SEVENTH FRAMEWORK PROGRAMME

Gentle remediation of trace element contaminated land
Greenland (FP7-KBBE-266124)

GREENLAND

Processing of plant biomass harvested at trace element-contaminated sites managed by gentle (phyto)remediation options

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WP2 Valorisation of plant biomass produced on TE contaminated sites

Objectives:

⇨to test the feasibility to use the various plant biomass collected from field sites of the Greenland partners, in existing and under development processes to assess advantages and limitations regarding technical aspects and regulations (pilot and lab scale assays).

⇨Interviews of companies using non-food plant biomass to identify the potential limitations (technical, economical, and regulatory) related to the admittance of plant biomass cultivated on TE contaminated lands in existing installations.

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Depending on the GRO set up on the polluted site and the type of plant used, **harvested plant parts may contain concentrations of TE** that may be higher than those found in similar vegetation grown on uncontaminated soils (phytoextraction).

⇨These plants may enter the **valuation pathways** if TE do not disturb the **functioning** and the **performance** of the process and if such plant use complies with current **regulation**.



A/ To test different various conventional and innovative technologies of biomass processing:

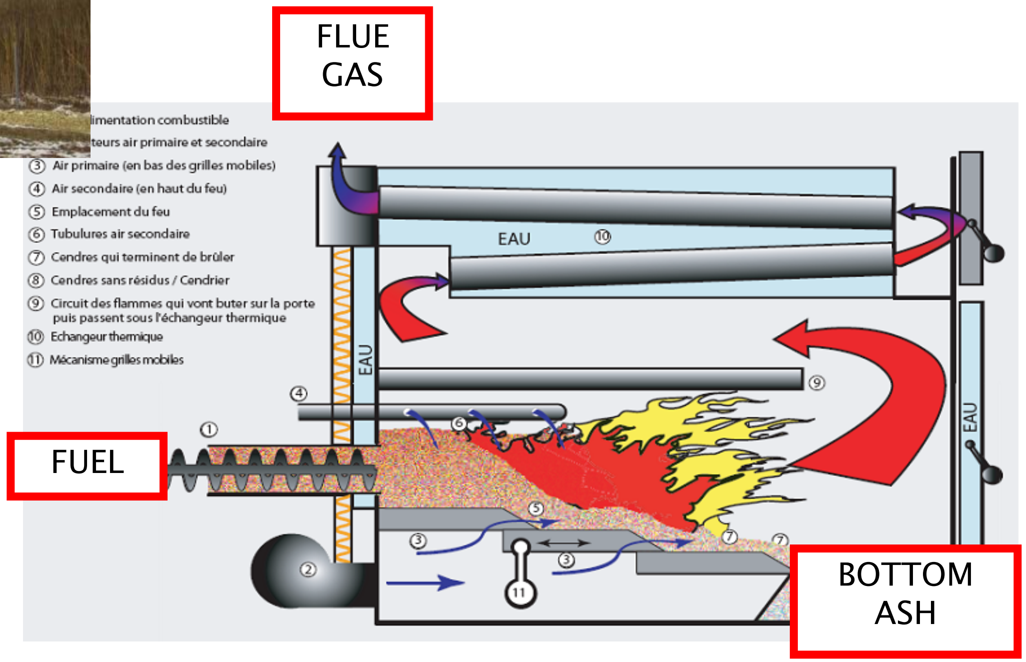
- **combustion**
- **solvolysis**
- **flash pyrolysis**

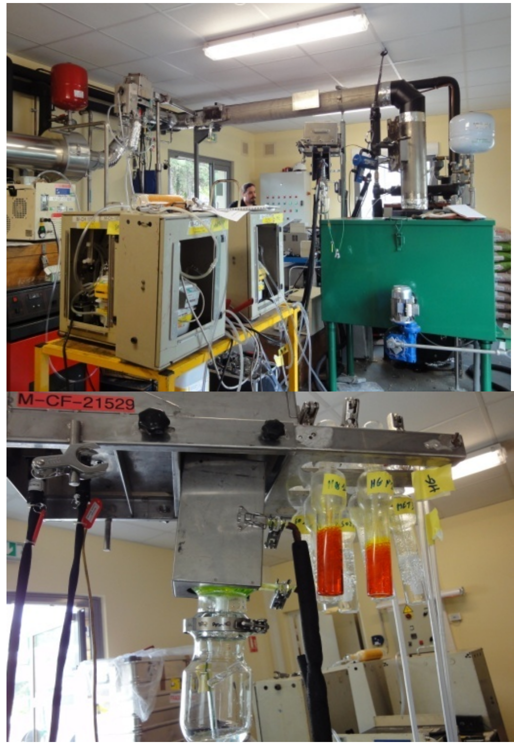
⇨To **determine the fate of the TE in the resulting products** of each conversion process.

Assays were carried out on a wide range of plant species cultivated at the field trials of the GREENLAND partners.

▶ Combustion of Cd-Zn enriched woody biomass (pilot scale – 40kW)

Thermochemical decomposition of biomass at 800-1000°C in presence of oxygen resulting in bottom ash and flue gas (fly ash and gaseous fraction).





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▶ Combustion of Cd-Zn enriched woody biomass

Table 1. Zinc and Cd concentrations in willow and poplar wood ships used in combustion assays (mean (SD)).

(mg kg^{-1} DW)	Sweden		Germany		Belgium		
	C *Salix* 'Tora'	Phytoextr.	C *Populus* 'Max3'	Phytoextr.	C *Salix alba*	C *Populus trichocarpa*	Phytoextr.
Zn	53 (8)	91 (18)	91 (2)	102 (0,8)	20 (3)	103 (7)	929 (236)
Cd	1,9 (0,2)	2 (0,4)	2,2 (0,0)	3,9 (0,1)	0,2 (0,0)	2,1 (0,1)	39 (9)

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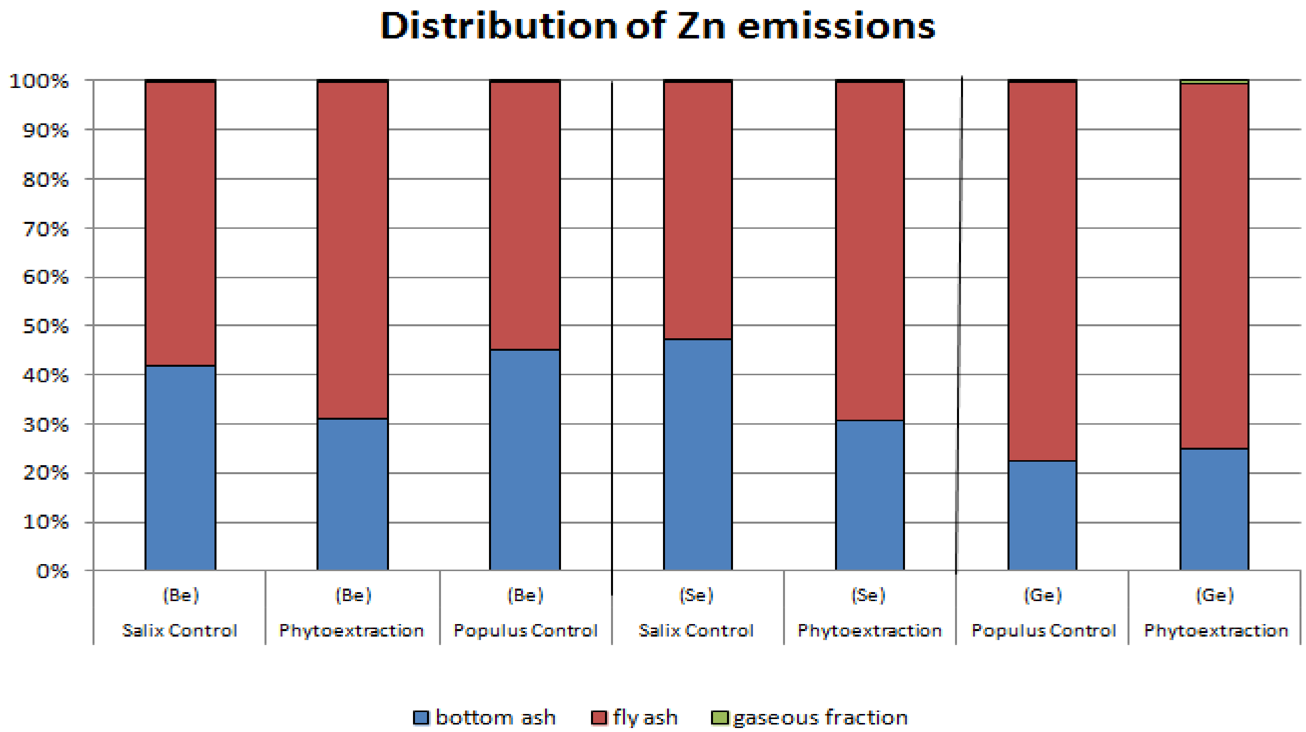
▶ Combustion of Cd-Zn enriched woody biomass



- For all assays, Zn occurred > 50% in the fly ash.
- Fly ash > bottom ash > gaseous fraction.
- The distribution is not depending on the initial burnt wood, i.e. virgin wood (control) or Zn enriched wood (phytoextraction).

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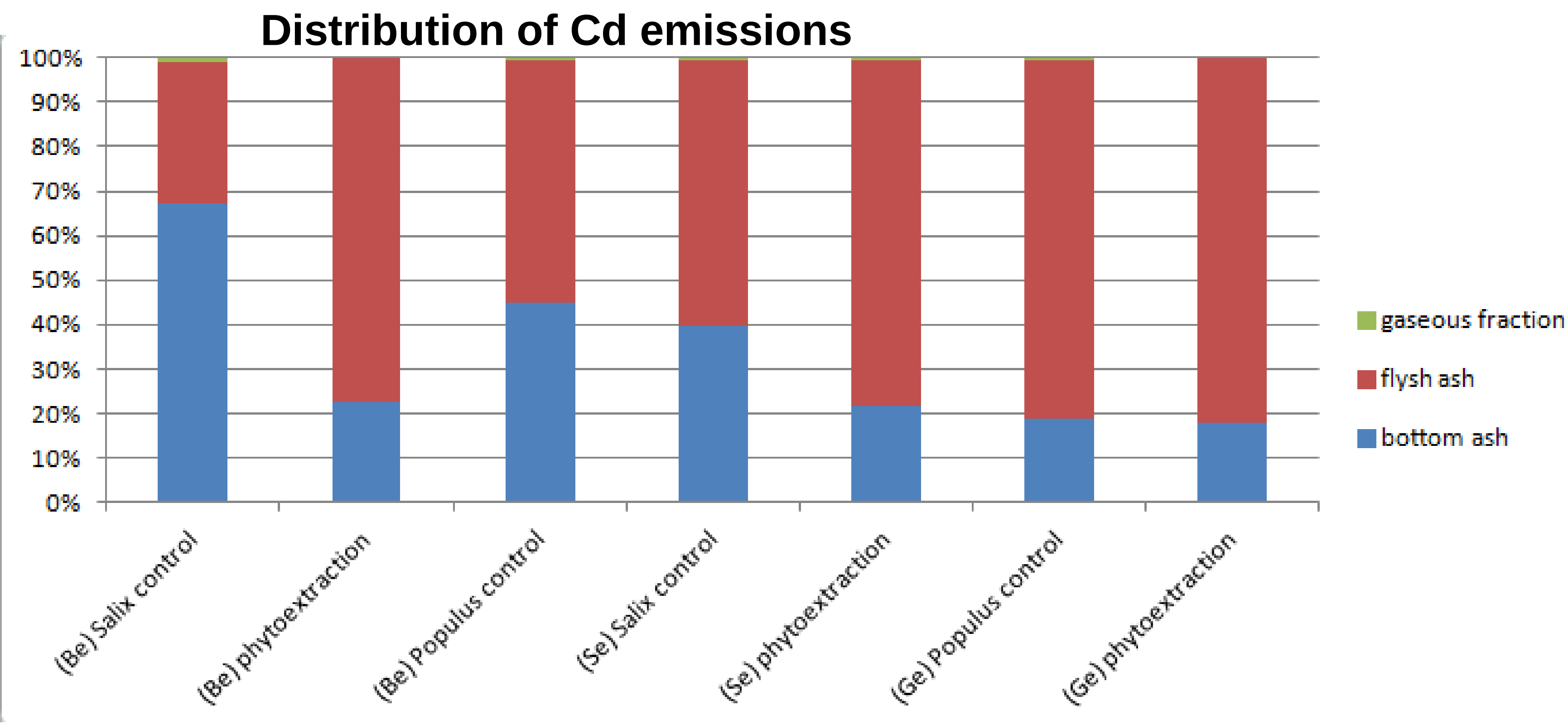
▶ Combustion of Cd-Zn enriched woody biomass



- Except in the (Be) Salix control assay, Cd occurred > 50% in the fly ash.
- Fly ash > bottom ash > gaseous fraction.
- The distribution is not depending on the initial burnt wood, i.e. virgin wood (control) or Cd enriched wood (phytoextraction).

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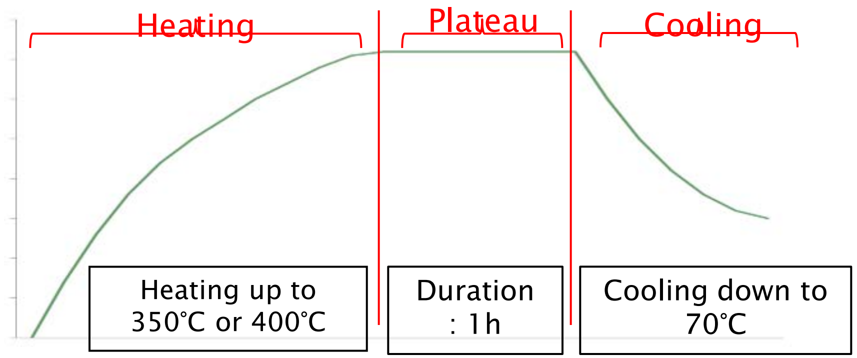
Conclusions

Combustion:

• Zn and Cd are mostly recovered in fly ash then in bottom ash.

• It might be possible to burn plant biomass enriched with metals in industrial or collective boilers as they are normally equipped with efficient filters to avoid air pollution and if bottom ash can be valuated despite TE content.

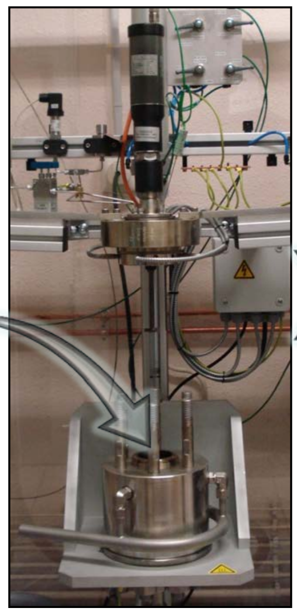
▶ Solvolysis of Cu and Zn-Cd enriched tobacco (lab scale)



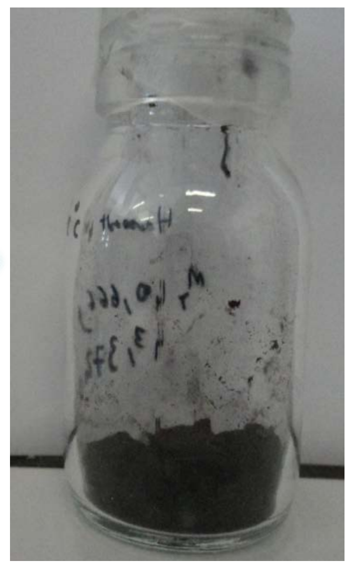
Chemical decomposition of biomass
with a solvent (water)
and under pressure
(~ 250 bars).

Biomass + water

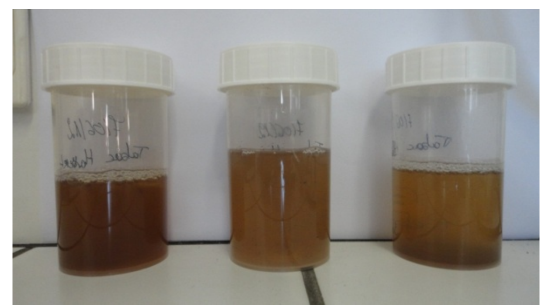
Reactor



Residual solid



Liquid phase

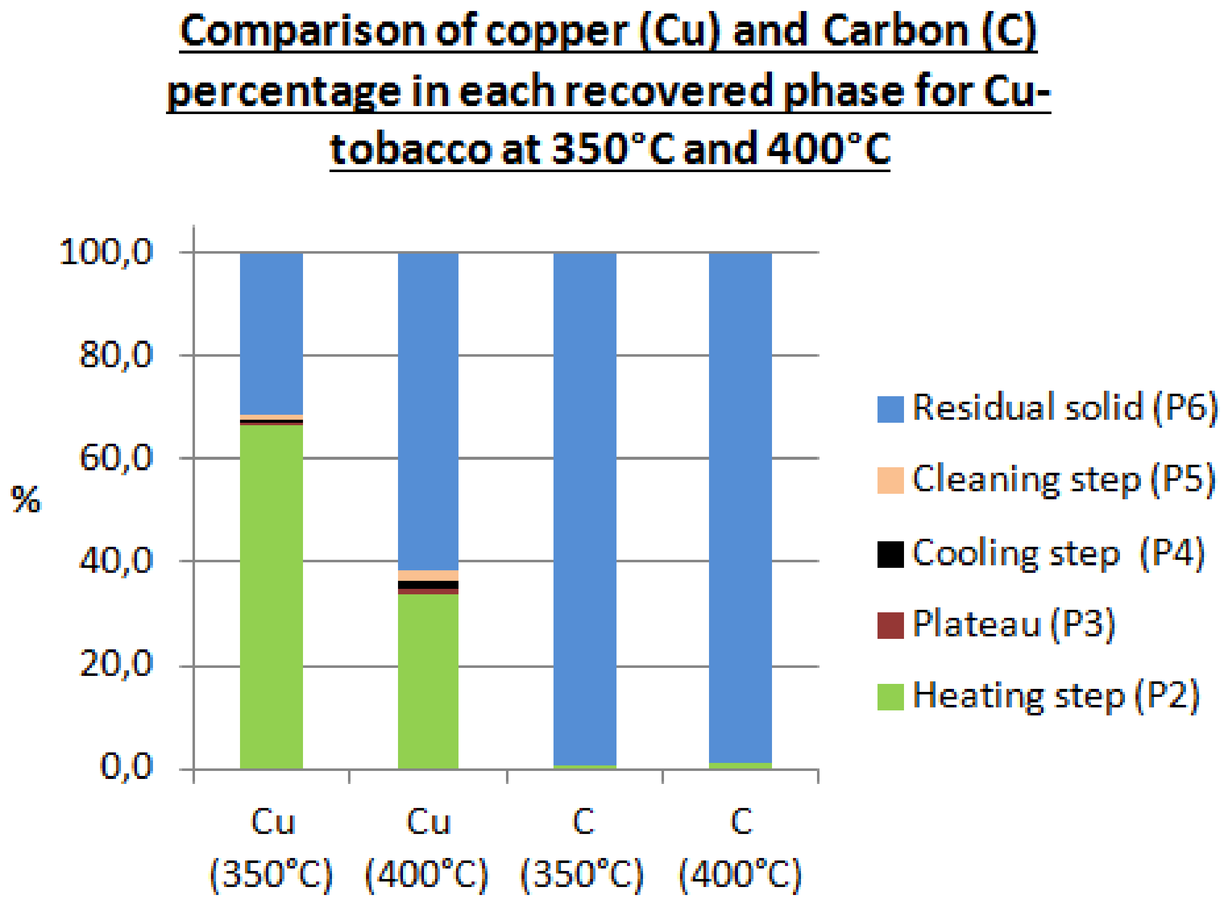


Solvolysis of Cu and Zn-Cd enriched tobacco

Table 4. Copper, Zn and Cd concentrations in Cu or Zn and Cd enriched tobaccos used in solvolysis assays. C = carbon.

$(mg.kg^{-1}$ DW)	Cu	Zn	Cd	C
Cu-Tobacco	16,162	34,343	<QL	78,45
Zn-Cd-Tobacco	14,363	847,397	8,977	72,27

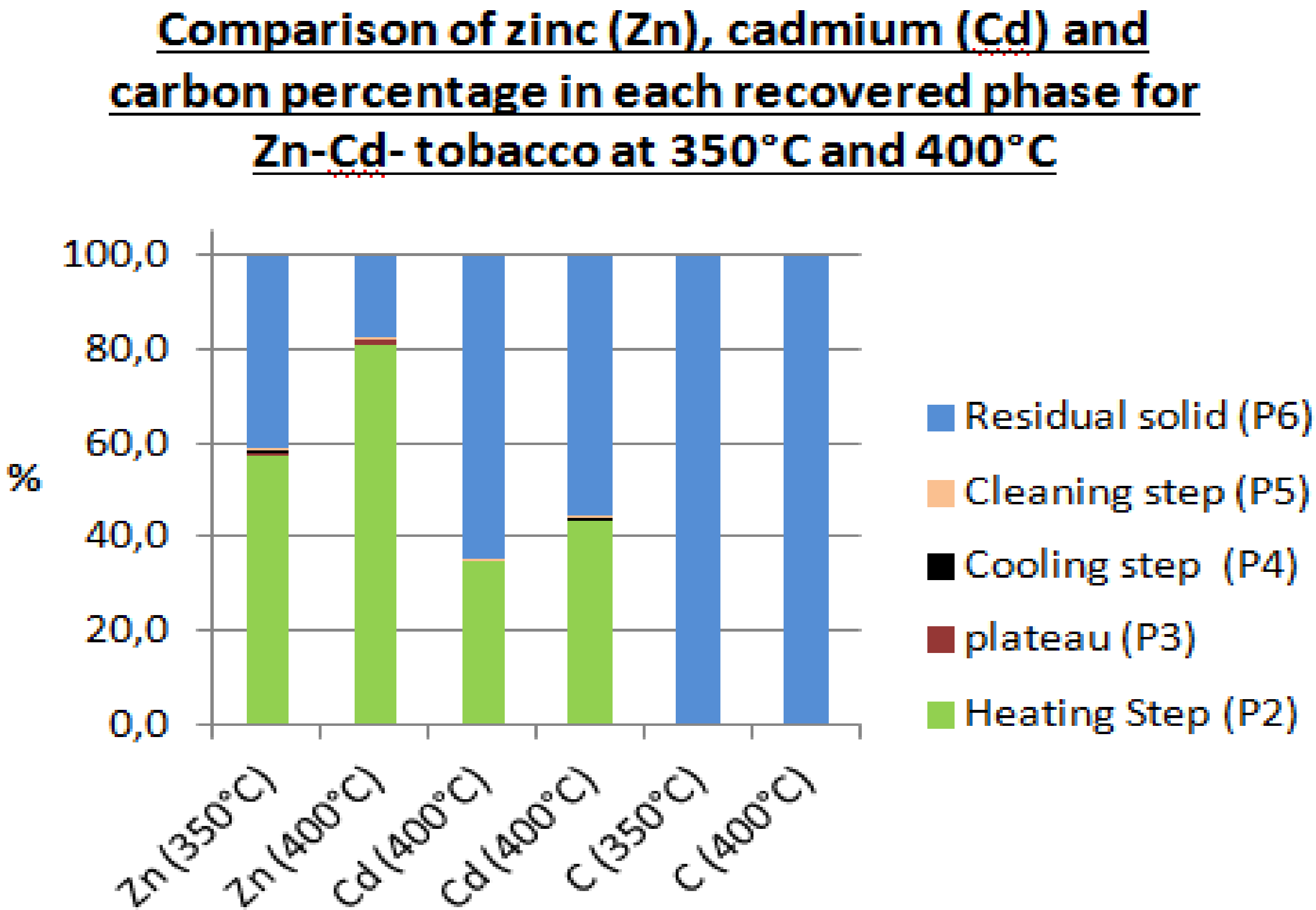
▶ Solvolysis of Cu enriched tobacco



• Cu is mainly found in the liquid phase during the heating step or in the residual solid, depending on the temperature.

• Carbon is almost exclusively found in the residual solid (> 99%).

▶ Solvolysis of Zn-Cd enriched tobacco

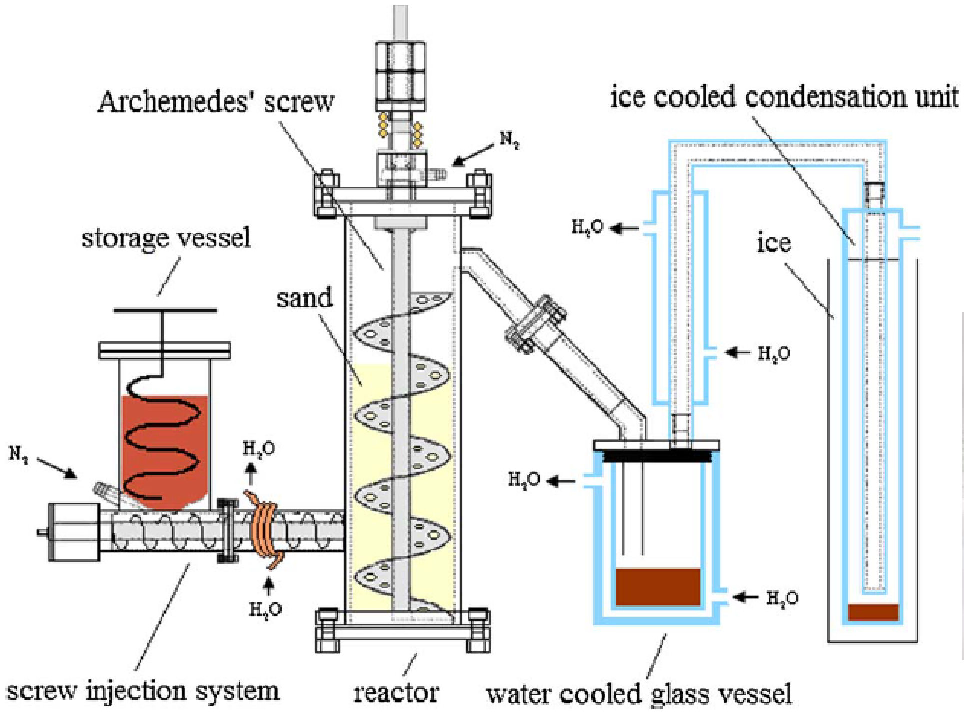


- Zn is mainly found in the liquid phase during the heating step.
- Cd is mainly found in the residual solid.

- Carbon is almost exclusively found in the residual solid (> 99%).

Flash pyrolysis Cd-Zn or Cu enriched willow, tobacco and sunflower (lab scale)

Thermochemical decomposition of biomass at 450 – 600°C in oxygen deficient conditions resulting in char, oil and gas.
Flash pyrolysis targets the pyrolysis liquid as end product.



Pyrolysis liquid
(tar and aqueous fractions)

▶ Flash pyrolysis Cd-Zn or Cu enriched willow, tobacco and sunflower (lab scale)

Table 2: Cadmium, Zn and Cu concentrations in biomass used for flash pyrolysis (mean (SD)) .

	Target TE (mg kg^{-1} DW)		
	Cd	**Zn**	**Cu**
Willow clone 1	14.2 (1.0)	508 (26)	< 10.0
Tobacco high Cd/Zn	1.5 (0.1)	390 (28)	23 (3)
Sunflower low Cd/Zn	< 1.1	112 (5)	18 (1)
Sunflower Cu	< 1.1	51 (2)	22 (1)
Tobacco Cu	< 1.1	25 (5)	36 (4)

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Flash pyrolysis Cd-Zn or Cu enriched willow, tobacco and sunflower (lab scale)

Table 3: Cadmium, Zn and Cu concentrations in pyrolysis liquid (aqueous and tar fractions) after flash pyrolysis (mean (Recovery of heavy metals in pyrolysis liquid, expressed as %wt of the heavy metals present in the original biomass)) .

	Aqueous fraction			Tar fraction		
	Target heavy metals (mg kg^{-1} DW)			Target heavy metals (mg kg^{-1} DW)		
	Cd	Zn	Cu	Cd	Zn	Cu
Willow clone 1	2.22 (7.2)	12.8 (1.2)	12.8 (-)	/	/	/
Tobacco high Cd/Zn	0.75 (12.3)	10.2 (0.7)	6.1 (6.8)	1.2 (11.6)	73.0 (2.8)	7.0 (4.6)
Sunflower low Cd/Zn	< 0.5 (-)	6.5 (1.4)	3.8 (5.1)	< 0.6 (-)	42.8 (4.9)	6.9 (5.0)
Tobacco Cu	< 0.5 (-)	4.9 (4.6)	4.5 (2.9)	< 0.7 (-)	14.3 (6.3)	25.0 (7.5)
Sunflower Cu	< 0.6 (-)	9.3 (3.1)	3.1 (2.4)	< 0.8 (-)	16.9 (3.7)	7.9 (4.0)

- For willow, the pyrolysis liquid was a dark brown single-phased liquid.

In contrast, the pyrolysis liquid of the tobacco and sunflower was two-phased (a tar and an aqueous fraction).

- Cd is the most recovered metal in the pyrolysis liquid compared to Zn and Cu and relatively to the metal concentrations in the biomass (Cd > Cu >Zn).

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Conclusions

Emerging valorisation processes (solvolysis, flash pyrolysis):

• The usage of metal-enriched plant biomass as feedstock depends on multiple factors :
→ the desired end product (e.g. liquid or solid phase),
→ the amount and quality of this end product (e.g. energy content),
→ the threshold concentrations of contaminants in this end product,
→ regulation and standards.

• **Flash pyrolysis**: 'phytoextracting' crops may be used for flash pyrolysis resulting in a liquid oil with a normal energy content, but with metals. To be used as a renewable fuel, the physicochemical properties of the liquid must be investigated as well as the potential impact and constraints associated to the presence of the metals for this usage.

• **Solvolysis**: the distribution of TE between the liquid and solid phases depends on the element and the temperature of the treatment. Work in progress addresses the question of metal distribution (liquid or solid phase? To do what?).

B/ Interviews of operators of anaerobic digestion (AD) platforms

- Selection of AD platforms that use plants in their process (digestion, structuring matter to make compost)

- Interviews of 11 operators (France: 5; Germany: 4; Austria: 2).

- Questionnaire
  - Characteristics of installation
  - Characteristics of plants used
  - Performed analyses
  - Phytotechnologies (knowledge, conditions for using plants from phytotechnologies)

Interviews of operators of anaerobic digestion (AD) platforms

	FR1	FR2	FR3	FR4	FR5	GE1	GE2	GE3	GE4	AU1	AU2
	farm	municipal utilities	municipal utilities	farm	farm	farms	municipal utilities	municipal utilities	farms	farm	farm
Type of plant used	Rye sunflower sorgho	Grass trees shrubs	Grass trees shrubs	Rye sorgho ray-grass maize naked oat	Lawn mowing woody residues	Maize silage lawn mowing cereals	Maize silage lawn mowin g	Maize silage	Maize silage grasses cereals	Clover alfafa grasses legumes law moving maize	Lawn mowing maize
Use of plants	D	Compost	D	D	D compost	D	D	D	D	D	D
% of plants used	-	20	25	20	30 10	14	86	67	8	>80	>80

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Interviews of operators of anaerobic digestion (AD) platforms

Biogas injection into natural gas network

Compost production

Input: biodegradable waste + plant residues

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Interviews of operators of anaerobic digestion (AD) platforms

Input:
agricultural wastes, lawn mowings, intermediate crops

Co-generation, heat used on site and electricity sold to the general electricity network

Digestate production (direct spreading)

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Interviews of operators of anaerobic digestion (AD) platforms

⇨ Phytotechnologies (knowledge, conditions for using plants from phytotechnologies)

• 8 over 11 operators don't know phytotechnologies

• all can accept plants from phytotechnologies under certain conditions

• differences in plant acceptance related to phytotechnologies (phytostabilisation versus phytoextraction)

Phytostabilisation:

•acceptance of phytostabilising plants (10 to 50%)

→after extensive TE analyses
→ If economic interest
→ If no negative effect observed on equipment and AD biology (microorganisms) and performance (gas yield)

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Interviews of operators of anaerobic digestion (AD) platforms

Phytoextraction:

•2 over 11 will not accept plants from phytoextraction

• 9 accept with caution
→ no diversification of providing source needed
→ too risky
→ additional control and analyses needed
→ waste treatment assimilation (image)

• acceptance of phytoextracting plants (10 to 35%)

→after extensive TE analyses to validate the use of digestate and compost
→ If economic interest
→ If no negative effect observed on equipment and AD biology (microorganisms) and performance (gas yield)

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Conclusions

Operator point of view (AD):

• Results show that plant biomass from phytotechnologies could be used in AD process.

• In theory, better acceptance of plants used in phytostabilisation or phytoexclusion than in phytoextraction.

• The acceptance is under conditions: TE control, economical interest, no negative effect on AD process and products.

C/ Regulation aspects: example of combustion

Biomass definition (IED 2010/75/UE)

'biomass' means any of the following:

(a) products consisting of any vegetable matter from agriculture or forestry which can be used as a fuel for the purpose of recovering its energy content;

(b) the following waste:

(i) vegetable waste from agriculture and forestry;

(ii) vegetable waste from the food processing industry, if the heat generated is recovered;

(iii) fibrous vegetable waste from virgin pulp production and from production of paper from pulp, if it is co-incinerated at the place of production and the heat generated is recovered;

(iv) cork waste;

(v) wood waste with the exception of wood waste which may contain halogenated organic compounds or heavy metals as a result of treatment with wood preservatives or coating and which includes, in particular, such wood waste originating from construction and demolition waste;

New requirements for French combustion plants using biomass

French regulation regarding combustion plants depends on (Autumn 2013):

- the total rated thermal input
- the type of fuels used

2910-A Declaration (<20 MW)	2910-B Registration (<20 MW)	2910 A & B Authorization (>20 MW)
a – b(i) – b(iv) b(v) : related product sawmill « biomass originated from waste » (end-of-waste procedure)	b(ii) – b(iii) b(v) : exception of related product sawmill	a – b(i) to b(v)

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Combustion plants: requirements regarding metals

	ash	Air ELVs on metals	Fuels
2910A Declaration	<u>Bottom</u> ash (only) may be spread < 5000 t/y Spreading requirements : - interest for soil and plants - study regarding environmental constraints - « spreading plan » Requirements on max metal content in <u>bottom</u> ash (if spreading) and metal load spread over 10 years	No ELVs on metals	No constraints
2910B Registration	Requirements on max metal content in <u>flying</u> ash and monitoring (2 times/y)	Elvs on metals (art. 67)	Biomass covered by b(v) : -requirements on max metal content in <u>biomass</u> -Identification of the origin of each biomass -Monitoring of the biomass content each 1000t/supplier or type of biomass or per year
2910 A&B Authorization	Separated storage of each by-product Valorization of by-products authorized if demand exists Ash : systematic spreading plan or end-of-waste procedure (fertilizer)	Elvs on metals (art. 13)	Monitoring program Constant characteristics of the fuel Max metal content in fuels authorized in the permit (based on data recorded by operator)

Requirements on max metal content

in fuels (b(v) end-of-waste biomass; 2910B Registration) and fly ash

TE	Max content in biomass (mg/kg DW)	'Phytoextraction' wood (used in combustion assays)			Max content in fly ash (mg/kg DW)	'Phytoextraction' wood (used in combustion assays)		
		Salix (Se)	Poplar (Ge)	Mix (Be)		Salix (Se)	Poplar (Ge)	Mix (Be)
Cd	**5**	2	3.9	39	**130**	759	436	6279
Zn	**200**	91	102	929	**15 000**	38476	12154	247868

in bottom ash if spreading (2910A-declaration and 2910B-registration)

TE	Max content in bottom ash (mg/kg)	Bottom ash from 'phytoextraction'		
		Salix (Se)	Poplar (Ge)	Mix (Be)
Cd	**10**	11.7	18.1	42.4
Zn	**3000**	946	766	2608

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Conclusions

Combustion:

• Plant biomass from phytotechnologies are not specifically addressed in regulation (French and European level).

• From the current French regulation, 3 options could be possible to classify such plant biomass – only hypotheses.

• Consequently, constraints or limitations related to their usage in combustion are not clearly stated.

• Results of the regulation study and the combustion assays performed on plant biomass used in phytoextraction highlighted the need to separate fly ash from bottom ash (in countries where it is not already done)
→to valuate bottom ash more easily
→to manage fly ash accordingly to their TE content.

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General conclusions

Finally:

• Knowledge related to the fate of metals in end products of the biomass processed is essential to anticipate metal transfer and potential limitations of end product use.

• Biomass processing aspects (technical, social, regulatory) have to be taken into consideration at early steps when phytotechnologies are envisaged.

• The choice of the valorisation process can help to make a decision in selecting the relevant plant (s) for a particular phytoremedion option.

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