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Combustion of *Salix* used for phytoextraction: The fate of metals and viability of the processes

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ABSTRACT

Phytoextraction may reduce the environmental risk posed by contaminated sediments while simultaneously providing an economic return via bioenergy production. There is a lack of information on the combustion of metal enriched willows used for phytoextraction. This work aimed to determine the Cd phytoextraction efficiency of *Salix* on a case study in France and elucidate the distribution of metals in the end products of the combustion process. Three willow clones were cultivated in short rotation coppice (SRC) on a metal contaminated dredged sediment landfill site. Combustion assays were performed in a biomass boiler of 40 kW with a Zn and Cd enriched *Salix* wood 'Tora' harvested from a part of the SRC and a commercial 'Tora', for comparison. In a best-case scenario, phytoextraction could reduce total Cd burden of the sediment from 2.39 mg kg^{-1} DW to 2 mg kg^{-1} DW in 19 years. Combustion experiments showed that Cd and Zn occurred at the highest concentrations in the particulate fraction of the flue gas (flyash), rather than in the bottom ash. Combustion of 'Tora' from phytoextraction resulted in Cd and Zn concentrations in flue gas emissions that exceeded French regulation. This was also observed for Cd in the flue gas of the commercial 'Tora'. Irrespective of the wood provenance, the use of industrial or collective boilers, equipped with efficient filters, is required to minimize air pollution. Given this constraint, wood produced during phytoextraction should be usable for bioenergy production. The possible uses of bottom ash are discussed.

1. Introduction

Human activities during the last decades have contaminated canal sediments with various organic and inorganic pollutants. Those of most concern are metal(loid)s, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and mineral oils. The dredging of canal sediments is necessary to facilitate navigation, to prevent flooding and to maintain a minimum water flow during dry periods. In Northern France, mining and metal smelting have deposited trace elements (Cd, Zn, Pb, Cu, As) in the canal sediments. European Community policy encourages sediment recovery [1]. Nevertheless, due to the high concentration of pollutants and their potential toxicity, contaminated dredged sediments cannot be

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used in civil engineering as raw material or the deposit cannot be used to produce biomass for human and animal feeding. Many treatments are available for contaminated sediments, but relatively few are applicable to metal(loid) pollution. Currently, treatment and reuse of metal contaminated dredged materials are not a cost-effective alternative to disposal at landfill sites [2]. In Northern France, disposal onto land is the current management practice for these polluted sediments. The regional division of Voies Navigables de France (VNF) developed a management strategy for its disposal sites. This strategy includes the implementation of an environmental management system which aims to meet best practices and comply with regulation in the fields of human health and the environment. Metal immobilization in metal contaminated sediments at some landfill sites may contribute to this environmental management strategy [3]. Phytoextraction combined with bioenergy production may be another way to contribute to such a strategy.

Phytoextraction may reduce the environmental risk posed by these sediments and allow the economic valorization of the contaminated sediments via the sale of the produced biomass. Phytoextraction may be combined with bioenergy production to provide a benefit to the land owner while ensuring that environmental parameters do not breach current regulation [4–8]. One phytoextraction strategy is based on cultivation of rapidly growing trees, such as willow, with high trace element (TE) accumulation ability in short rotation coppice (SRC). After the cultivation of appropriate tree species on the contaminated site, enriched TE harvestable plant parts are removed from the site.

Various energy-recovery techniques such as combustion, gasification and pyrolysis may be suitable for high-biomass trees such as *Salix* [9–15]. Combustion, the most important energy conversion route for biomass produced on uncontaminated soils, results in bottom ash and stack emissions. There is a lack of information on the combustion of metal enriched willows used for phytoextraction. To our knowledge, few combustion experiments have been performed on willows planted on contaminated sites [9,15] and none in an industrial boiler. Nevertheless, the theoretical fate of metals during combustion is rather well documented [16]. Keller et al. [9] simulated a combustion assay in a glass tube reactor with Zn and Cd enriched *Salix* leaves. Zinc was found in the bottom ash whereas Cd was volatized during the combustion process. Syc et al. [15] performed a fluidized bed combustion test in a reactor on *Salix caprea* enriched with Cd and Zn and studied metal distribution between bed ash, cyclone ash and flyash. Most Zn and Cu were retained on ashes (bottom ash and bed material) whereas Cd was partly retained on cyclone and flyash and partly volatilized. After comparison with legal thresholds, Keller et al. [9] and Syc et al. [15] concluded that ash could not be applied as fertilizers.

The aims of this study were to assess the Cd phytoextraction efficiency of *Salix* 'Tora' cultivated in SRC on a metal contaminated dredged sediment landfill site in France. We also sought to perform a combustion experiment with a *Salix* 'Tora' sample harvested from this phytoextraction site to determine the fate of the metals in the products of the combustion process. The viability of the processes, i.e. phytoextraction with *Salix* 'Tora' combined with combustion for bioenergy production, was envisaged according to French regulation.

This is the first time that a combustion experiment performed at industrial scale with *Salix* 'Tora' used for phytoextraction on a metal contaminated dredged sediment disposal site is reported.

2. Materials and methods

2.1. *Historical and site description*

In 1993, as a result of a Deûle river maintenance operation, a 15 ha dredged sediment disposal site was created in Deûlémont (Northern France, 50°43′ N, 2°57′ E). In 1998, the regional division of Voies Navigables de France (VNF) in cooperation with the Association pour le Développement des Cultures Energétiques en Nord-Pas de Calais (ADCE) decided to test, on this disposal site, a management strategy based on phytoextraction and bioenergy production. A short rotation coppice (SRC) of three willow clones (*Salix viminalis* 'Tora', *S. viminalis* 'Jorr' and *Salix schwerinii* × *S. viminalis* 'Björn') was set up on 4.5 ha of this disposal site. Clones were selected for high biomass production and disease resistance, in particular against rust (*Melampsora sp.*). The planting density on 4.5 ha was 17,800 cuttings per hectare of which 14,000 'Tora', 31,320 'Jorr' and 34,710 'Björn'. Fig. 1 shows the planting design of SRC. It consisted of twin rows (0.75 m inter row distance) with a distance of 1.50 m between twin rows. Each clone was separated from 16 m. Biomass production was estimated four years after the plantation at 16.8 Mg ha^{-1} y^{-1} for wood and 1.7 Mg ha^{-1} y^{-1} for leaves [17]. After the plantation was ground in autumn 2006, the crushed wood was incorporated into the

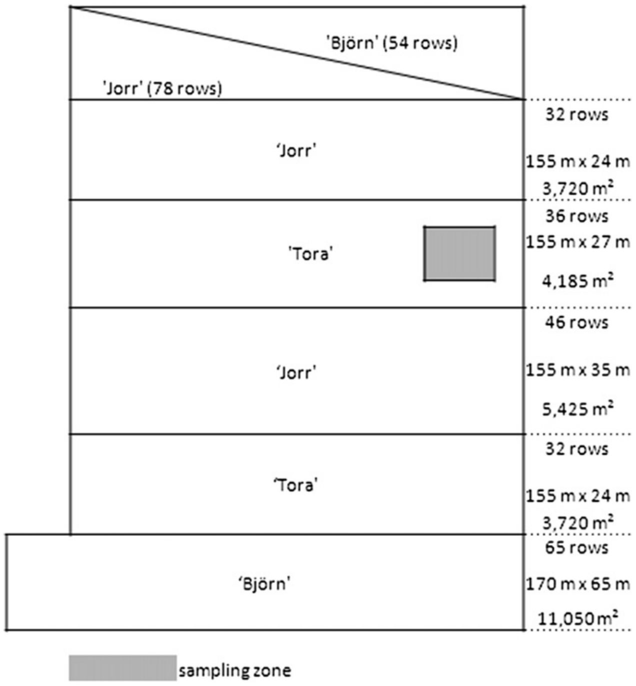

Fig. 1 – Planting design of the field trial with blocks and willow clones ('Tora', 'Jorr' and 'Björn') used for phytoextraction. For each block, the number of rows, length × width (m^2) and surface (m^2) are presented.

top sediment and willows regrew from spring 2007. In this work, the field study was performed on a part of the SRC (see "sampling zone" in Fig. 1) where the only clone present was 'Tora'.

The sediment was composed by sand (5.8%), clay (32.2%) and silt (62%). The pH_{water} was 7.89. Concentrations of organic carbon and nitrogen were 22.8 g kg^{-1} and 1.99 g kg^{-1}, respectively ($C/N = 11.46$).

2.2. *Plant and sediment sampling*

In April 2010, five samples of four years old above ground parts of 'Tora' (wood and foliage) and five samples of top sediments (0–20 cm depth), taken up at the foot of the sampled willows, were collected (Fig. 1, sampling zone, 50°43′46.209″ N, 2°57′2.265″ E). 'Tora' samples were collected above sediment samples to allow TE bioconcentration factor calculation. Top sediments were collected with a hand auger whereas wood samples were harvested with clippers. Sediments and 'Tora' samples were transported to the laboratory where they were stored at 4 °C until preparation and analysis. In addition, on 225 m^2 of the same SRC area (Fig. 1, sampling zone), above ground parts of 'Tora' (wood and foliage), were harvested with clippers, made up in bundles and transported to INERIS facilities where they were stored in an open shed until preparation for combustion experiment.

2.3. *Sediment analysis*

Pseudototal metal(loid) and extractable concentrations in sediment samples were determined. The five top sediment samples were dried at 40 °C in a forced air oven to a constant weight, ground with a grinder (agate mortar, Retsch RM100) and sieved to <200 μm (Retsch AS 200 digit). Pseudototal trace element concentrations (As, Cd, Pb, Zn, Cu) were measured using ICP-OES (Ultima 2, Jobin Yvon Horiba) following an *aqua regia* digestion according to the EN 13346 standard. To assess the analytical quality, a standard reference sediment material (Buffalo River Sediment, Standard Reference Material 2704) was subject to the same protocol. Recoveries were: 1 for Cd, 1.01 for Zn, 1.04 for Pb, 0.9 for Cu and 0.94 for As. Mercury concentrations in sediment samples were also measured using a mercury analyzer (AMA 254, LECO).

Extractable fraction of trace elements (As, Cd, Pb, Zn, Cu) was assessed with a $Ca(NO_3)_2$ (0.01 kg mol^{-1}) extraction procedure. Calcium nitrate extraction procedure was often suggested as the best predictor of trace element concentrations that is available for plant uptake [18,19]. Sixty grams of dried sediment were shaken (Heidolph Reax 2) with 120 mL of $Ca(NO_3)_2$ (0.01 kg mol^{-1}) for 48 h. Resulting sediment pastes were filtered on filtration units at 0.45 μm (MILLIPORE). Eluates were acidified to a pH of 2 for preservation and were analyzed by ICP-OES.

2.4. *Plant analysis*

TE concentrations in 'Tora' leaves and wood harvested on the sampling zone (Fig. 1) were determined. The five samples of above ground parts of willows were dried at 40 °C in a forced air oven to a constant weight. Leaves were separated from the stems. Stems with barks were ground and digested (microwave Mars Xpress, CEM) using *aqua regia*. Leaves were ground and digested in an HNO_3 solution (65%). Extracts were filtered using 0.45 μm Whatman filter paper and analyzed using ICP-OES for trace elements. Two 'BCR-679' standard references of plant material (white cabbage; community bureau of reference) were included for analytical quality control. Recoveries were, for example, 1.2 for Cd and 1.1 for Zn. Mercury concentrations in above ground parts of plants were measured using a mercury analyzer (AMA 254, LECO).

2.5. *Combustion experiments*

Combustion assays were performed with two different 'Tora' samples. One was harvested on Deûlémont's sediment disposal (named "phytoextraction") whereas the second was bought at a wood producer (Salix society, Thugny-Trugny, France) (*S. viminalis* 'Tora' named "control"). *S. viminalis* 'Tora' was cultivated on an uncontaminated agricultural soil for commercial purpose and chosen as a "control" because it was the clone harvested in the SRC for the combustion experiment. It was 4 years old at harvest. Wood samples were dried at 40 °C in a forced air oven until a moisture content of 15%, ground and riddled (35 mm). In June 2010, combustion assays were carried out with a biomass boiler of 40 kW (HKRST/V-FSK type, REKA), built to the EN 303-5, which allowed the extrapolation of the results to industrial and collective boilers. The boiler used for these experiments had an efficiency of 88% and belongs to class 3, the most efficient class. The boiler was cleaned before combustion. Sixty-three kilograms of "control" and 54 kg of "phytoextraction" were burnt using the same boiler program.

Woody stems were sampled before combustion to assess moisture content (EN 14346 standard), lower and higher heating value (LHV and HHV, respectively; ISO 1928 standard) and elemental analysis (C, H, O, N, S, Cl) and analyzed for trace element concentrations as described for stems (see Section 2.4). After each test, the bottom ash was collected, weighed and representative samples were ground (agate mortar, RM100, Retsch) and sieved at 200 μm (AS 200 digit, Retsch) for analysis by ICP-OES. Elemental (C, H, O, N, S, Cl) and moisture content (EN 14346 standard) analyses were performed on these samples.

In the absence of Emission Limit Values (ELVs) for metals in the French regulations for small combustion plants, such as the one used in this study, we referred to the French regulation concerning large combustion plants (thermal power > 20 MW) [20]. The following trace elements were analyzed in flue gas: As, Ba, Cd, Cr, Cu, Mn, Mo, Pb, Se, Sn, Te, Tl, Zn, Co, Ni, Hg, Sb and V. Flue gas comprises particulate (flyash) and gaseous fractions. Particulate matter and trace elements were measured according to EN 13284 and EN 14385 standards. Trace elements in the gaseous fraction (2 L min^{-1} flow rate) were trapped into adsorption solutions (HNO_3/H_2O_2) and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (Elan 6 100, Perkin Elmer Sciex). To assess the analytical quality, a standard reference water material (Standard Reference Material 1643e) was subject to the same protocol. Recoveries were between 0.8 and 1.08. On the gaseous fraction, common pollutants (SO_2, NO_x, CO) were continuously analyzed using Fourier transfer infrared spectrometry (FTIR) (DX4000, GASMET). In addition, analyses for dioxins, furans, PCBs and PAHs were performed on the gaseous and particulate fraction of the "control" to complete the set of pollutants which could affect air quality. Mercury and HCl were compared to the EN 13211 and EN 1911 standards. Flue gas was passed through a $K_2Cr_2O_7$ (5%)/HNO_3 (20%) solution for Hg analysis and H_2O without chloride solution for HCl analysis. Adsorption solutions for Hg were analyzed by the Flow Injection Mercury System (FIMs 100, Perkin Elmer). Adsorption solutions for HCl were analyzed by ionic chromatography (DX600, DIONEX).

3. Results and discussion

3.1. *Trace elements in sediments*

Table 1 shows the pseudototal concentrations in sediments. Only Cd exceeded the French guideline value for dredged sediments management (>2 mg kg^{-1} DW; [21]). Mercury was below the quantification limit (Hg $\leq$ 20 ng kg^{-1}). Based on coefficients of variation, there were large variations in the pseudototal concentrations (60% for As, Cu, Pb and Zn; 25% for Cd) showing the heterogeneity of the trace element pollution.

Table 1 also presents the 0.01 kg mol^{-1} $Ca(NO_3)_2$ extractable trace element concentration in sediments. The $Ca(NO_3)_2$ extractable fraction represented just 0.02% for Pb and 0.03% for Zn of pseudototal Pb and Zn concentrations in the sediment, respectively. For As, Cu and Cd, the extractable fraction represented 0.18%, 0.15% and 0.83% respectively. These results indicate that a greater fraction of the total Cd was available than other metals for plant uptake.

3.2. *Trace element concentrations in* Salix *'Tora' and phytoextraction efficiency*

Table 1 presents trace element (As, Cd, Cu, Pb, Zn) concentrations in leaves and stems of *Salix* 'Tora' harvested in the sampling zone (Fig. 1) of the sediment landfill site. As expected [22,23], the higher Zn and Cd concentrations were found in leaves than in stems of *Salix*. Zinc and Cd concentrations in above ground parts of willows were highly variable. Coefficients of variation for stems were 57% for Cd and 33% for Zn and for leaves they were 40% for Cd and 27% for Zn. Arsenic and Pb contents were below quantification limits of ICP-OES (2 mg kg^{-1}), indicating that these two elements are not transferred to the above ground parts of willows. The same result was obtained for Hg. To assess phytoextraction efficiency, the bioconcentration factors (BCFs), defined here as the plant/soil metal concentration quotient, were calculated (Table 1). BCFs for Cd and Zn were greater than 1. For Cd, BCFs were 3 and 5 in stems and leaves, respectively. These results indicate that *Salix* 'Tora' is an efficient phytoextractor tree for Cd, and to a lesser extent for Zn, on the metal contaminated sediment landfill site of Deûlémont. For comparison, *Alnus glutinosa*, which is able to grow on this polluted site, has a low BCF (0.01) and is therefore unsuitable for Cd phytoextraction [24]. These results confirm the choice for *Salix* 'Tora' to reduce the pseudototal concentration of Cd, Cd being the only TE that may pose environmental problem as shown by the French guideline value for dredged sediment management [21]. Vervaeke et al. [22] reported BCF values for *S. viminalis* L. 'Orm' planted on a metal contaminated dredged sediment landfill site. Cadmium was the only metal that showed BCFs >1 in leaves (1.4) and wood (1.2). These values would have been higher if the willow clone had been selected for metal uptake, which was not the purpose of their study [22]. In another study on *Salix triandra*, Vervaeke et al. [25] found comparable BCFs as ours (3.5 and 4.8 for wood and leaves, respectively). The results obtained for Cu confirmed that *Salix* 'Tora' is not efficient for the extraction of this element.

Like any remediation technique, the effectiveness of phytoextraction is assessed by comparing the residual trace element concentration in the soil to the environmental requirements [26]. Extraction calculations were based on the yield obtained at the end of the first rotation cycle (3 years). The result was then expressed per year according to Robinson et al. [27] from Cd concentrations in stems, in leaves, and in stems and leaves, and according to various scenarios (Table 2). Yield values used for calculations were 5.6 Mg ha^{-1} y^{-1} and 1.7 Mg ha^{-1} y^{-1} for stems and leaves, respectively [17]. In these calculations, we considered that willow stems and leaves are harvested every year, even if it is not realistic. These calculations permitted to compare with literature [6,23]. Supposing a linear decrease of trace element contents should be possible,

Table 1 – Metal concentrations (mg kg^{-1} DW) in the sediment, stems and leaves of *Salix viminalis* 'Tora'.

Element	Sediment concentrations (mg kg^{-1} DW)		Willow stems concentrations (mg kg^{-1} DW)	BCF stems	Willow leaves concentrations (mg kg^{-1} DW)	BCF leaves
	(Pseudo) total fraction	Ca $(NO_3)_2$ extractable fraction				
As	22 ± 14	0.04 ± 0.01	<QL		<QL	
Cd	2.4 ± 0.6	0.02 ± 0.00	7.3 ± 4.2	3.0	11.8 ± 4.7	5.0
Cu	33 ± 19	0.05 ± 0.02	3.0 ± 0.1	0.1	10.1 ± 1.4	0.3
Pb	88 ± 59	0.02 ± 0.00	<QL		<QL	
Zn	228 ± 140	0.07 ± 0.04	285 ± 95	1.3	412 ± 113	1.8

<QL: below quantification limit. All data were presented as mean of five replicates (*n* = 5) ± standard deviation. BCF were calculated with average value.

Table 2 – Calculated Cd phytoextraction potential of *Salix viminalis* 'Tora'.

	Cd (mg kg^{-1} DW)	BCF	Biomass yield (Mg ha^{-1})	Cd removal (kg ha^{-1} year^{-1})	Cleanup time (year)	Cd removal per harvest (kg ha^{-1})	Number of harvest	Number of SRC
Scenario 1 (2.39 mg kg^{-1} DW to 2 mg kg^{-1} DW)								
Willow stems	7.3	3.1	16.8	0.04	62	0.12	21	3
Willow leaves	11.8	4.9	1.7	0.02		0.02		
Willow stems + leaves				0.06	41	0.14	18	2
Scenario 2 (2.39 mg kg^{-1} DW to 2 mg kg^{-1} DW)								
Willow stems	13.9	4.4	16.8	0.07	33	0.23	11	2
Willow leaves	33.1	10.5	1.7	0.05		0.05		
Willow stems + leaves				0.13	19	0.29	9	2
Scenario 3 (3.16 mg kg^{-1} DW to 2 mg kg^{-1} DW)								
Willow stems	13.9	4.4	16.8	0.07	97	0.23	32	4
Willow leaves	33.1	10.5	1.7	0.05		0.06		
Willow stems + leaves				0.13	56	0.29	26	4

Data are Cd concentrations in aerial parts (mg kg^{-1} DW), bioconcentration factor (BCF; calculated as wood metal concentration over sediment metal concentration), biomass production (Mg ha^{-1}), Cd removal per year (kg ha^{-1} year^{-1}) and per harvest (kg ha^{-1}) and predicted cleanup time supposing a linear extraction expressed as years, harvest number and SRC cycles needed to reduce the sediment Cd concentration to the guideline value (2 mg kg^{-1} DW). This calculation is based on 50 cm soil depth with a sediment density of 1.3. One short rotation coppice cycle represents 8 harvests on 24 years duration.

Scenario 1: average Cd concentrations for sediment and aerial parts of plants (stems, leaves, stems and leaves).

Scenario 2: average Cd concentrations for sediment and maximum Cd concentrations in aerial parts of plants (stems, leaves, stems and leaves).

Scenario 3: maximum Cd concentrations for both sediment and aerial parts of plants (stems, leaves, stems and leaves).

time needed to reduce Cd concentration in the upper 50 cm from 2.39 mg kg^{-1} DW to 2 mg kg^{-1} DW sediment with a density of 1.3 (French regulation that fixed guideline values for sediments management, [21]) will be at least 41 years if stems and leaves are removed from the site. The duration of phytoextraction increases to 62 years when just stems are removed (scenario 1). Due to high variability found for sediment and biomass, Cd concentrations and extraction calculations were also performed with maximum concentrations both for sediment and biomass (scenarios 2 and 3). When maximum Cd concentrations of stems and leaves were used for the calculation, the time needed to reduce the Cd concentration in the upper 50 cm soil from 2.39 mg kg^{-1} DW to 2 mg kg^{-1} DW will be 19 years if both stems and leaves are removed or 33 years if just the stems are removed. When the calculation was carried out with maximal concentration values in the sediment (3.16 mg kg^{-1} DW instead of 2.39 mg kg^{-1} DW) and the biomass, duration increased to 56 years for leaf and stem removal and 97 years for stem removal (scenario 3). These results confirm that the best phytoextraction efficiency is obtained when stems and leaves are harvested together. This result was in accordance with those reported in the literature [23,28]. Mertens et al. [28] reported that willows (*S. triandra* and *Salix fragilis*) would reach the Cd Flemish threshold for reuse of the sediments as soil in nearly 50 years. In the study of Vangronsveld et al. [23], Cd concentrations were higher in leaves (60 mg kg^{-1} DW) than in twigs (24 mg kg^{-1} DW). The time needed to reduce Cd in the upper 50 cm soil from 5 mg kg^{-1} DW to 2 mg kg^{-1} DW ranged from 67 years when both stems and leaves were removed and 117 years when just stems were removed. However, the Cd phytoextraction reported in that study was more efficient due to higher biomass production (8 Mg ha^{-1} y^{-1} for wood and 2.4 Mg ha^{-1} y^{-1} for leaves) and highest Cd concentrations in leaves and stems [23]. Mertens et al. [28] pointed out the seasonal changes of trace element accumulation in willows and the decrease with the age stand of willow. In their study, Cd and Zn concentrations in stems and leaves increased toward the end of the growing season which indicates that the harvest should be performed at the end of the growing season and before leaves fall to remove the highest amount of trace elements [28]. This option would have the advantage of minimizing the metal impact on food chain and ecosystem. As the harvest of willows before leaves fall is not a usual practice in SRC, it should be investigated whether this option is feasible.

Because the sediment landfill site was only slightly contaminated with Cd, the time required to decontaminate sediment to standard was not excessive (19 years) and might not be a constraint for applying phytoextraction.

The decontamination efficiency was also calculated from extractable Cd in sediment as discussed in Ref. [23]. In this case, time needed to extract the total Cd extractable fraction ranged from 1 to 2 years depending on the above ground part of harvested willow. This calculation does not assume that there is a replenishment of soil solution Cd from the bulk Cd. This result shows that it may be relevant to focus on the "bioavailable metal" contamination in soil rather than total metal contamination that is plant available [23,29]. However, this is not possible yet, as current regulation in Europe is based on total metal concentrations, rather than the bioavailable fraction.

To provide a more realistic scenario of SRC, we recalculated the potential of Cd phytoextraction of *Salix* 'Tora' by taking into account the number of possible harvests in a rotation and considered that stems and leaves are harvested only every three years. The results are presented in Table 2. To decrease the Cd concentration in the sediment from 2.39 mg kg^{-1} to 2 mg kg^{-1}, 9 harvests of stems and leaves are necessary, which represents 1 SRC if 9 cycles of 3 years are possible. The number of harvests increased to 11 if only stems are collected. To decrease the Cd concentration in the sediment from 3.16 mg kg^{-1} to 2 mg kg^{-1}, 32 harvests of stems are necessary, which represents 4 SRCs (8 cycles of 3 years). These results indicate that the time scale for Cd phytoextraction will be acceptable only if biomass production becomes an objective of the plantation. As suggested by Voets et al. [7], Wenzel [29], Thewys et al. [30] and Witters et al. [31], one option for the wood produced on the contaminated sediment landfill site is its sale to an energy producer. The sustainability of this approach was assessed in Belgium [30,31]. Based on a multicriteria decision analysis, they concluded that although SRC of willow has a high potential as an energy and remediating crop, SRC plantations are unlikely to be implemented without subsidies for the SRC growers. The economics of phytoextraction combined with bioenergy production (gasification and pyrolysis) based on SRC plantation is under investigation [7,30].

3.3. *Combustion experiments*

In this work, combustion was tested as a possible conversion route for *Salix* ‘Tora’ harvested biomass, which was used to extract Cd from the contaminated sediment landfill site of Deûlemont. The combustion experiments had two objectives. The first was to understand the behavior of the trace elements during the combustion of metal enriched biomass. This knowledge is necessary to assess potential environmental impacts of end products on combustion process. The second objective was to compare results of combustion tests performed with a metal enriched *Salix* wood ‘Tora’ (“phytoextraction”) and a ‘Tora’ (“control”) cultivated on an uncontaminated soil usable as a commercial fuel (in our case: natural biomass chemically untreated, according to the French regulation definition), according to the French regulation on combustion plants which may consider biomass produced during phytoextraction comparable if similar characteristics were obtained during combustion. No regulatory threshold was used to make this comparison. Only departments of the French Ministry of the environment can judge whether the results of combustion experiments are similar.

3.3.1. *Operational parameters during combustion*

All results are expressed in standardized conditions, i.e. 273.15 K and 1013 hPa. The CO emissions of “control” (1050 mg m^{-3}) were higher than those for the “phytoextraction” (800 mg m^{-3}), which may indicate that the “phytoextraction” woodchips were burnt in better conditions than the “control”. The NO_x emissions were 345 mg m^{-3} for “control” and 480 mg m^{-3} for “phytoextraction” which corroborates CO emission results. The SO_2 emissions were low for both experiments (“control”: 5 mg m^{-3}; “phytoextraction”:13 mg m^{-3}). Particulate emissions for “phytoextraction” (300 mg m^{-3}) were higher than for “control” (200 mg m^{-3}) due to excessive primary air supply in the boiler.

3.3.2. *Trace element concentrations and properties of processed “phytoextraction” and “control” woods*

As expected, the Cd and Zn concentrations in the “phytoextraction” stems were higher than those in the “control” stems (Table 3). Copper, Co, Se and Mn concentrations were also higher in “phytoextraction” stems than in “control” stems (Table 3). For the others trace elements (As, Cr, Ni, Pb, Sn, Tl, V and Mo), concentrations were below quantification limits of ICP-OES (2 mg kg^{-1} for As, Ni, Pb and V; 1 mg kg^{-1} for Cr; 4 mg kg^{-1} for Sn, Tl and Mo). Concentrations of trace elements in shoot tissues of *S. viminalis* grown on uncontaminated soil have been reported [32–35]. According to these studies, Cd and Zn concentrations in stems of *S. viminalis* clones ranged from 0.2 mg kg^{-1} DW to 1.4 mg kg^{-1} DW and 96.7 mg kg^{-1} DW to 200 mg kg^{-1} DW, respectively. Compared to these data, the Cd and Zn concentrations in the “control” (*S. viminalis* ‘Tora’) were similar to willows grown on uncontaminated soil.

Lower heating values (LHV) were similar for both types of wood (17 MJ kg^{-1} and 17.1 MJ kg^{-1}, for “control” and “phytoextraction”, respectively). Results of elemental analysis were similar for both types of wood (data not shown) and to those of several studies on willow [11,13]. The chloride concentration was below detection limits in both woods (<0.1 mg kg^{-1}).

3.3.3. *Trace elements in bottom ash and flue gas*

3.3.3.1. *Cadmium and zinc.* Cd concentrations in the gaseous fractions of the flue gas were below quantification limits of ICP-MS or low in the case of Zn (Table 4). In the flue gas, most Zn and Cd were found in the particulate fraction (flyash) (Table 4). For both combustion experiments, the temperature inside the boiler was around 900 °C–1000 °C. Consequently, the boiling points of Zn (907 °C) and Cd (767 °C) were reached, leading to the volatilization of Zn and Cd. Volatilized Cd and Zn may condense mainly on small particles which may explain that the major part of Cd and Zn were found in the particulate fraction of flue gas.

Zinc and Cd concentrations were 8 times greater in the “phytoextraction” particulate fraction than in “control” particulate fraction (Table 4). French regulation does not state metal input values in fuels. Rather, metal emissions of the fuel to be tested must be comparable to those of a commercial fuel.

Table 3 – Trace element concentrations of processed willow stems (“control” and “phytoextraction”).

mg kg^{-1} DW	Cd	Zn	Cu	Co	Se	Mn
“Control”	1.4	38.0	1.1	0.4	0.6	2.2
“Phytoextraction”	7.3 ± 4.2	285 ± 94	3.0 ± 1.3	0.7 ± 0.1	1.2 ± 0.2	7.6 ± 2.6

All data were presented as mean of five replicates ($n = 5$) ± standard deviation except for control stem concentrations where $n = 1$.

Table 4 – Cd and Zn concentrations in bottom ash and flue gas (particle and gaseous fractions).

	Cd			Zn		
	Bottom ash (mg kg^{-1} DW)	Flue gas (mg m^{-3})		Bottom ash (mg kg^{-1} DW)	Flue gas (mg m^{-3})	
		Gaseous fraction	Particle fraction		Gaseous fraction	Particle fraction
"Control"	1.7 ± 0.1	<0.0004*	0.1164	164 ± 16	0.0679	6.1
"Phytoextraction"	4.4 ± 0.1	<0.0005*	0.9541	1160 ± 22	0.0583	53.9

All data were presented as mean of five replicates ($n = 5$) ± standard deviation except for control stem concentrations where $n = 1$. * values correspond to QL.
Results in the flue gas are expressed in mg m^{-3} in standardized conditions, i.e. 273.15 K and 1013 hPa.

These results showed that the two types of wood were not comparable. According to the French regulation on combustion plants, *Salix* biomass produced during phytoextraction could not legally be used as a commercial fuel.

In contrast to Cd, Zn concentrations were higher in bottom ash than in stems (Tables 4 and 3, respectively). These results can be explained by the boiling points of Cd and Zn. Zinc and Cd concentrations in the "phytoextraction" bottom ash were higher than those in "control" bottom ash (Table 4) which can be explained by the initial Zn and Cd concentrations, highest in "phytoextraction" willow stems (Table 3).

Cadmium and Zn mass balance for the combustion process confirms that most Cd and Zn were found in flue gas (Table 5). For "control", 1.4% of Cd and 3.9% of Zn of the initial willow stems content were concentrated in bottom ash (Table 5). For "phytoextraction", bottom ash concentrated 0.8% of Cd and 5.3% of Zn of the initial willow stems content (Table 5). Seventy-one percent for "control" and 86% for "phytoextraction" of the initial Cd willow stems content were found in the flue gas. Zinc concentration in gases exceeded 100% for "phytoextraction" and "control". An overestimation of this element in the particulate fraction may partially explain this result. The error on the mass balance must be attributed to uncertainties during the recoveries of the ash from the installation and the measurement of the different fractions. Depending on the process chosen for metal enriched wood (combustion, pyrolysis, gasification) and the conditions associated to these processes (reducing or oxidizing environment, temperature), a different distribution of metals in the different fractions resulted in differences in the process products. For example, after pyrolysis of poplar and willow stems at low temperature (450 °C) a char/ash residue enriched with Cd and Zn was produced [13] whereas after gasification of willow wood, flyash was enriched in Cd and Zn [10]. Bert et al. [36] performed an incineration test with *Arabidopsis halleri*, a Cd and Zn hyperaccumulator, and found that Cd occurred in the flue gas whereas Zn was concentrated in the residue. This result was explained by the temperature used for the incineration test (800 °C) and the different boiling points of trace elements. After a combustion experiment performed in a glass tube reactor at about 850 °C on *Salix* leaves, an enrichment of Zn in bottom ashes compared to initial *Salix* leaves concentration was observed whereas Cd was volatilized [9]. Syc et al. [15] performed a fluidized bed combustion test in a reactor on *S. caprea* enriched with Cd and Zn and studied metal distribution between bed ash, cyclone ash and flyash. After a test at 850 °C, more than 90% of Zn was retained on ashes (bottom ash and bed material) whereas less than 50% of Cd was retained on cyclone ash and flyash. The rest of Cd left the system volatilized. Similar results were obtained for forest residues (mostly pines) processed in a full-scale circulating fluidized bed boiler [37]. At 830 °C, Cd was nearly absent in the bottom ash (<1%) whereas Zn was enriched in the bottom ash (65 %–68 %). In flue gas, Cd was found in the gaseous fraction in small amounts (1 %–8 %) whereas Zn was nearly nonexistent. Cd and Zn were found predominantly in particles, and particularly in coarse flyash particles (>0.5 μm).

In absence of metal Emission Limit Values (ELVs) for boiler <2 MW, trace elements in flue gas (gaseous and particle fractions) trapped at the chimney of the combustion plant were compared with French ELV for more than 20 MW combustion plants [20]. Cadmium concentrations in the flue

Table 5 – Concentrations and mass fractions of Cd and Zn in bottom ash and flue gas of "control" and "phytoextraction".

		"Control"		"Phytoextraction"	
		Concentration (mg kg^{-1} DW)	%	Concentration (mg kg^{-1} DW)	%
Cd	Stems	1.4	100	7.3 ± 4.2	100
	Bottom ash	0.02	1.4	0.06	0.8
	Flue gas	1	71	6.3	86
Zn	Stems	38	100	285 ± 94	100
	Bottom ash	1.5	3.9	15	5.3
	Flue gas	50	131	358	126

Results for bottom ash and flue gas were expressed in emission factor (mg kg^{-1} of stems burnt).
Percentages are estimated recovered amounts relative to metal input through wood.

gas of the “control” and the “phytoextraction” exceeded Cd ELV (0.05 mg m^{-3} in standardized conditions). The result for the “control” was unexpected. The Cd concentration exceeded Cd ELV in the commercial wood even though the Cd concentrations in the stems were similar to those measured in *Salix* wood grown on uncontaminated soil (i.e. normal Cd concentration as reported in Refs. [32–35] of Section 3.3.2). This result highlights the need to burn commercial *Salix* wood in combustion plant equipped with efficient filters to trap Cd. Zinc concentration in “phytoextraction” flue gas was higher than the Zn ELV (20 mg m^{-3} in standardized conditions, expressed as (Sb + Cr + Co + Cu + Sn + Mn + Ni + V + Zn)). To respect ELV policy, large combustion plants are equipped with efficient filtration systems. If these plants should burn metal enriched biomass such as the one studied in this work, Cd and Zn in the particle fraction of the flue gas will be intercepted by these filters.

3.3.3.2. Other combustion products. “Control” and “phytoextraction” bottom ashes were enriched in Cu, Cr, Co, Ni and Mn which indicate low volatilization for these elements, consistent with their high boiling points (Table 6).

Compared to “phytoextraction” bottom ash, “control” bottom ash shows elevated Mn, Ni, Cr and Co concentrations whereas initial concentrations are lowest in “control” willow stems (Mn, Co) or below quantification limits in both willow stems (0.2 mg kg^{-1} for Ni; 0.5 mg kg^{-1} for Cr). Selenium, Mo, Sn, Te and Tl were below QL in the bottom ash of both willows (0.4 mg kg^{-1} for Se and Te; 4 mg kg^{-1} for Mo and Tl; 2.5 mg kg^{-1} for Sn).

In the gaseous fractions of the flue gas, trace elements were below QL (0.5 µg L^{-1} for As, Se, Sn, Te and V, 0.8 µg L^{-1} for Co, Mo and Tl) or low (Cr, Mn, Cu, Ba, Ni, Pb) (data not shown). Mercury concentrations were also below the quantification limit (0.5 µg L^{-1}). Arsenic, Cr, Cu, Mn, Pb and Se were mostly found in the particulate fraction (data not shown).

Mercury, Tl, As, Se and Pb concentrations in flue gas of both types of processed woods were below ELV (0.05 mg m^{-3} for Hg and Tl, 1 mg m^{-3} for As + Se, 1 mg m^{-3} for Pb in standardized conditions).

The PAH emissions in the gases of the “control” combustion were 660 µg kg^{-1} of stems burnt (DW) whereas PCB content was 25.9 pg TEQ$_{\text{OMS}}$ kg^{-1} (TEQ: Toxic Equivalent Quantity, [38]). In an industrial boiler, the average dioxin/furan emission factor for natural wood combustion is approximately 0.8 ng TEQ$_{\text{OMS}}$ kg^{-1}. Dioxin/furan emission factor for the “control” combustion was below this value (0.49 ng TEQ$_{\text{OMS}}$ kg^{-1}) and confirmed that “control” can be used as a reference. Small quantities of hydrocarbons (ethane, propane, formaldehyde, hexane…) were emitted during both combustion experiments (data not shown).

3.3.4. *Ash disposal*

The combustion of 63 kg and 54 kg of willow stems resulted in the production of 0.6 kg and 0.7 kg bottom ash, respectively (Table 5). Thus, 0.95% (“control”) and 1.29% (“phytoextraction”) of the weight of the processed wood was recovered as bottom ash. These values are in accordance with those reported in Obernberger et al. [39]. In the study of Keller et al. [9], combustion reduced *Salix* leaves to 10% of its original weight. For comparison, gasification reduced willow wood to 6% of its original weight [10]. In these studies, the material processed, the process temperature, operational conditions and equipment were different and may have affected the percentage of ash produced.

Currently, most bottom ash is reused in civil engineering, disposed in landfills or applied to soils. However, the use of ash should not result in environmental degradation, such the accumulation or leaching of metals [40,41]. Studies on utilization routes for bottom ash from biomass are limited. As wood bottom ash contains nutrients such as Ca, P, Mg and K, it could be recycled as fertilizers on agricultural soils and forests. In France, there is no policy that regulates the use of wood ash. Its use may be regulated on threshold values for trace elements in basic mineral amendments (NF U 44-001 standard) or inorganic fertilizers (NF U 42-001-1).

Thus far, there is no category in the French standard (NF U 44-001) for wood ash. Standards require that wood ash must be recognized officially as a mineral basic amendment by proving, for instance, the stability of its composition. Depending on the liming material category considered (e.g. calcic lime, manganese oxides, slag, etc.), Cd and Zn range from 1.5 mg kg^{-1} to 41 mg kg^{-1} and 18 mg kg^{-1} to 530 mg kg^{-1}, respectively. In our study, the Cd concentrations in the bottom ash of the “control” and the “phytoextraction” (Table 4) might not exceed most of these threshold values. Similarly, the Zn concentration in the bottom ash of the “control” might be also suitable (Table 4). Contrary to “control”, the Zn concentration

Table 6 – Trace element (TE) concentrations in the bottom ash following willow combustion, boiling points of TE and threshold values related to liming materials and inorganic fertilizers.

	As	Cr	Cu	Co	Pb	Ni	Mn
“Control” (mg kg^{-1} DW)	<QL	19.3 ± 0.6	176 ± 17	7.1 ± 0.3	2.4 ± 0.3	19.5 ± 1.2	1930 ± 55
“Phytoextraction” (mg kg^{-1} DW)	3.1 ± 0.4	7.3 ± 0.2	143 ± 21	4.4 ± 0.2	<QL	9.7 ± 0.5	590 ± 11
Boiling points (°C)	613	2672	2562	2870	1740	2732	1962
Range of threshold values (NFU 44-001: liming materials)[a]	2–83	12–1200	8–63	–	4–33	16–686	–
Threshold values (NFU 42-001-1: inorganic fertilizers)	60	120	–	–	150	120	–

All data were presented as mean of five replicates ($n = 5$) ± standard deviation.

[a] NFU 44-001: liming materials: range of values for different liming materials (calcic lime, manganese oxides, slag, etc.).

in the bottom ash of "phytoextraction" (Table 4) exceeded the highest Zn threshold value. For other metals (As, Cr, Cu, Pb, Ni), threshold values are not exceeded (Table 6). The bottom ash from "phytoextraction" may thus not be applied as basic mineral amendment to soils due to Zn.

For inorganic fertilizers standard, wood ash may come under the category of ash from combustion of vegetation. Zinc threshold values do not exist while Cd is set at 90 mg kg^{-1}. However, this Cd concentration is not directly comparable with Cd concentration in wood ash as in the standard Cd is expressed as Cd P_2O_5. For other metals (As, Cr, Pb, Ni), threshold values are not exceeded (Table 6).

Vervaeke et al. [10] compared the trace element concentrations in the bottom ash of *S. viminalis* after gasification to the threshold values of the Flemish legislation and found Cd and Zn above these threshold values. They concluded that theses ashes could not be used as a fertilizer. In the study of Keller et al. [9] who compared Zn, Cd and P concentrations of *Salix* leaves bottom ash to the limits set by the Swiss Ordinance on environmentally dangerous substances, it was concluded that *Salix* bottom ash could not be used as mineral fertilizer due to the high Zn concentration that limits the recycling of ash in agriculture. Similarly, bottom ash from a fluidized bed combustion test performed on Cd and Zn enriched *S. caprea* could not be applied as fertilizers due to its high metal content [15].

Even if there is more bottom ash than flyash, the possible reuse of flyash was investigated by several authors [42–44]. As they may contain trace elements, they should be carefully assessed for their risks to the environment and human health.

The goal of phytoextraction is to remove metals such as Cd from soils by transferring them to the harvestable parts of the plants. By combusting metal enriched wood, Cd and other metals may be dissipated to the environment through ash recycling. This would contradict the phytoextraction goal of removing harmful pollutants from soils. Depending on the energetic process used (e.g. combustion, pyrolysis, gasification), volatilization temperatures of metals and equipment used for filtration, a significant fraction of a metal-free ash may be obtained, either the bottom ash, the cyclone ash or the filter ash [16,38]. Ash management may have to consider just the small volume of metal rich ash, with the remainder of low-metal ash recycled as raw material for agricultural and forestry with respect to regulation [38].

4. Conclusions

The most optimistic scenario led to a reduction of the total Cd content of the sediment from 2.39 mg kg^{-1} DW to 2 mg kg^{-1} DW in 19 years. When the calculation was based on extractable Cd rather than pseudototal Cd, time needed to decontaminate the extractable Cd decreased to less than 2 years, assuming that there is no replenishment of soil solution Cd from the bulk Cd. Because the sediment landfill site was only slightly contaminated with Cd, the time required to decontaminate sediment to regulatory thresholds was not excessive and may not be a constraint in this case, especially if phytoextraction could be combined with the production of valuable biomass. In this case, 9 harvests of stems and leaves are necessary, which represents 1 SRC if 9 cycles of 3 years are possible.

In this study, we have tested combustion as a possible conversion route for the harvested *S. viminalis* 'Tora' while accumulating Cd. Combustion experiments performed on this metal enriched *Salix* and a commercial *Salix* 'Tora' used as a "control" showed that, for both types of wood, Cd and Zn occurred at a higher concentration in the particulate fraction of the flue gas (flyash) than in the bottom ash.

The Cd and Zn concentrations in flue gas of *Salix* 'Tora' from phytoextraction were higher than those of the commercial *Salix* 'Tora'. Consequently, with the combustion test mentioned in the French regulation which only consists to compare the wood tested with a commercial wood, *Salix* produced during phytoextraction could not be considered as a fuel but as a waste. The classification of the biomass from phytoextraction is important because it can affect the viability of the overall process, i.e. phytoextraction combined with bioenergy production. In any case, biomass derived from phytoextraction is insufficient as a sole source of fuel for a combustion plant. Co-combustion with coal or other fuel products could be envisaged if regulation is respected.

According to French policy concerning metal Emission Limit Values (ELV) for 20 MW combustion plants, Cd concentration in the flue gases of "phytoextraction" and "control" woods exceeded the Cd ELV, which was unexpected for the "control" wood. To avoid air pollution, combustion of *Salix* wood, irrespective of its provenance, should only occur in industrial or collective boilers equipped with efficient filters.

Our study showed that options to recycle bottom ash would be to use it as basic mineral amendments or inorganic fertilizers. The legality of the first option depends on the insertion of wood ash into French standard as a new category of basic mineral amendment.

The viability of phytoextraction based on SRC plantation combined with bioenergy production raised questions of cleanup duration, biomass yield and valorization route, pollutant impact and dispersion in the environment, sustainability, policy and economics. Most of these questions are investigated in the ongoing FP7 GREENLAND project.

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