62 ± 0.06 bc	0.50 ± 0.09 a	0.585 ± 0.14 a	1.12 ± 0.14 a	0.56 ± 0.04 b	70.37 ± 6.93 a
DS4	0.66 ± 0.01 b	0.54 ± 0.15 a	0.583 ± 0.07 a	1.25 ± 0.12 a	1.00 ± 0.13 a	78.77 ± 4.82 a
DS6	0.52 ± 0.04 c	0.38 ± 0.05 a	0.546 ± 0.05 a	1.12 ± 0.22 a	0.68 ± 0.09 b	77.76 ± 11.59 a

[a] Values for the same element followed by the same letter do not differ ($p < 0.05$) according to a Tukey's test.

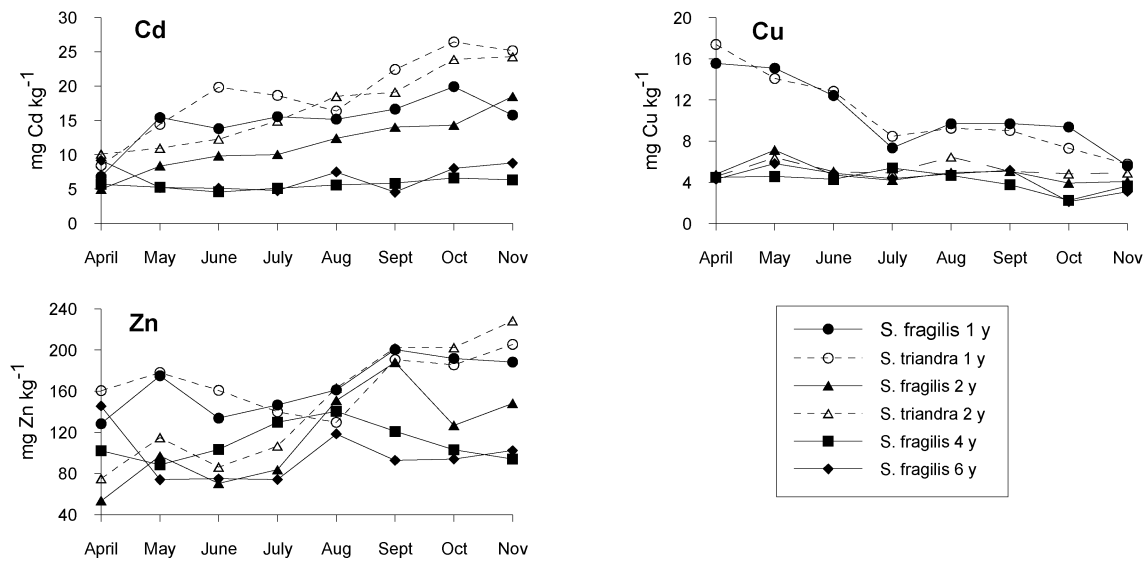

FIGURE 1. Seasonal changes in the wood Cd, Cu, and Zn concentrations.

a mean concentration of 0.5 ± 0.2 mg kg^{-1} for all stands was found. 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, 0.5 ± 0.1 mg kg^{-1}, was measured in July.

Bark Metal Concentrations. Metal concentrations measured in the bark were consistently higher compared to the wood concentrations. Bark Cd concentrations of the 2-year-old stands increased over the course of the growing season (Figure 2). However, such an increase was not detectable for the other stands. The Cu concentrations of the 2-, 4-, and 6-year-old stands were fairly constant over the growing season with a slight decrease toward the end. Concentrations in the 1-year-old stands exhibited higher levels in the beginning of the growing season and a more pronounced decline toward the end. The same trends were also observed for the Cu wood concentrations. Zn concentrations of the 1- and 2-year-old stands increased slightly. The Cd and Zn concentrations of the older 4- and 6-year-old stands remained fairly constant over the growing season. Mean Cd concentrations over the growing season were 19 ± 2 mg kg^{-1} for the 4-year-old stand and 23 ± 4 mg kg^{-1} for the 6-year-old stand. For Zn these concentrations were 606 ± 77 and 573 ± 100 mg kg^{-1}. Cr concentrations ranged from 0.21 to 0.91 mg kg^{-1}, and Ni concentrations ranged from 0.4 to 2.0 mg kg^{-1}. Measurements of both elements, however, were characterized with high standard deviations.

Foliar Metal Concentrations. All metal concentrations were highest in the leaves compared to wood and bark concentrations. The differences in metal concentrations over the growing season were also more pronounced (Figure 3). The foliar Zn concentrations particularly increased toward 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 these two stands also increased, from, respectively, 7.4 ± 1.8 and 20.1 ± 2.6

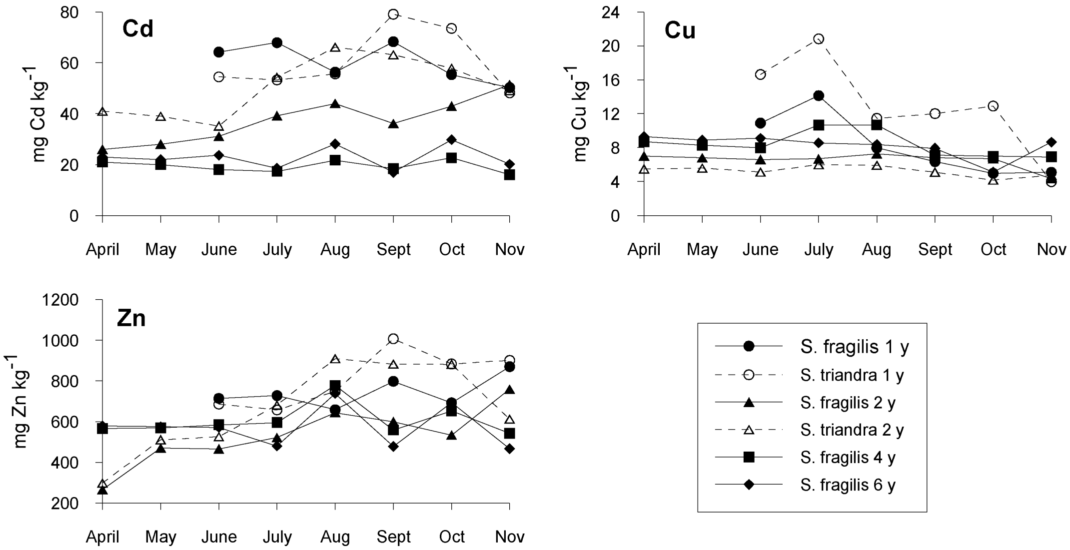

FIGURE 2. Seasonal changes in the bark Cd, Cu, and Zn concentrations.

to 74 ± 21 and 44.8 ± 4.4 mg kg^{-1}. At the end of the growing season the Cd and Zn concentrations seemed to decrease slightly before leaf fall.

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 remained fairly constant over the next months until summer. Before leaf senescence both Cr and Ni concentrations increased in the two oldest stands, and to a lesser extend in the younger *S. fragilis* stands. In the 1- and 2-year-old *S. triandra* stands, Cr and Ni concentrations decreased instead in the last month before total leaf fall. Cu concentrations in all stands remained constant over the course of the growing season.

Discussion

Seasonal Changes in Metal Concentrations. Seasonal changes in biomass metal concentrations suggest that either the availability of metals in the soil showed a seasonal pattern and/or growth dilution and/or shunting occurred in plant tissues. Leaf concentrations showed the highest fluctuations over the season: the Cu, Cr, and Ni concentrations dropped in the beginning of the growing season for all stands after which they increased again toward leaf senescence. Similarly, Dinelli and Lombini (*26*) 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, associated with C-assimilation, which diluted the concentrations. A 2-year study of the metal concentrations in leaves of a mature birch stand (*27*) showed that Cu and Ni contents decreased at the beginning of the growth period. These authors attributed this to a dilution effect resulting from increased dry weight of the leaves.

Other studies have confirmed the accumulation of metals in leaves of deciduous trees prior to shedding (*28*). A sharp increase in foliar Zn concentration was observed in a *S. cinerea* stand growing on dredged sediment (*29*). This increase in metal concentrations is generally interpreted as metal shunting occurring in the plant tissues prior to senescence. It is argued that this phenomenon might be part of an excretion mechanism of excess metals by the tree (*30*).

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 translocation mechanisms 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 (*31*).

In the 1- and 2-year-old stands 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 4- and 6-year-old stands wood Cd and Zn concentrations remained fairly constant. This would imply that in these younger stands Cd and Zn were progressively accumulated throughout the growing season. One explanation for this can be that the fast developing root systems in these young stands explore more substrate with relatively more available Cd and Zn. Another possibility is that Cd and Zn in the sediment became more available over the course of the growing season. While this would be very likely in freshly disposed sediments, sediments used in the trial were completely oxidized. Nevertheless, significant shifts in available fractions during the growing season in the first year cannot be excluded. No study yet closely examined changes in metal availability during a growing season in the field.

Stand Age. The data suggest that metal concentrations in willow biomass compartments tend to decrease with stand age. Several other studies came to a similar conclusion when investigating Cd accumulation over several growing seasons (*8*, *32*). This trend may be attributed to the general notion that metal accumulation primarily occurs in actively growing tissues such as shoots and young leaves. Subsequently, accumulated metals are diluted with increased biomass production. Klang-Westin and Perttu (*33*) reported an opposing and very consistent relationship between stem biomass and stem Cd concentration. Our finding and these reports suggest that the potential to remove metals from contaminated site will decline 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.

Phytoremediation. The data suggest that harvesting at the end of the season will remove the greatest amount of metals. For most elements, the concentrations in the wood and the bark remained quite constant over the season or increased toward the end of the season. Also, the produced biomass increases toward the end of the season. To correctly assess the potential amount of exportable trace metals and

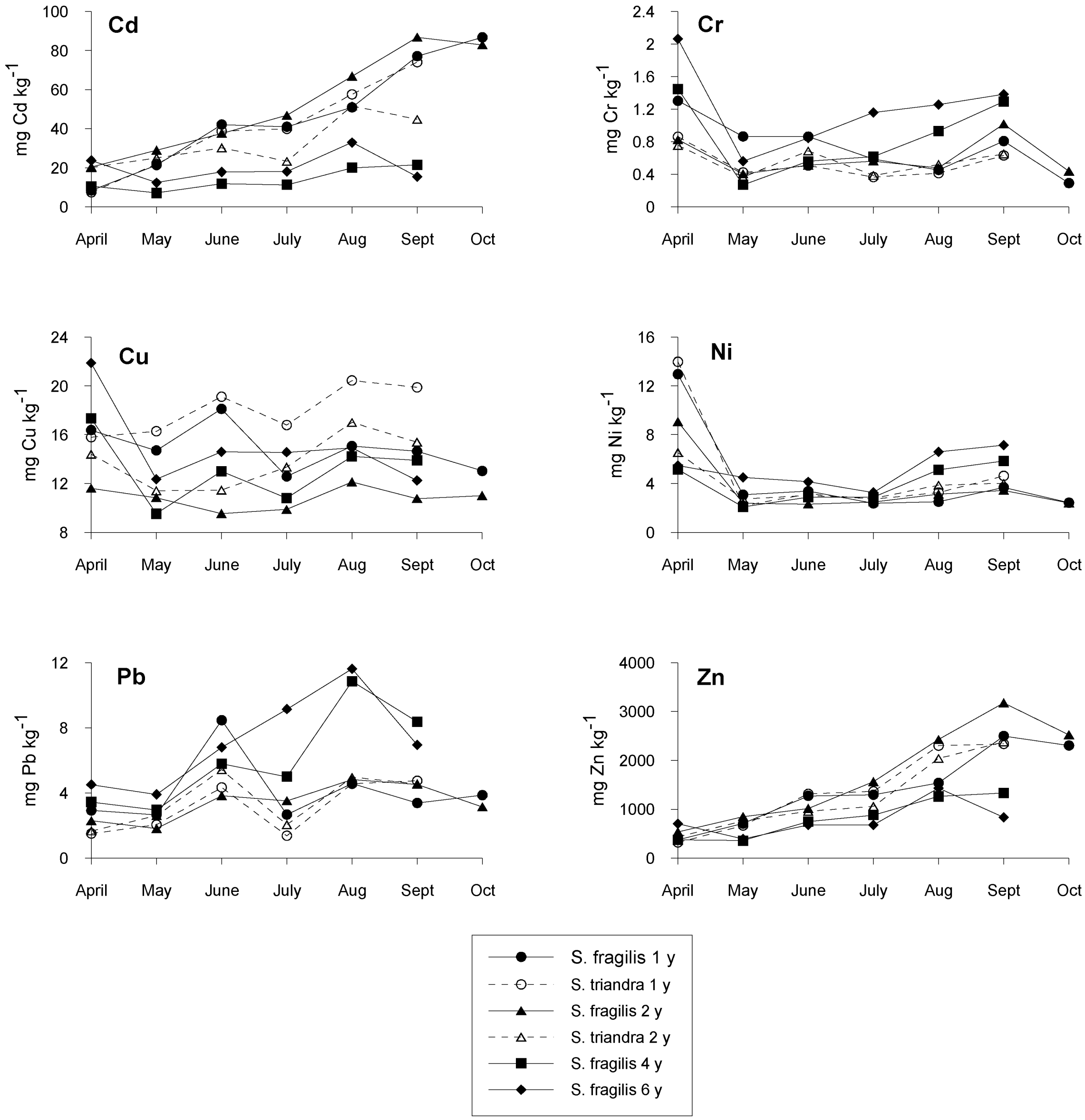

FIGURE 3. Seasonal changes in the foliar Cd, Cr, Cu, Ni, Pb, and Zn concentrations.

the recycling of metals with leaf fall, sampling should be performed close to the harvest and leaf senescence.

The metal extraction ratio was calculated as the proportion of the metal stock in the biomass compartments to the metal stock in the rooted soil profile (*34*). Metal stocks in the biomass were calculated taking into account the concentrations and the biomass. Biomass production was between 8.4 and 13.9 metric ton stems (wood and bark) $ha^{-1}{\cdot}y^{-1}$, and between 1.7 and 7.6 ton DM leaves $ha^{-1}{\cdot}y^{-1}$ (Table 5, Supporting Information). The amount of metals in the soil was calculated from the mean metal concentration for the 4 disposal sites assuming a 0.5 m profile with 1.3 g cm^{-3} bulk soil density. We assumed the upper 0.5 m profile to contain the majority of the active roots. This ratio allows an estimation of the percentage of metals which can be exported from the site with harvest (Table 4).

The highest annual metal extraction ratio was found for Cd in the 2-year-old *S. triandra* stand: 1.2% of the amount of Cd in the upper 0.5 m of the soil was taken up in the aboveground wood biomass. Co-harvesting of the leaves will increase the annual uptake ratio to about 1.6%. Compared to the amount of Cd that should be removed from the soil to meet criteria for reuse as soil in Flanders, up to 2.4% could be exported per year.

Assuming that the trees will take up a similar amount of metals every year, it would take nearly 50 years to reach the threshold value. For Zn it would take at least 100 years and for Cu it seems beyond reach. For Cr and Ni, the concentrations were below threshold values but the metal extraction ratio is in the order of magnitude of Cu.

Cd seems thus to be the only element which might be targeted for cleanup using willow cultures as was already indicated by several authors (*35*). Nevertheless, there are different reasons to assume that the calculated period of 50 years needed to reach the threshold value is underestimated. It is known that Cd availability in the soil can decrease with time but the rate of this decline is poorly known. In our experiment, the extractable concentration on the 1- and 2-year-old plots was about 17−18% of the total concentration, while on the 4-year-old plot it was 13%, and on the 6-year-old plot it was only 6%. For the other elements, the extractable fraction was very similar among the plots of different ages. Eriksson and Ledin (*36*) 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. This decrease in available Cd might partly be compensated because metal availability in the vicinity of willow roots can increase compared to unrooted bulk soil

TABLE 4. Metal Uptake Ratio: Mean Percentage (%) of the Soil Metals in the Upper 0.5 m Profile that are Taken Up by the Biomass on Yearly Basis

	Cd		Cr		Cu		Ni		Pb		Zn	
	wood	wood + leaves	wood	wood + leaves	wood	wood + leaves	wood	wood + leaves	wood	wood + leaves	wood	wood + leaves
						S. fragilis						
DS1	0.70	1.23	0.0001	0.0002	0.0095	0.0149	0.0012	0.0031	0.0018	0.0030	0.10	0.21
DS2	0.89	1.47	0.0000	0.0002	0.0093	0.0182	0.0014	0.0043	0.0023	0.0042	0.08	0.28
DS4	0.33	0.82	0.0001	0.0005	0.0127	0.0229	0.0027	0.0085	0.0034	0.0067	0.08	0.29
DS6	0.21	0.44	0.0002	0.0013	0.0096	0.0222	0.0050	0.0248	0.0026	0.0069	0.06	0.27
						S. triandra						
DS1	1.10	1.58	0.0001	0.0002	0.0121	0.0164	0.0014	0.0026	0.0021	0.0032	0.12	0.24
DS2	1.22	1.56	0.0001	0.0002	0.0122	0.0142	0.0017	0.0029	0.0024	0.0032	0.13	0.28

(*37*). Pulford et al. (*38*) 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 topic certainly needs further investigation as it is important for the feasibility of phytoremediation.

Furthermore, it is doubtful if biomass production will remain constant for every rotation period. From 3 to 6 year rotations it can be expected that this will be true, based on reports on traditional short rotation forests (SRF) practices (*39*). Short rotation forests managed this way are generally characterized with constant biomass production for every rotation as long as soil fertility is maintained. Only toward the end of the 20 year period in which SRF stands are generally operated can a decline in production 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 (*40*). 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.

While a large percentage of soil Cd accumulated in the *Salix* stands, considerable amounts of metals were recycled to the stand surface with leaf fall. For example, on the 4- and 6-year-old sites, harvesting after 4 or 6 years would result 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 would reach the stand surface compared to the amount of Zn in wood and bark. Up to now, the recycling of trace metals with leaf fall and the associated risks have received little attention in the literature on the evaluation of willow species for phytoremediation purposes. A possible management option is to harvest the leaves in addition to the wood. This would reduce the risk of food chain accumulation. In general, willows in SRF systems are harvested in winter when leaves have already fallen (*40*). One option to remove the leaves is to collect them from the site surface after the harvest of the wood. For rotations longer than 1 year this can result in practical problems as it implies that leaves have to be removed in the years between harvests. Another option 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 physiological disorders and that resprouting is severely affected. However, Hammer et al. (*8*) 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, in this study of Hammer et al., willows were grown on a fertile substrate which received additional fertilization may be an explanation for their findings. As the dredged sediment was also very fertile, it should be investigated whether annual harvesting, including stems and leaves, is feasible.

Acknowledgments

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Supporting Information Available

Wood, bark, and leaf biomass (mean value ± standard deviation) values of the different stands. This material is available free of charge via the Internet at http://pubs.acs.org.

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