

# *The use of bioavailability in selecting remediation technology to preserve soil quality*

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# The site

Cyanides

As

Heavy metals

PAH

VOC

**Manufactured Gas Plant utilized for over eighty years (1908–1994) Gas production was performed by coal gasification and catalytic reforming processes of petroleum light derivatives, with production of large quantities of wastes: organics, arsenic and heavy metals**



# Heavy metal concentration mg/kg

Metals	Soil			
	I 10	I 16	I 4	11 SS
Lead	3625 ± 111	600 ± 28	750 ± 41	245 ± 22
Zinc	2975 ± 204	250 ± 36	275 ± 38	146 ± 18
Arsenic	10.3 ± 2.4	276 ± 45	67 ± 9.0	700 ± 54

- Italian remediation values mg/kg

R I

- Zn 150 – 1500
- Pb 100 – 1000
- As 20 - 50

# Clean-up technologies for heavy metal contaminated sites

- Soil washing ←

- Electrokinetic

- Inertization

- Excavation and landfilling

- Phytoremediation ←

sand (49%)

gravel (19%)

clay (4%)

organic matter (1.9%)

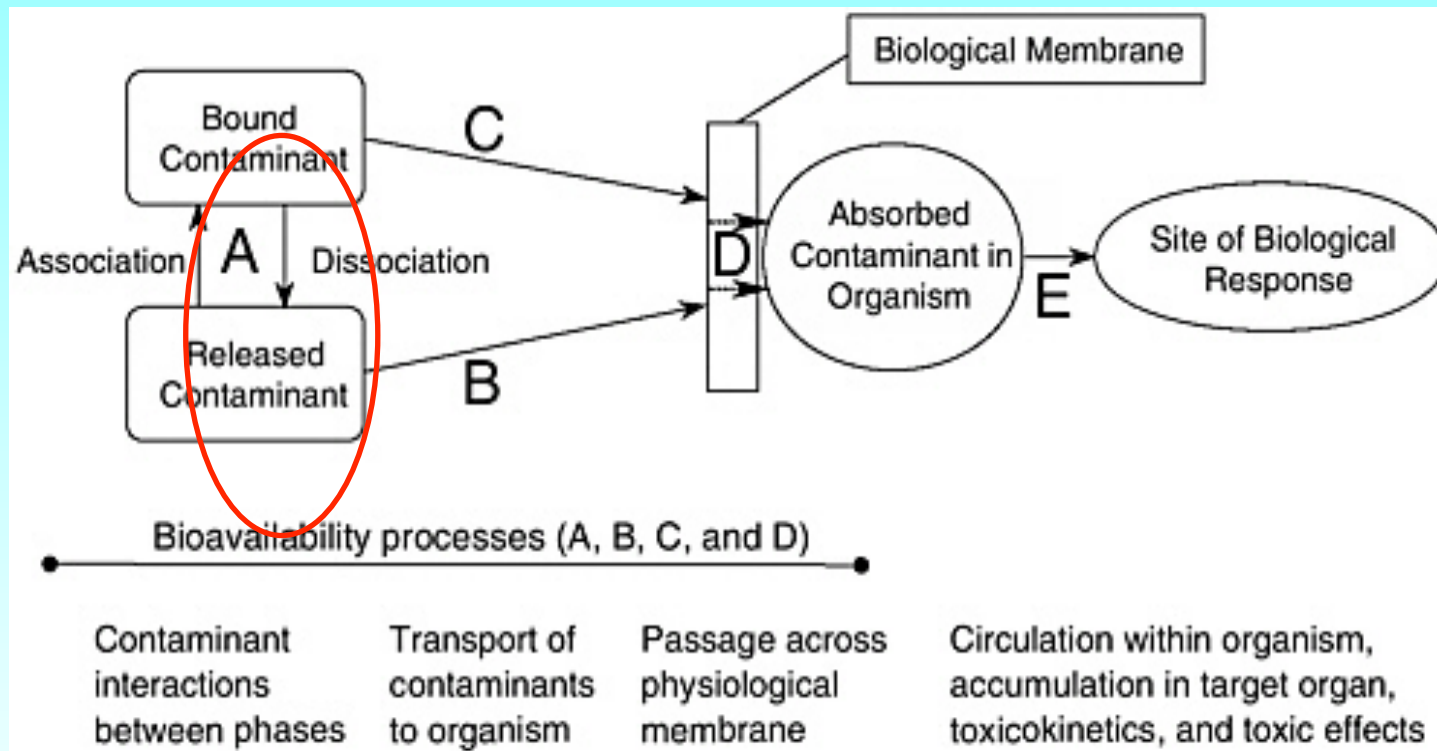
C.E.C. 12.2 meq/100 g

soil,

pH 7.4.

# Bioavailability processes

*Committee on Bioavailability of Contaminants in Soils and Sediments  
(2003)*





# Sequential extraction procedure

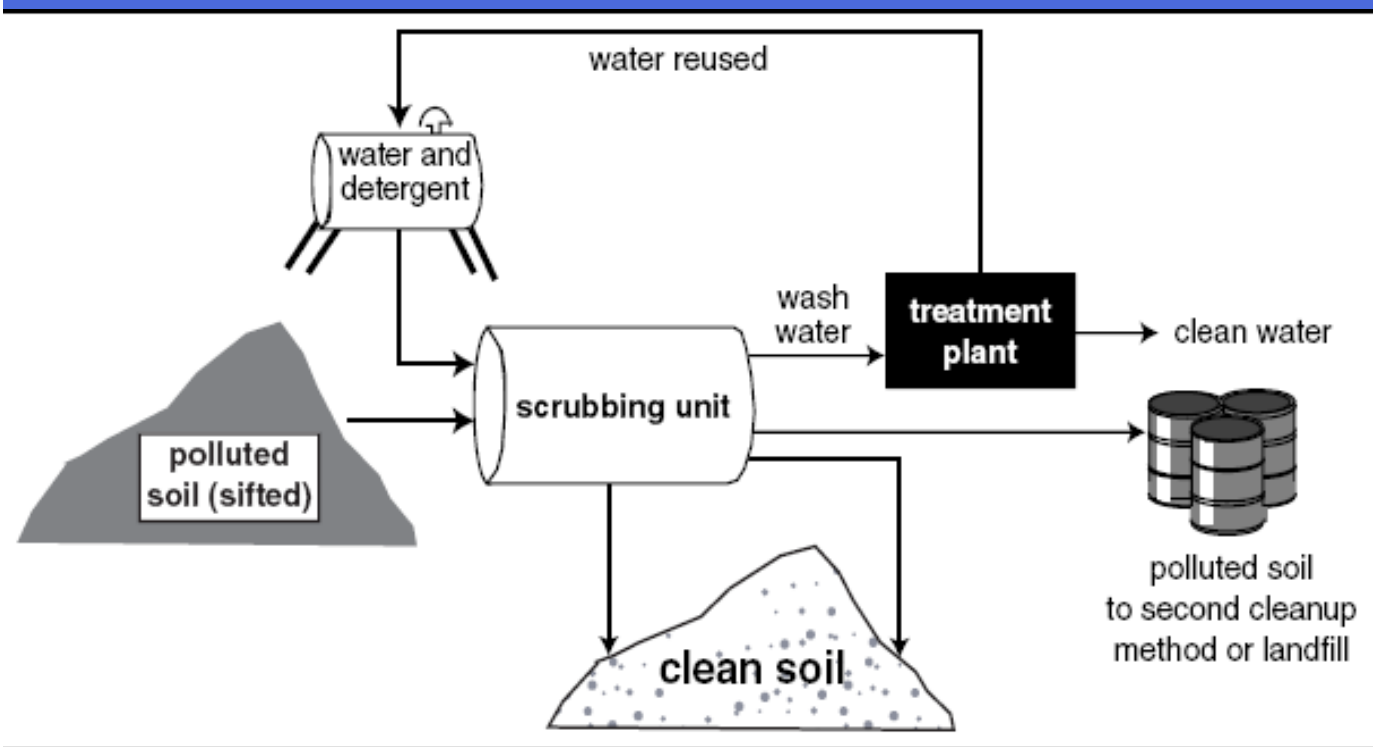
- Immediately soluble metals in the form of free cations, or soluble complexes, extractable with water.  
 $\text{H}_2\text{O}$
- Cations retained on sites with permanent charges on clay surfaces with non-specific electrostatic forces.  
 $\text{KNO}_3$  1M
- Metals “adsorbed and/or complexed” different surfaces and much greater bonding forces are involved.  
EDTA 1%

# Zn and Pb concentration in the different fractions from SEP (mg/kg ss) *Soil washing*

Soil	H <sub>2</sub> O	KNO <sub>3</sub>	EDTA
I 10	0.05 ± 0.01	1.5 ± 0.02	600 ± 31
I 16	0.02 ± 0.01	1.0 ± 0.01	35.7 ± 2.8
I 4	0.02 ± 0.01	1.1 ± 0.01	21.0 ± 1.5
11 SS	0.01 ± 0.00	1.1 ± 0.01	18.5 ± 1.2

Soil	H <sub>2</sub> O	KNO <sub>3</sub>	EDTA
I10	0.01 ± 0.00	11.5 ± 0.9	750 ± 42
I 16	0.01 ± 0.00	10.0 ± 1.1	115 ± 21
I 4	0.01 ± 0.00	10.1 ± 1.4	140 ± 11
11 SS	0.05 ± 0.01	12.5 ± 1.2	48.5 ± 3.3

# Soil washing



**Most contaminants tend to bind to the fine fraction of a soil (i.e., clay and silt). Thus, separating the fine clay and silt particles from the coarser sand and gravel soil particles concentrates the contaminants into a smaller volume of soil that can then be further treated or disposed.**



# Percentage of weight distribution of the different particle size fractions of soils

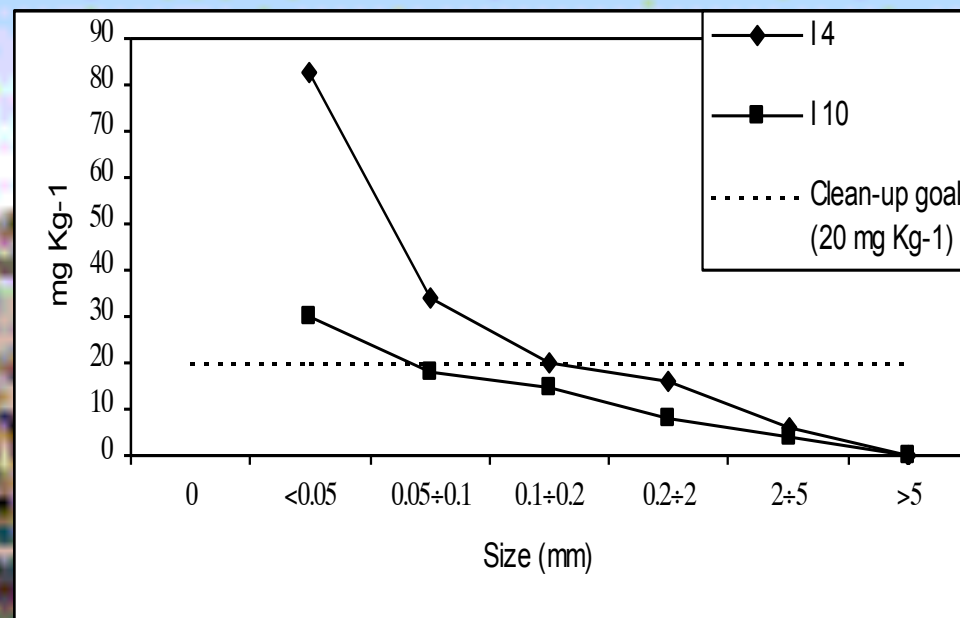
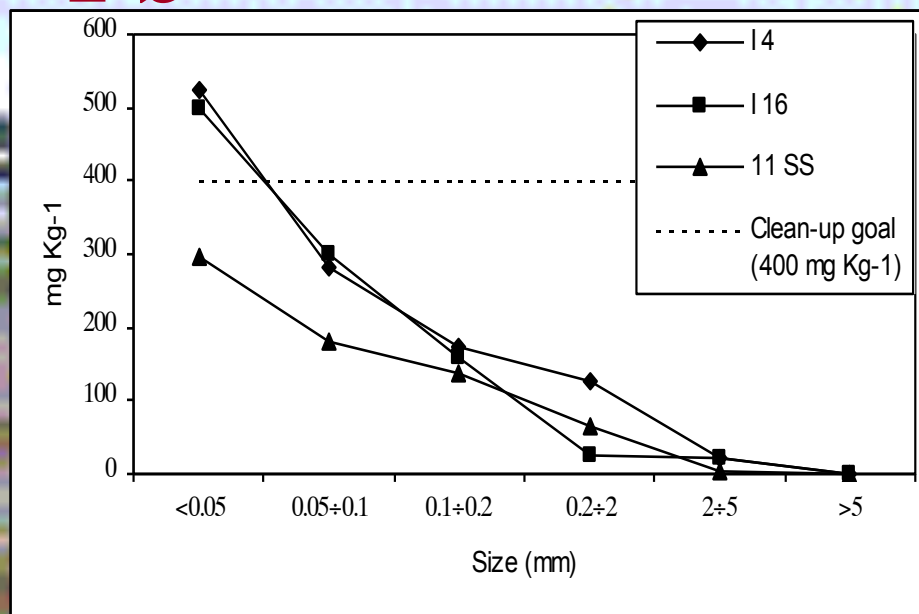
Size fraction (mm)	Soil			
	I 16	I 10	I 4	11 SS
> 5	52.8	55.6	53.7	54.0
5 - 2	9.38	11.1	11.8	12.0
2 - 0.2	20.1	16.7	17.6	17.4
0.2 - 0.1	2.1	2.8	3.4	3.1
0.1 - 0.05	2.6	2.6	2.1	3.0
< 0.05	13.0	11.2	11.4	10.5

# Lead distribution in soil fractions

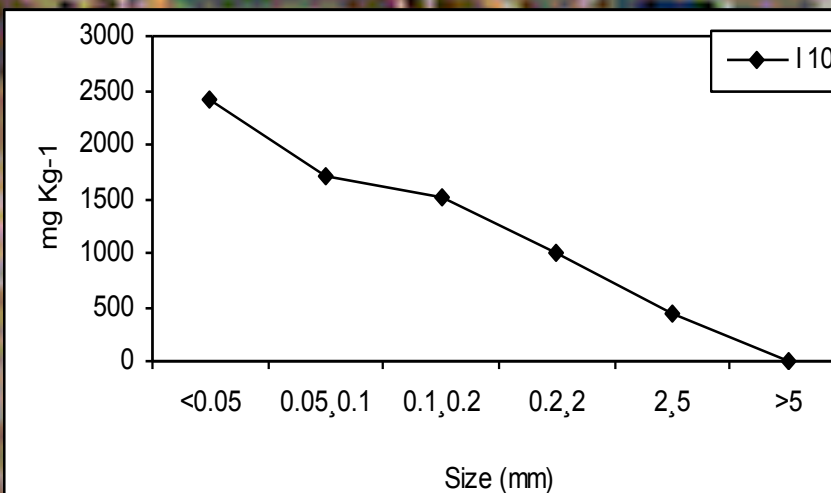
Terreno	Frazione					
	>0.5 cm,	>2 mm,	>200µm	>100µm	>50µm	<50µm
I 16	< 1	20.4	25.0	160	300	500
I 10	< 1	166	820	1075	1200	1550
I 4	< 1	20	125	175	281	525
11 SS	< 1	5	65	137	180	295

# Results from S.W.treatability test

**Pb**



**Zn**



**As**

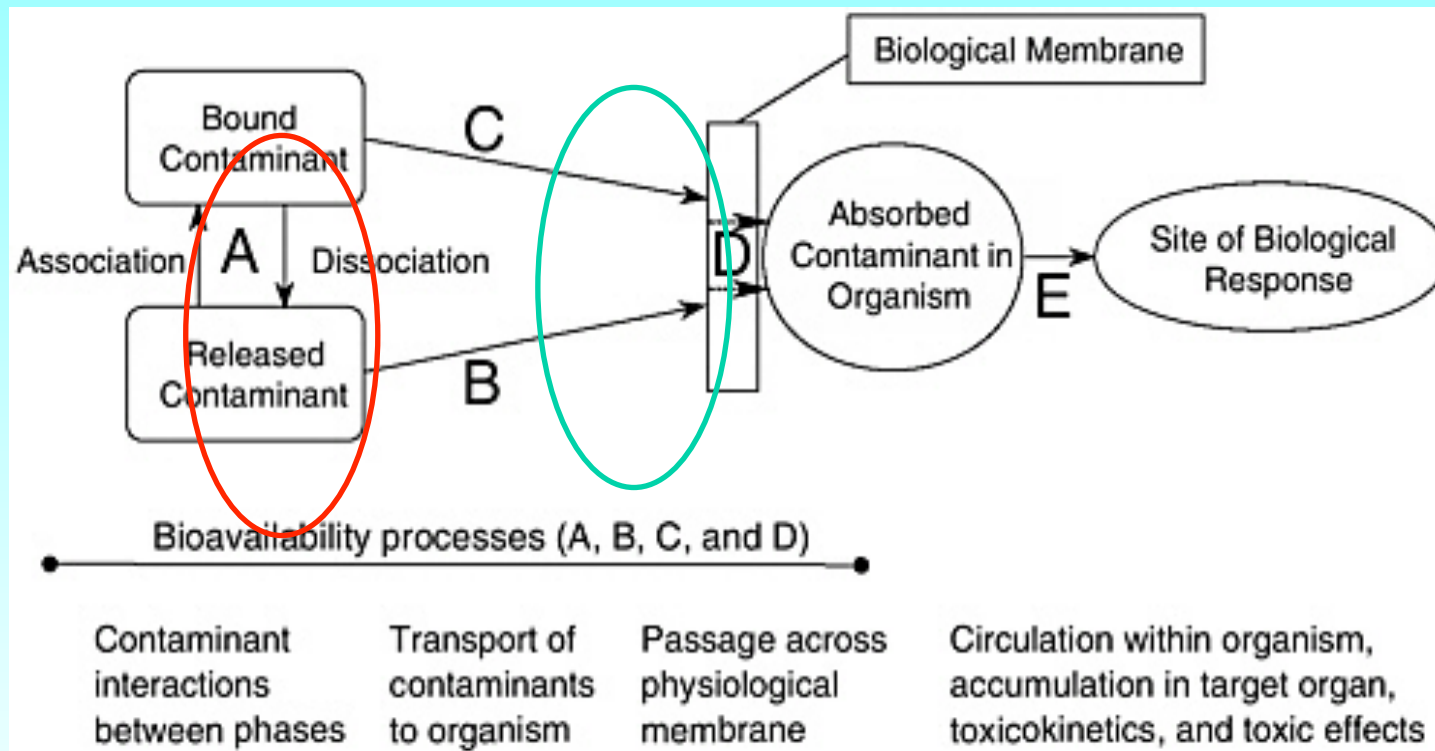


Efficiency of soil washing considering the  $> 2$  mm fraction only. Data are expressed as percent of metal removal in the respect to the total concentration in the original unwashed soil.

Metal	Soil			
	I 10	I 16	I4	11 SS
Pb	96.6%	95.4 %	92.7 %	97.9 %
Zn	84.1 %	94.0 %	92.7 %	84.5 %
As	85.7 %	63.0 %	89.1 %	52.8 %

# Bioavailability processes

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(2003)*



## *SEP for Phytoremediation*

Zn

Soil	H <sub>2</sub> O	KNO <sub>3</sub>	EDTA
I 10	0.05 ± 0.01	1.5 ± 0.02	600 ± 31
I 16	0.02 ± 0.01	1.0 ± 0.01	35.7 ± 2.8
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Pb

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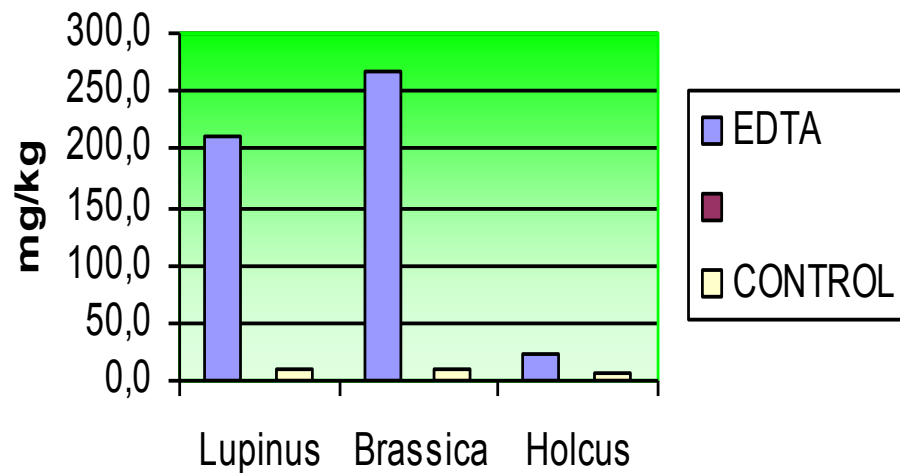


# Microcosm scale

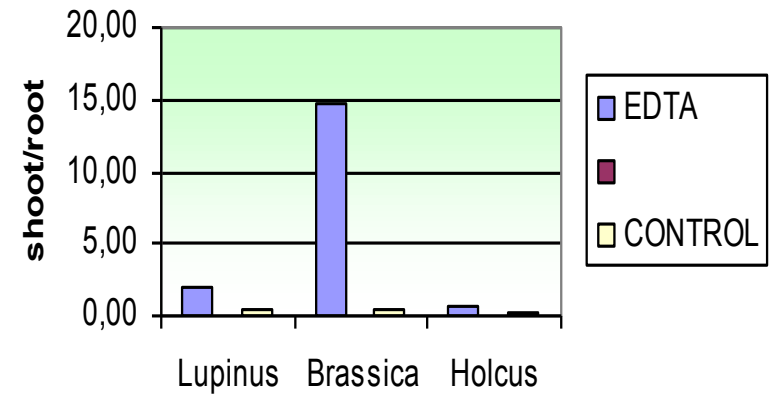


# Pb accumulation and translocation

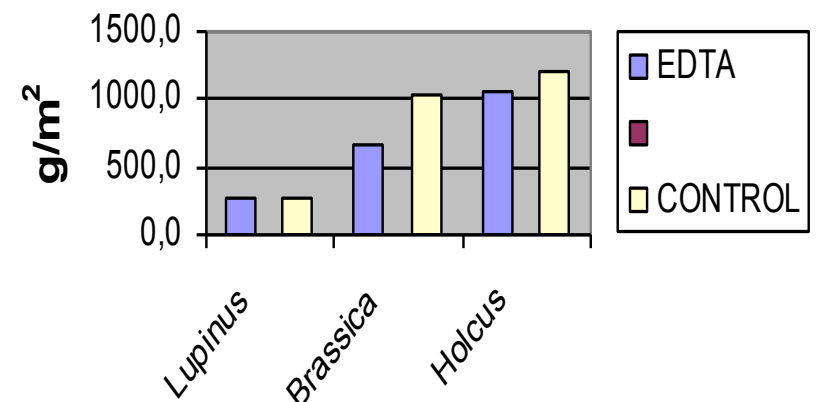
## Pb concentration in shoots



## translocation factor



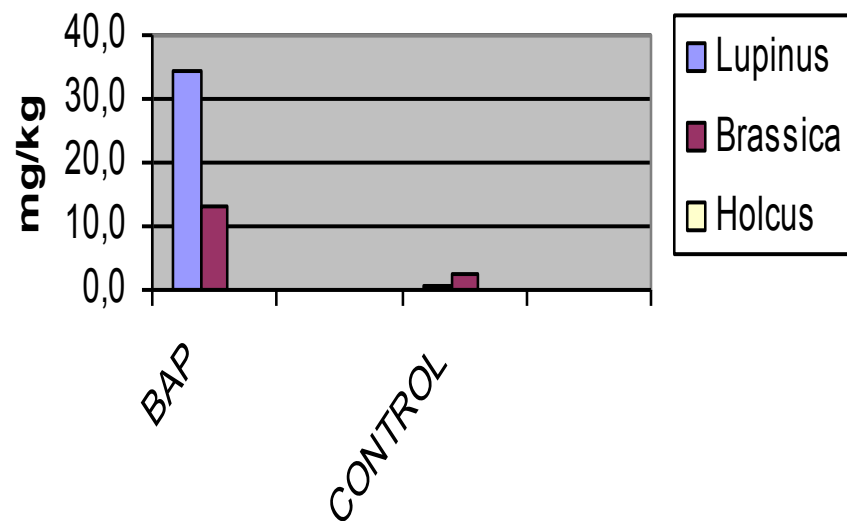
## crop production



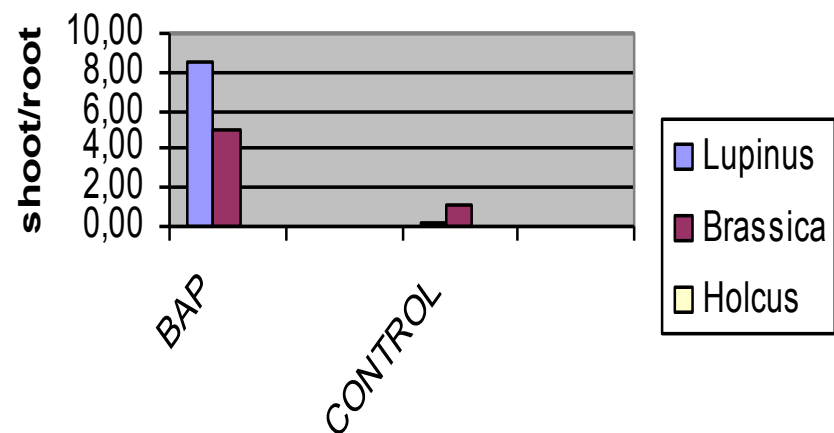


# Biomass production and As phytoextraction

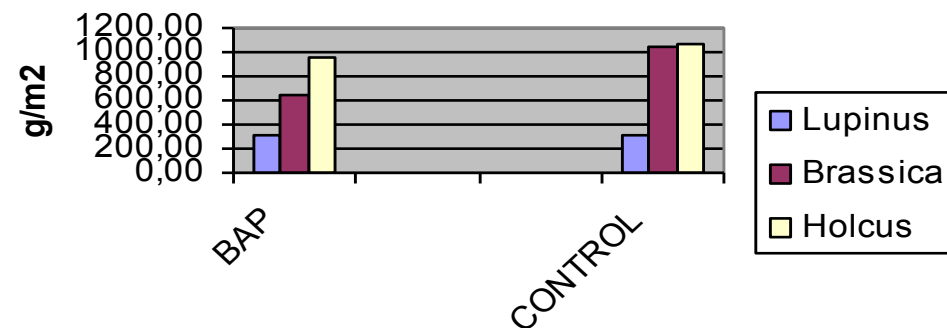
## As content in shoots



## As translocation factor



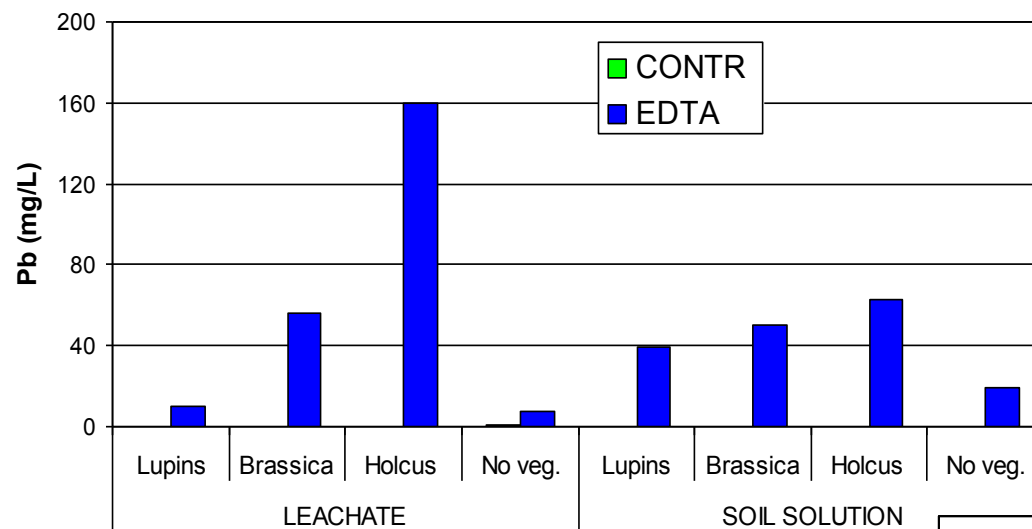
## Crop production



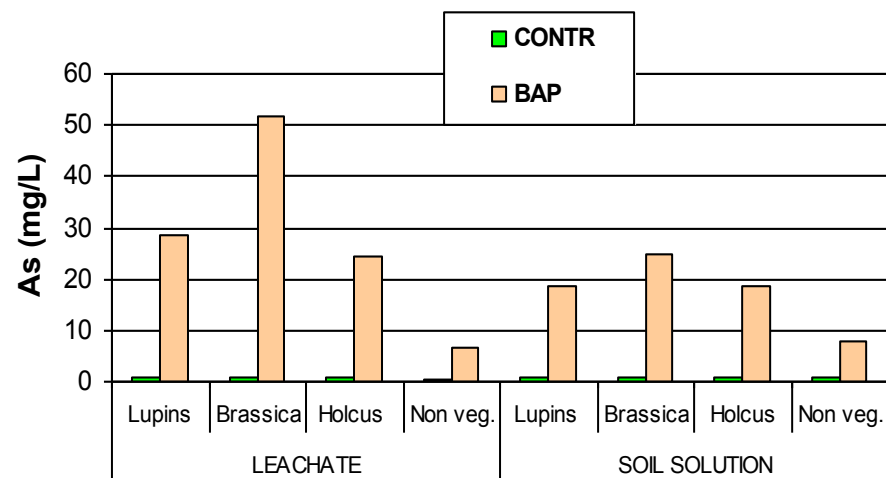


# Leaching processes

**Pb content in leachate and soil solution after treatment**

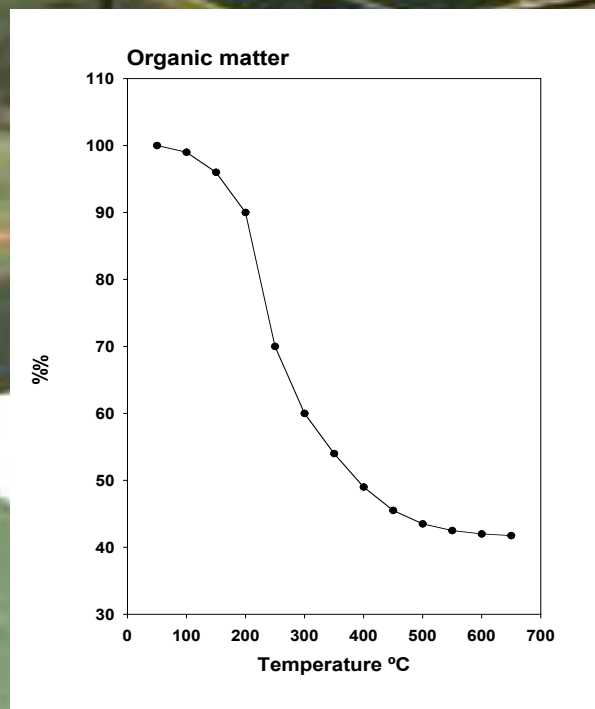


**As content in leachate and soil solution after treatment**



# Risk associated with residual contamination

## Soil quality after th



Heavy metal extractability ( $\text{H}_2\text{O} + \text{KNO}_3$ ) after thermal treatment at different temperatures

Metal	25°	500°	900°
Cu	n.d.	1.5	n.d.
Zn	n.d.	3.1	0.5
Cd	n.d.	n.d.	n.d.
Pb	n.d.	3.2	0.5
Ni	n.d.	1.0	0.6
Cr	n.d.	0.5	4.0

Heavy metal extractability (EDTA 1%) after thermal desorption at different temperatures (zone A)

metal	25°	500°	900°
Cu	36.4	52.5	n.d
Zn	52.2	222	0.5
Cd	0.01	n.d.	n.d.
Pb	77.3	265	7.5
Ni	11.1	3.0	2.0
Cr	n.d	14.5	12.0



# Bioavailability in soil remediation

There are various factors that can determine whether or not it is the case to take into account the processes of bioavailability in remediation strategies

- When only some chemical forms of the contaminants are a source of risk for the site.
- When default assumptions regarding bioavailability are not suitable because of the site's specific characteristics.
- When there is a substantial difference in the remediation goals if the bioavailability of the pollutants is taken into account.
- When it is foreseen that the final destination of the site will not be modified at least in the near future.



# Bioavailability as a tool in remediation strategies

- Selecting appropriate remediation technologies,

*Bioavailability evaluation is an essential step in the treatability tests.*

- Risk associated with residual contamination

*More attention can be given to impacts on soil quality*

- Improving the risk assessment procedures

*Inserting bioavailable values instead of total*