



Management strategies of organic wastes for environmental protection against trace metal contamination

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- ◆ Definition and origin of heavy metals in soils
- ◆ Ecotoxicological considerations of heavy metals in soils
- ◆ Environmental risk of the agronomic use of organic wastes
- ◆ Data mining in the prediction of heavy metal accumulation in soils
- ◆ New processes in the treatment of organic wastes

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Definition

Heavy metals or **Trace Elements** is a term that applies to the group of metals and metalloids with atomic density $> 5 \text{ g cm}^{-3}$ (Alloway, 2010)

The periodic table is annotated with the following groups:

- s-group:** Elements in groups 1 and 2 (Alkali and Alkali earth elements).
- d-group:** Transition elements in groups 3 through 10.
- p-group:** Elements in groups 13 through 18.
- f-group:** Lanthanide and Actinide series.

A diagonal arrow labeled "Metallic character" points from the top-left (Hydrogen) towards the bottom-right (Polonium), indicating that metallic character increases in this direction.

Alkali elements 1a												Alkali earth elements 2a					2	
1 H																2 He		
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne	
11 Na	12 Mg	d-group Transition elements										13 Al	14 Si	15 P	16 S	17 Cl	18 Ar	
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr	
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe	
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn	
87 Fr	88 Ra	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112	113	114	115	116	p-group				
Lanthanide		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	f-group	
Actinide		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

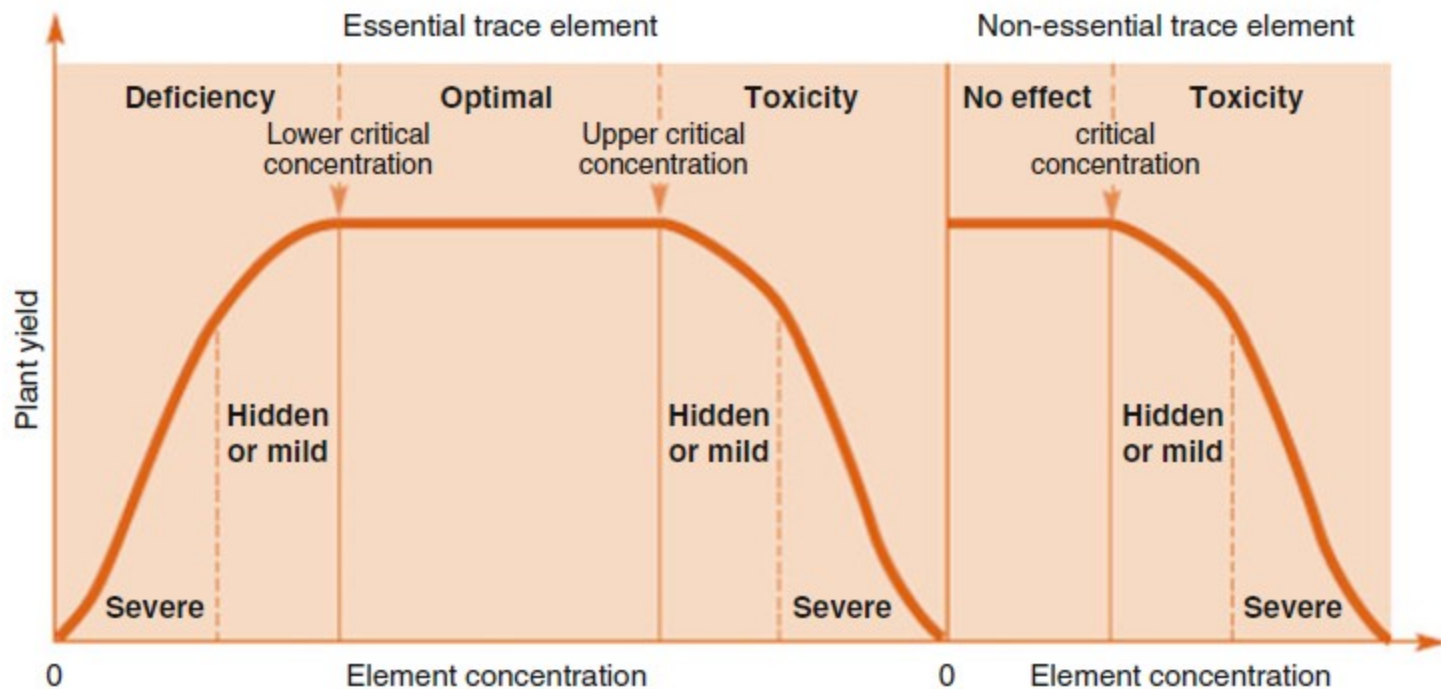


Most are toxic to humans, even at low concentrations

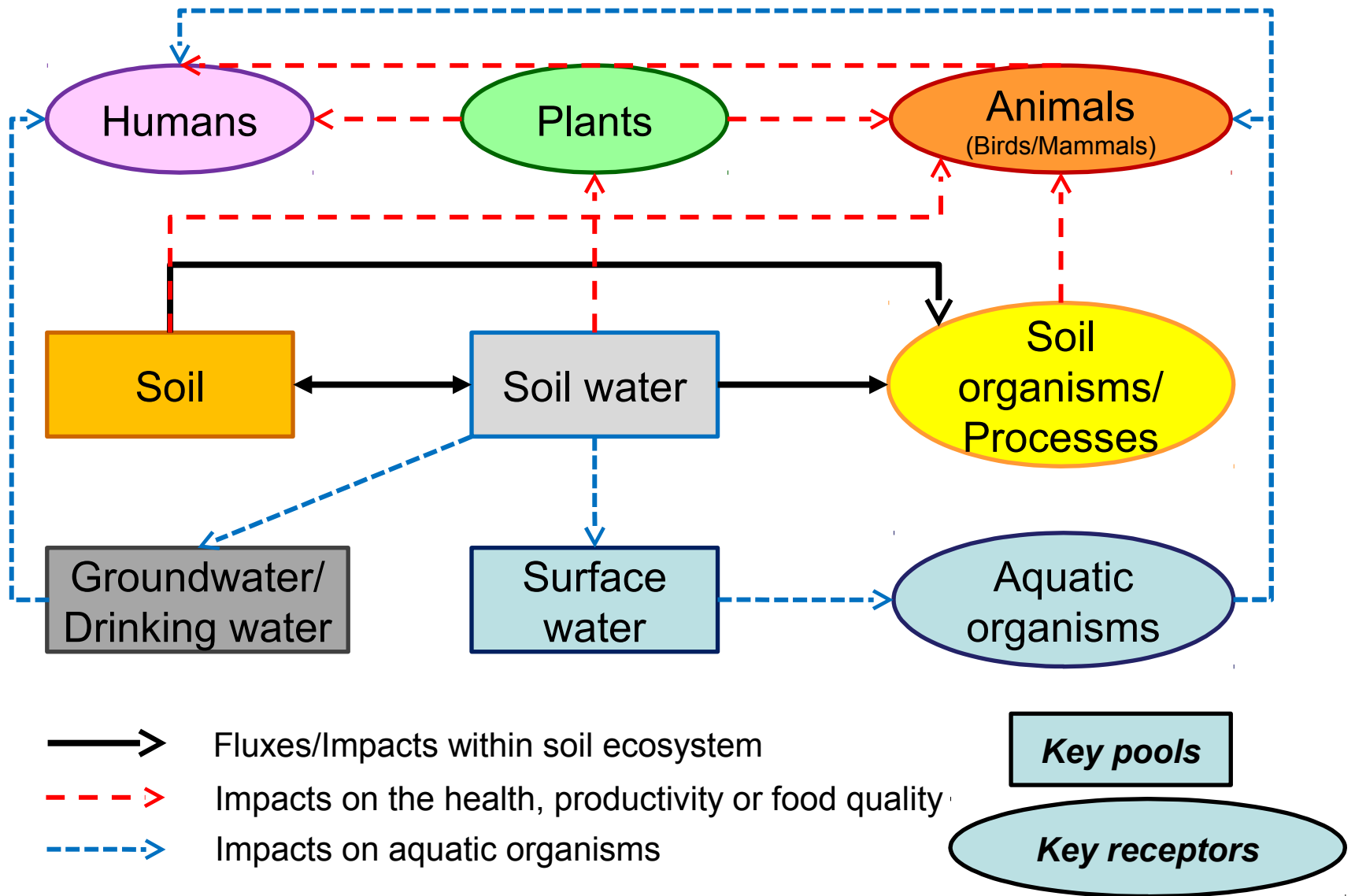
Two main groups:

- **Essential Trace Elements**, such as B, Cu, Fe, Mo, Ni, and Zn, which are necessary for plant growth, but become toxic to animals and plants when their concentrations exceed certain threshold levels
- **Non-Essential Trace Elements**, such as As, Cd, Hg, and Pb, which are not essential for plants or animals

Typical Dose-Response Curves for Essential and Non-Essential Trace Elements in Crops



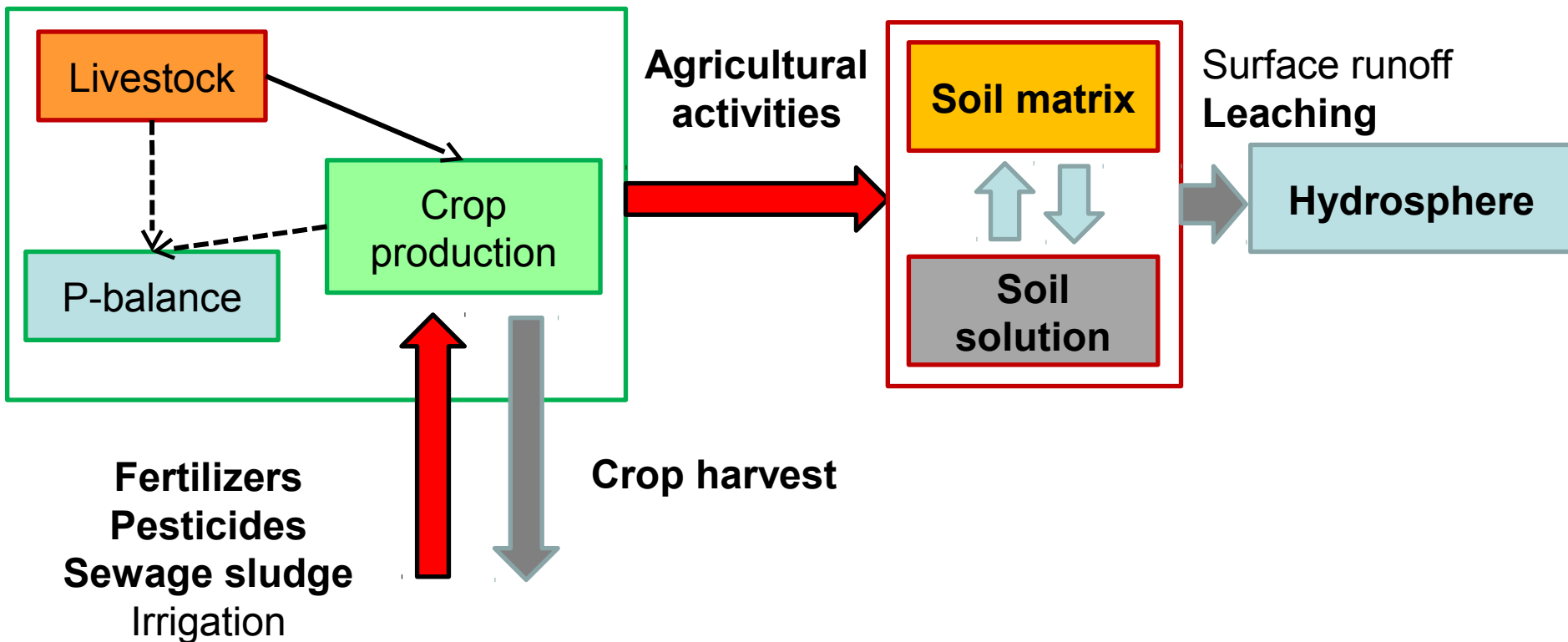
Fluxes and impact pathways of heavy metals



Sources of heavy metals in soils

- Weathering of soil minerals
- Land application of treated wastewater
- Sewage sludge and fertilizers
- Industrial activities

Land use systems



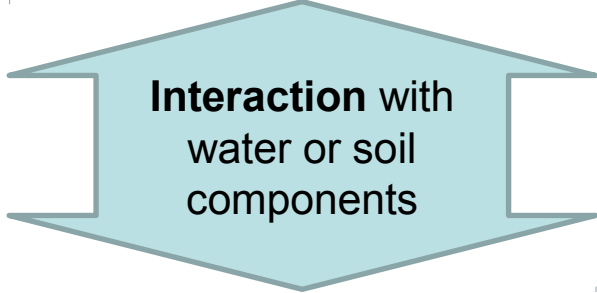
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Bioavalilability

Environmental Availability

Total Concentration in Soil/sediment



Soil / Sediment

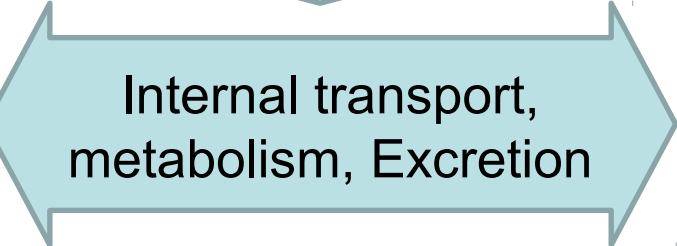


Environmental Bioavailability



Toxicological Bioavaliability

Bioaccumulation



Organism

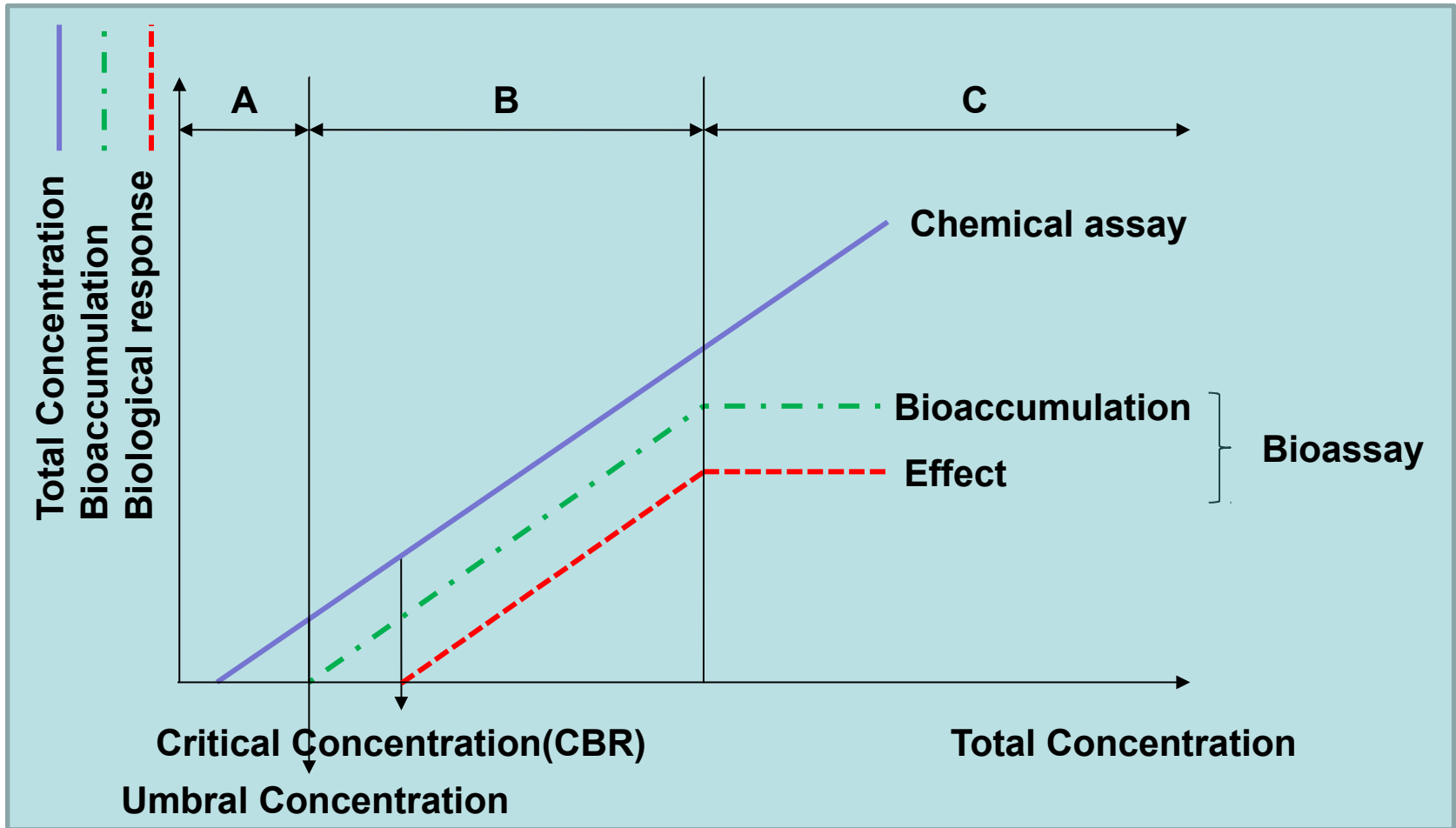
Biota

Trophic Web

Effect

Harmsen (2007) *Journal of Environmental Quality* 36,1420-1428.

Chemical assays / Bioassays:



Zone A: the contaminant is detected, no detectable effect

Zone B: concentration-response curves, useful surrogate test

Zone C: assays become nonlinear, correlation is lost.

Chemical assays:

Mechanism	Simulates	Pathway	Method	Calibrated		Recommended	Limitations
				Contaminant	Target		
Neutral extract	pore water concentration	direct contact with water	neutral water extract (NaNO ₃ ; KNO ₃ , NH ₄ NO ₃ ; CaCl ₂)	Cd/Zn/Ni	soil organisms, plant uptake	+	NH ₄ NO ₃ may reduce pH in low buffered soils CaCl ₂ may reduce dissolved organic carbon concentrations poorly soluble compounds depends on concentration of salt
		direct contact with water	extraction of pore water	Cd/Zn/Ni	soil organisms, plant uptake	+	pore water not available in dry soil Equilibration time if water is added
		transport uptake	leaching test DMT†, DGT‡	inorganic/organic inorganic	groundwater soil organisms, plant uptake	+ +	poorly soluble compounds specialized equipment
Acid extraction	potential soluble in water	uptake	acid extract (HNO ₃)	Cd/Zn/Ni	plant uptake after including soil characteristics	+	
		transport uptake	leaching test acid extract (pH of stomach or lower)	inorganic Pb	groundwater screening, human ingestion	+ +	gives a maximum of bioavailability because pH in the intestine system is higher
		uptake, transport	EDTA extract	heavy metals	plant uptake, groundwater		
Simulation of digestion	oral uptake	human uptake	stomach and intestine system	Pb/Cd/Zn/Ni/Hg/PCB/ PAH method comparison	human	+	
Adsorption to competitive adsorbant	amount in equilibrium with pore water	contact with pore water	adsorption to excess solid phase (TENAX, XAD, cyclodextrins)	PAH§	degrading organisms, uptake invertebrates	+	
	pore water concentration	contact with pore water	adsorption to solid phase (SPME††)	PAH/PCB¶/OCP#	uptake invertebrates	+	
Increasing solubility	amount in equilibrium with pore water	contact with pore water	mild (water + organic) solvent	PAHs	degrading organisms		
Partial oxidation of organic matter	amount of weakly bounded organic contaminants	easily attainable by microorganisms	oxidation with persulphate	PAHs	degrading organisms	+	

† DMT, Donnan membrane technique (Weng et al., 2005).

‡ DGT, differential gradients in thin films (Davison and Zhang, 1994).

§ PAH, polycyclic aromatic hydrocarbons.

¶ PCB, polychlorinated biphenyls.

OCP, organochlorine pesticides.

†† SPME, solid-phase micro-extraction.

Adapted and modified from ISO/DIS, 2006.

Standardized bioassays:

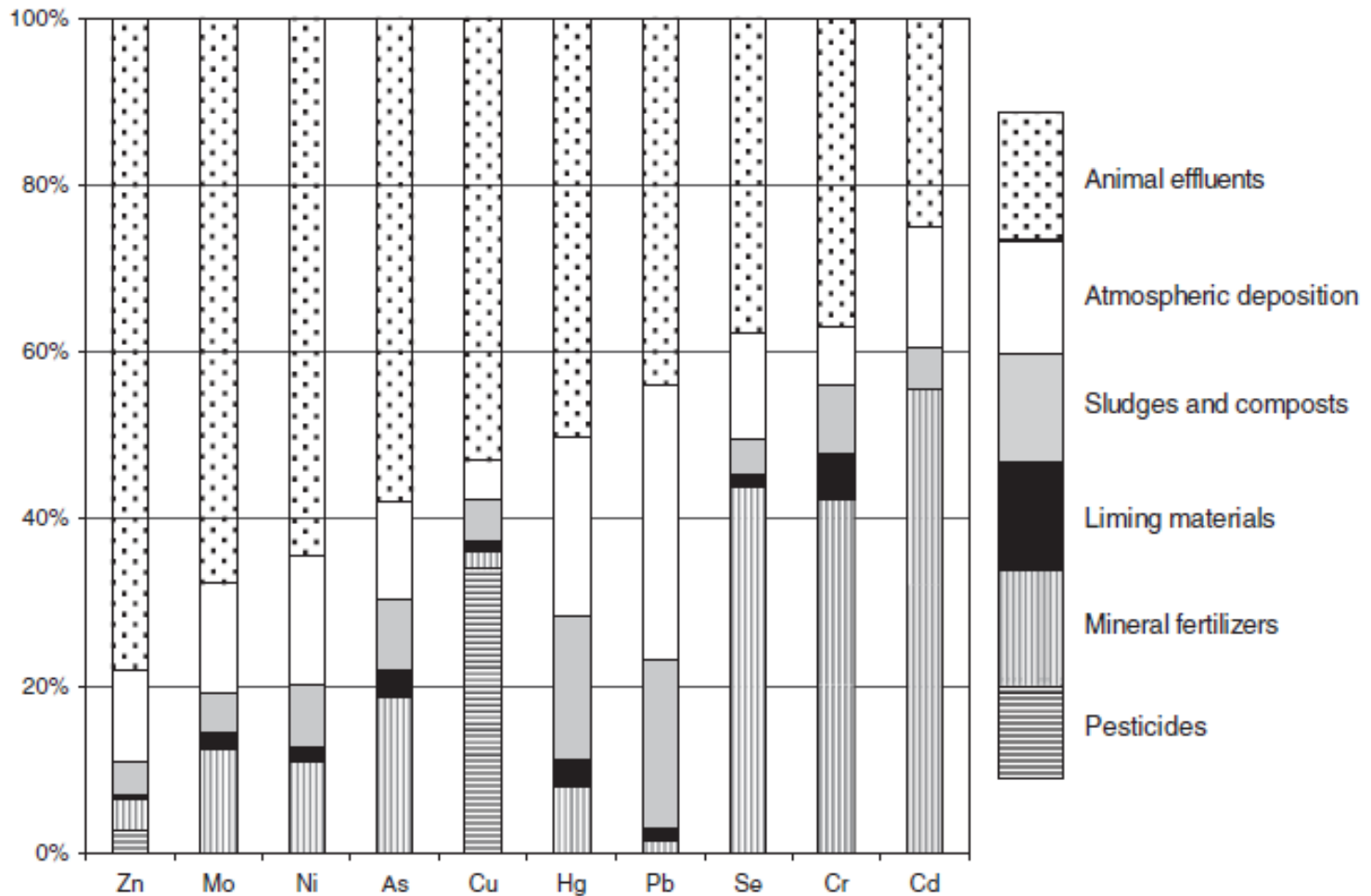
Organism	Measuring parameter	Habitat	Most important exposure route		Method
			Soluble substance	Poorly soluble substance	
Soil function affected: Habitat function					
Microorganisms	nitrification, N mineralization (incubation: 28 d)	water film of soil pores	pore water	pore water	ISO 14238
	ammonium oxidation				ISO 15685†
	respiration				ISO 17155†
	substrate induced respiration				ISO 14240-1
	biomass (fumigation-extraction)				ISO 17155†
	dehydrogenase activity				ISO 14240-2
<i>Enchytraeids: Enchytraeus albidus</i> (mesofauna)	reproduction	water film of soil pores	pore water	pore water	ISO 23753-1, -2
<i>Collembolans: Folsomia candida</i> (mesofauna)	reproduction	air-filled soil pores	pore water, air	pore water, feeding	ISO 16387†
Earthworms: <i>Eisenia fetida</i> (macrofauna)	mortality	bulk soil	pore water	pore water, feeding, skin uptake	ISO 11267†
	reproduction				ISO 11268-1†
	avoidance				ISO 11268-2†
Higher plants: <i>Mono-/dicotyledonous</i> species	emergence, growth	bulk soil	pore water	pore water	ISO/DIS 17512†
Juvenile land snails: <i>Helix aspersa aspersa</i>	growth	bulk soil	pore water	skin uptake, feeding	ISO 11269-2†
<i>Oxythyrea funesta</i>	mortality				ISO/FDIS 15952†
<i>Brassica rapa, Avena sativa</i>	growth, reproduction	bulk soil	pore water	pore water	ISO 20963
Soil function affected: Retention function					ISO 22030
<i>Vibrio fischeri</i> luminescent bacteria test—Parts 1 to 3	inhibitory effect of water samples on the light emission	surface water			ISO 11348
<i>Desmodesmus subspicatus, Pseudokirchneriella subcapitata</i>	growth inhibition	surface water			ISO 8692
<i>Daphnia magna</i> Straus (Cladocera, Crustacea)	inhibition of the mobility	surface water			ISO 6341
	reproduction and survival				ISO 10706
<i>Ceriodaphnia dubia</i>	reproduction and survival				ISO/CD 20665
<i>Brachionus calyciflorus</i>	reproduction and survival				ISO/CD 20666

† Test is validated for the assessment of soils (adapted from ISO/DIS, 2006).

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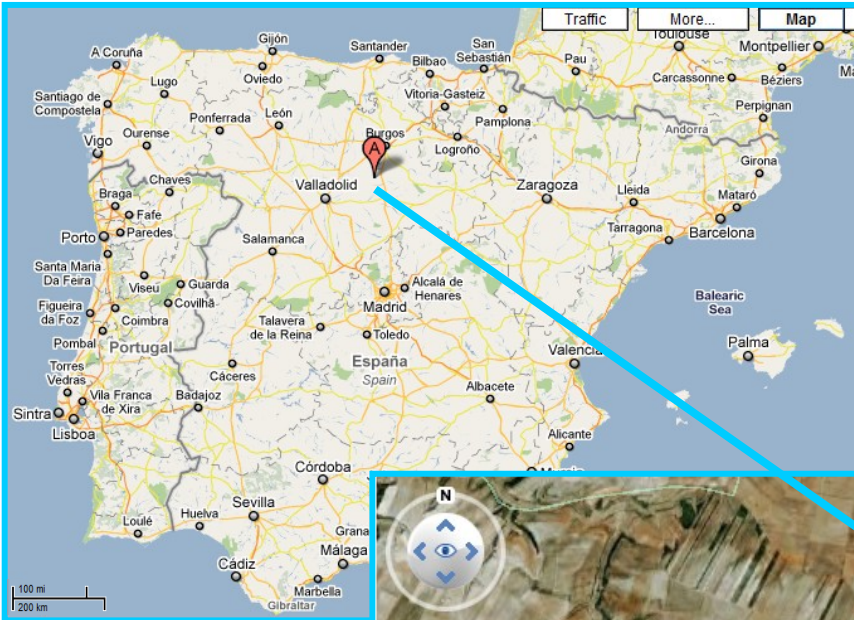
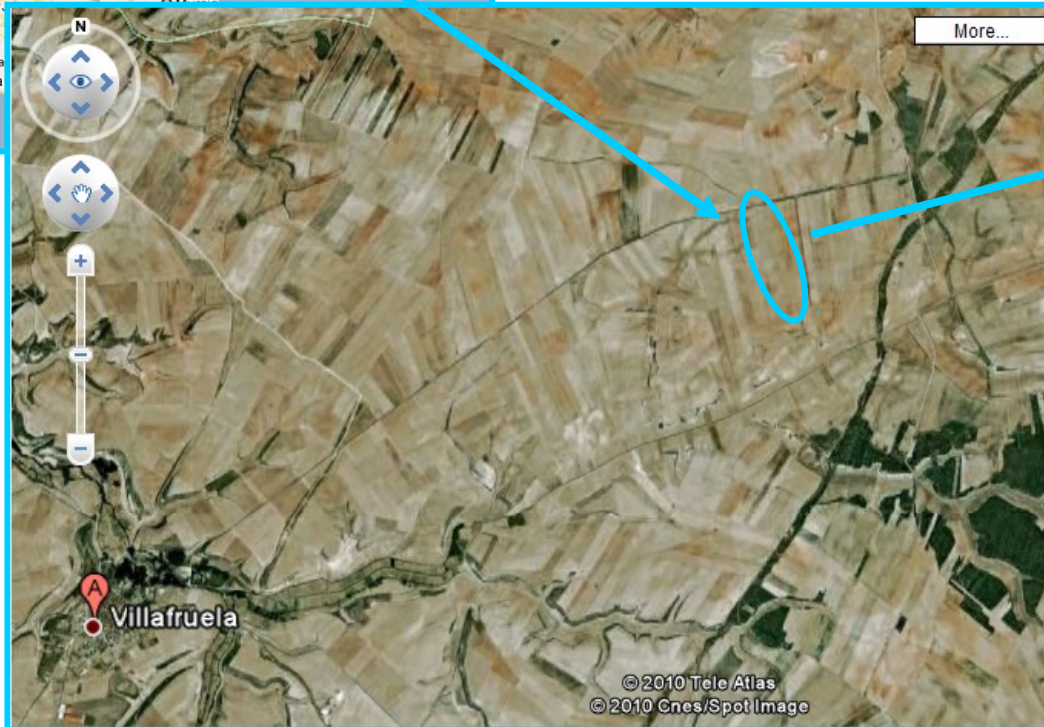
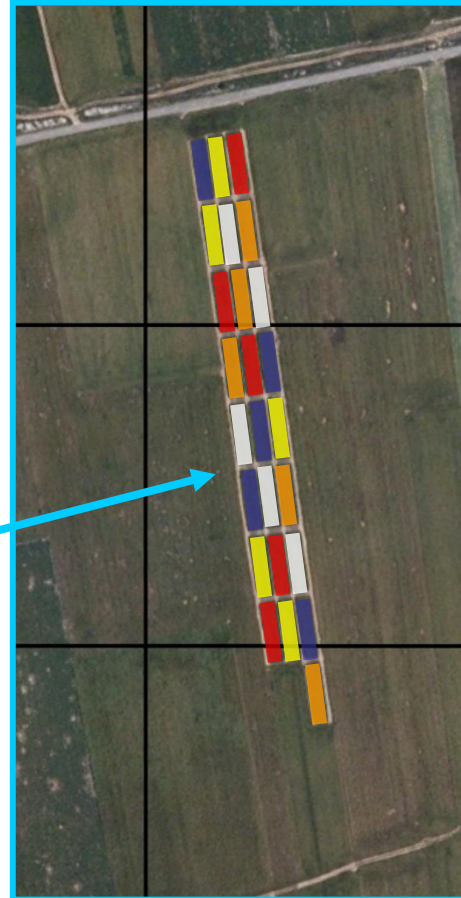
Sources of heavy metals in French agricultural soils



Agronomic use of compost of organic wastes

Villafruela (Burgos)

N: 41°56'32"
W: 3°51'13"

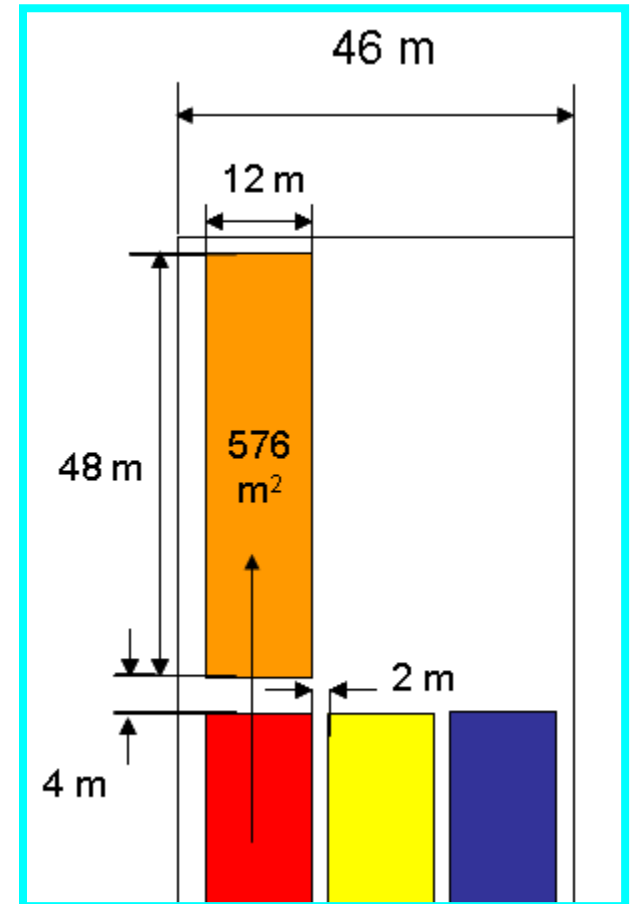


Experimental design

- Latin square design adapted
- Treatments: control, inorganic, three doses of compost of sewage sludge (CSS)
- Five replicates per treatment

Tratamientos	
(SC) Control	Blue
(SI) NPK 350 kg ha ⁻¹	Yellow
(SL ₁) CSS 3.5 t ha ⁻¹	Red
(SL ₂) CSS 7.5 t ha ⁻¹	White
(SL ₃) CSS 17.5 t ha ⁻¹	Orange

- Plots: 12x48 m divided for annually (SLL) or biannually (SL) CSS application
- 8 years of experiences
- Other soils from dryland or irrigated fields
- Other organic wastes: compost of municipal wastes, manure, dewatered pig slurry, injected pig slurry



Soil and CSS-compost characteristics

Chemical Parameters	Samples	
	Soil	CSS
pH (1:2.5 agua)	8.31 ± 0.07	7.50 ± 0.05
EC (1:5 agua 25°C dS m ⁻¹)	0.270 ± 0.024	1.420 ± 0.037
OM (% DM)	2.34 ± 0.13	26.51 ± 0.22
TN (% DM)	0.26 ± 0.02	1.77 ± 0.05
C.E.C. (meq/100g)	26.18 ± 2.08	---
Lime (% DM)	18.65 ± 4.66	---
N-NH ₄ ⁺ (% DM)	0.03 ± 0.001	0.32 ± 0.06
P Olsen (mg kg ⁻¹ DM) / Total (% DM)	58.76 ± 12.32	2.51 ± 0.74
K ⁺ exchan (mg kg ⁻¹ DM) / T (% DM)	421.7 ± 78.76	0.40 ± 0.07
Ca ⁺² exchan (mg kg ⁻¹ DM) / T (% DM)	4783.3 ± 167.3	11.29 ± 0.89
Mg ⁺² exchan (mg kg ⁻¹ DM) / T (% DM)	83.15 ± 12.50	0.78 ± 0.12
Na ⁺ exchan (mg kg ⁻¹ DM) / T (% DM)	3.68 ± 0.80	0.14 ± 0.04
Fe (mg kg ⁻¹ DM)	21916.2 ± 2219.0	12196.6 ± 769.4
Mn (mg kg ⁻¹ DM)	591.0 ± 41.5	288.3 ± 12.82
Cd (mg kg ⁻¹ DM)	1.45 ± 0.11	4.60 ± 0.39
Cr (mg kg ⁻¹ DM)	41.85 ± 3.92	716.2 ± 26.2
Cu (mg kg ⁻¹ DM)	12.51 ± 1,62	217.2 ± 7.8
Ni (mg kg ⁻¹ DM)	25.26 ± 2.98	45.70 ± 3.61
Pb (mg kg ⁻¹ DM)	27.81 ± 1.85	62.20 ± 8.36
Zn (mg kg ⁻¹ DM)	47.78 ± 4.49	507.4 ± 45.9

Legal limits in Spain and UE for sewage sludge

- Limit values of Heavy Metals in **sewage sludges**

Metal Pesado	V	
	Suelo	
Cd		
Cu	1.	
Ni		

- Limit values of **heavy metals in soils**

Metal Pesado	V _i	
	Suelo	
Cd		
Cu		
Ni		

Metal Pesado	Val _c kg
Cd	
Cu	
Ni	

- Limit values for amounts of **Heavy Metals which may be added annually** (average of 10-years)

Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture (**RD 1310/1990**, 29 October)

Legal limits in Spain for compost

- **Organic N:** 80% of Total N
- **Humidity:** maximum 14%
- **Granulometry:** 90% with $\varnothing < 10$ mm
- **Microorganisms:**
 - *Salmonella*, absent in 25 g
 - *Escherichia coli*, $< 10^3$ CFU/g

- **Heavy metals:**

Metal Pesado			
	(
Cd			
Cu			
Ni			

Class C, limited amount < 5 t/ha.año



DESARROLLO DE UN PROGRAMA DE INVESTIGACIÓN
SOBRE EL RECICLADO DE RESIDUOS ORGÁNICOS
(2004-2006)

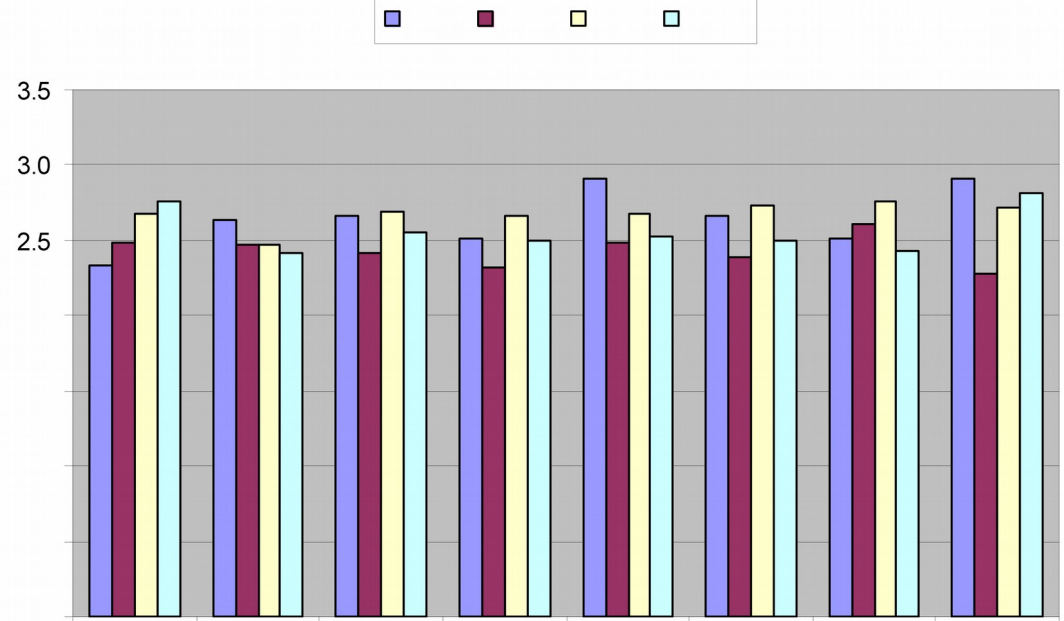
CONVENIO DE COLABORACIÓN
JUNTA CASTILLA Y LEÓN - UNIVERSIDAD DE BURGOS

Proyecto de investigación
10 de junio 2004
Cátedra de Suelos
Instituto Tecnológico de León

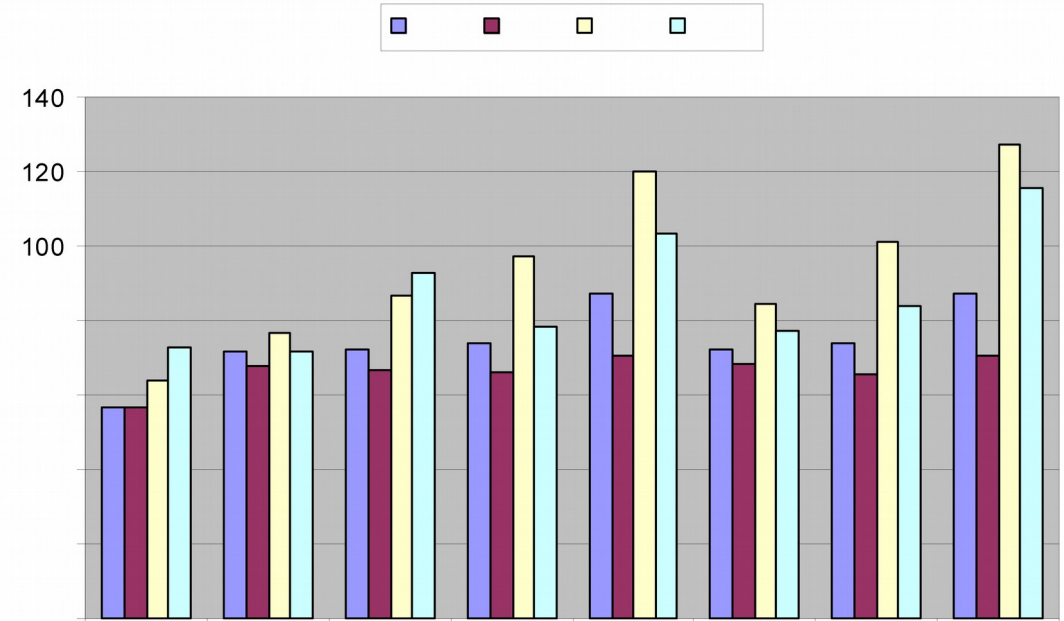
Junta de Castilla y León
Instituto Tecnológico de León

Universidad de Burgos

- Without clear effect in SOM



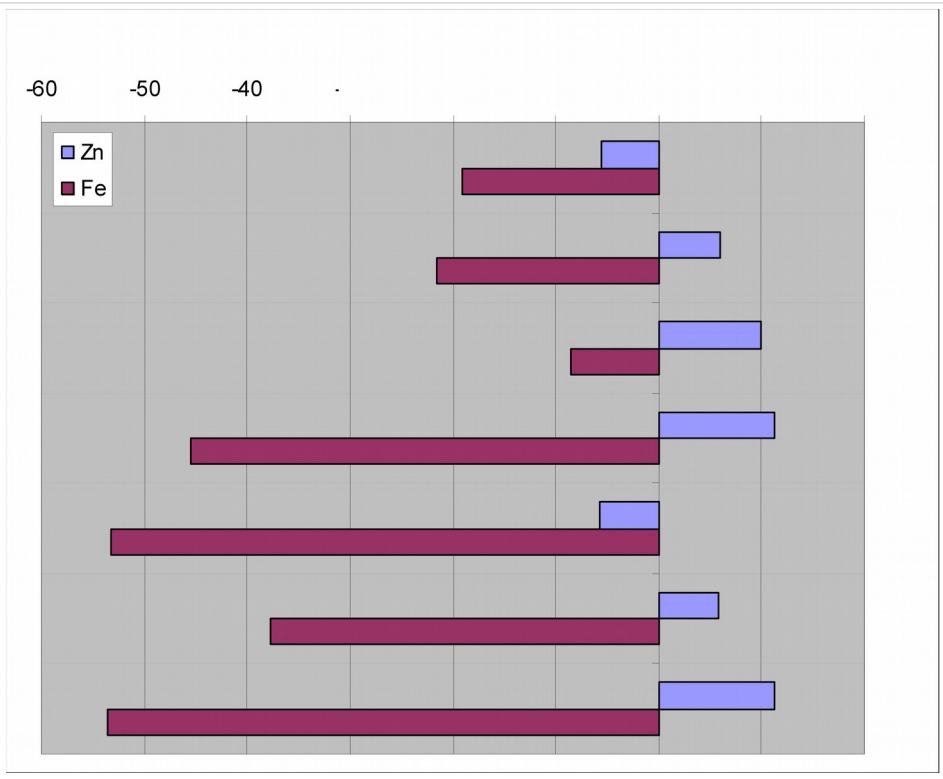
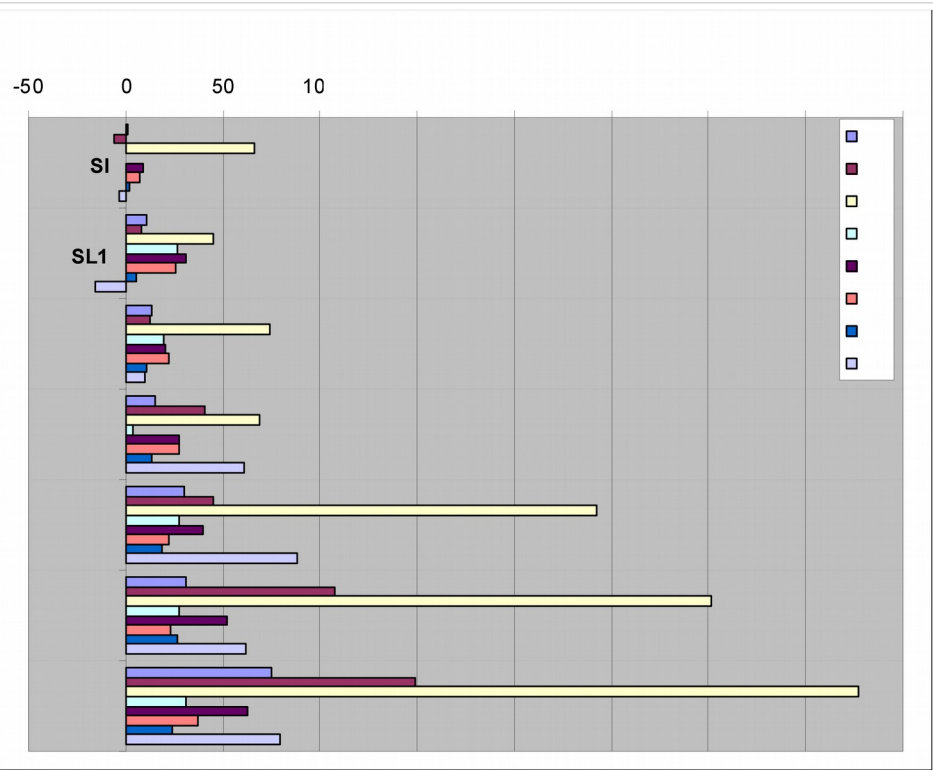
- High accumulation of available P in soil



Heavy metals in sunflower

- Above ground

- Seed

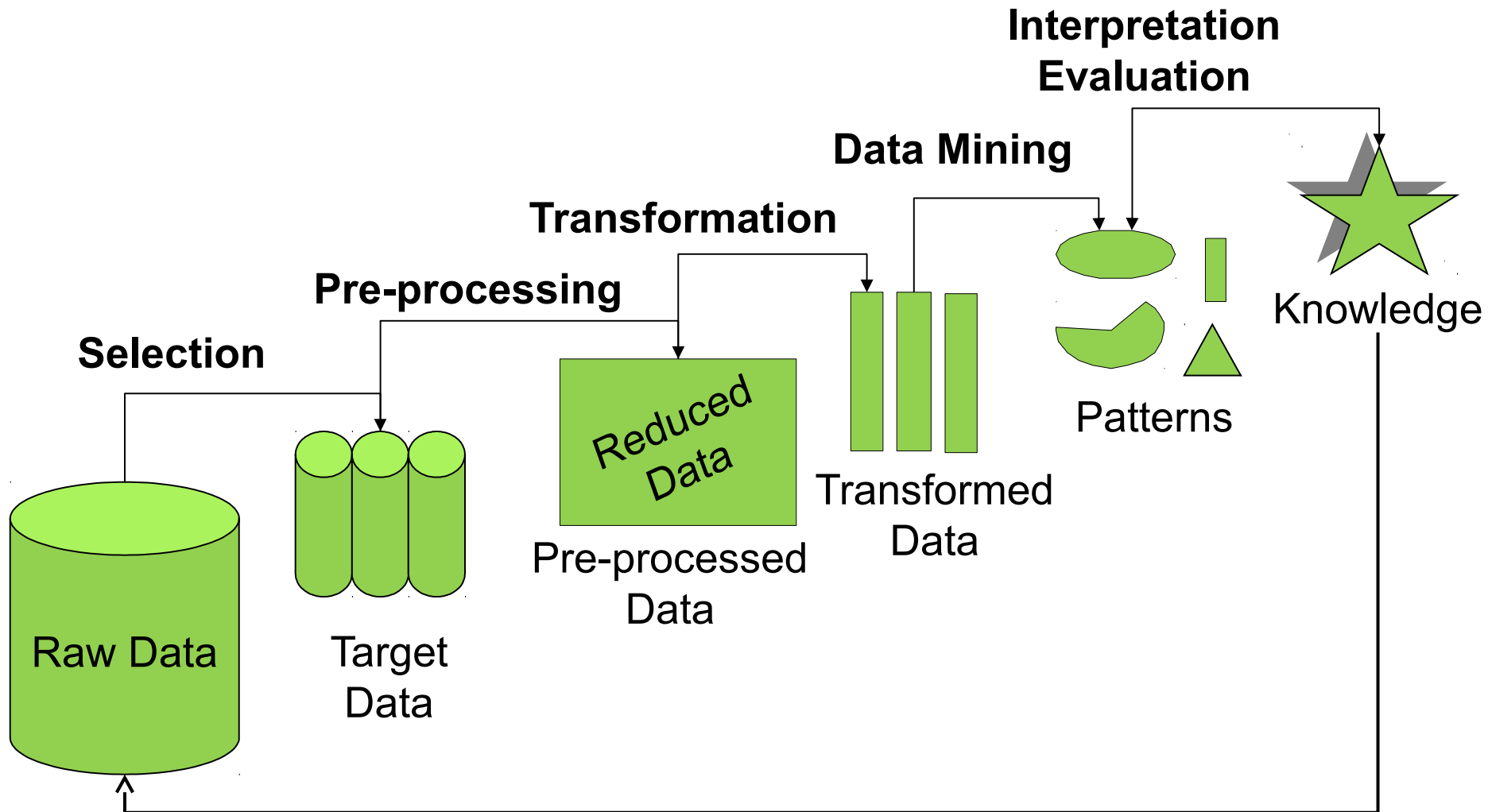


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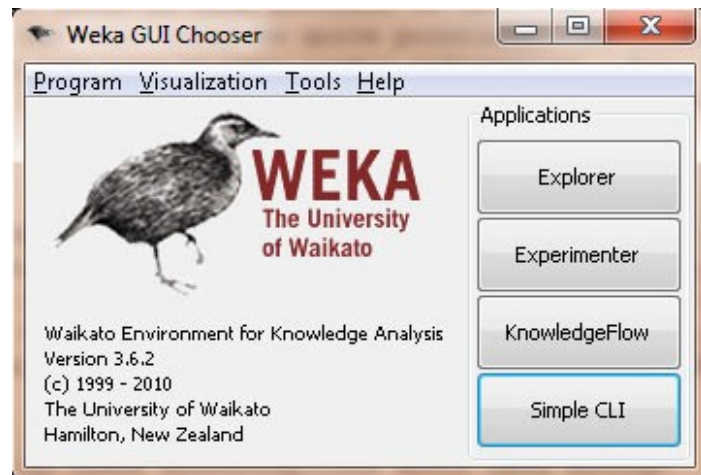
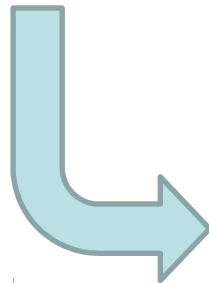
Knowledge Discovery in Databases, KDD

Supervised algorithms that predict unknown data from other known data called training set.



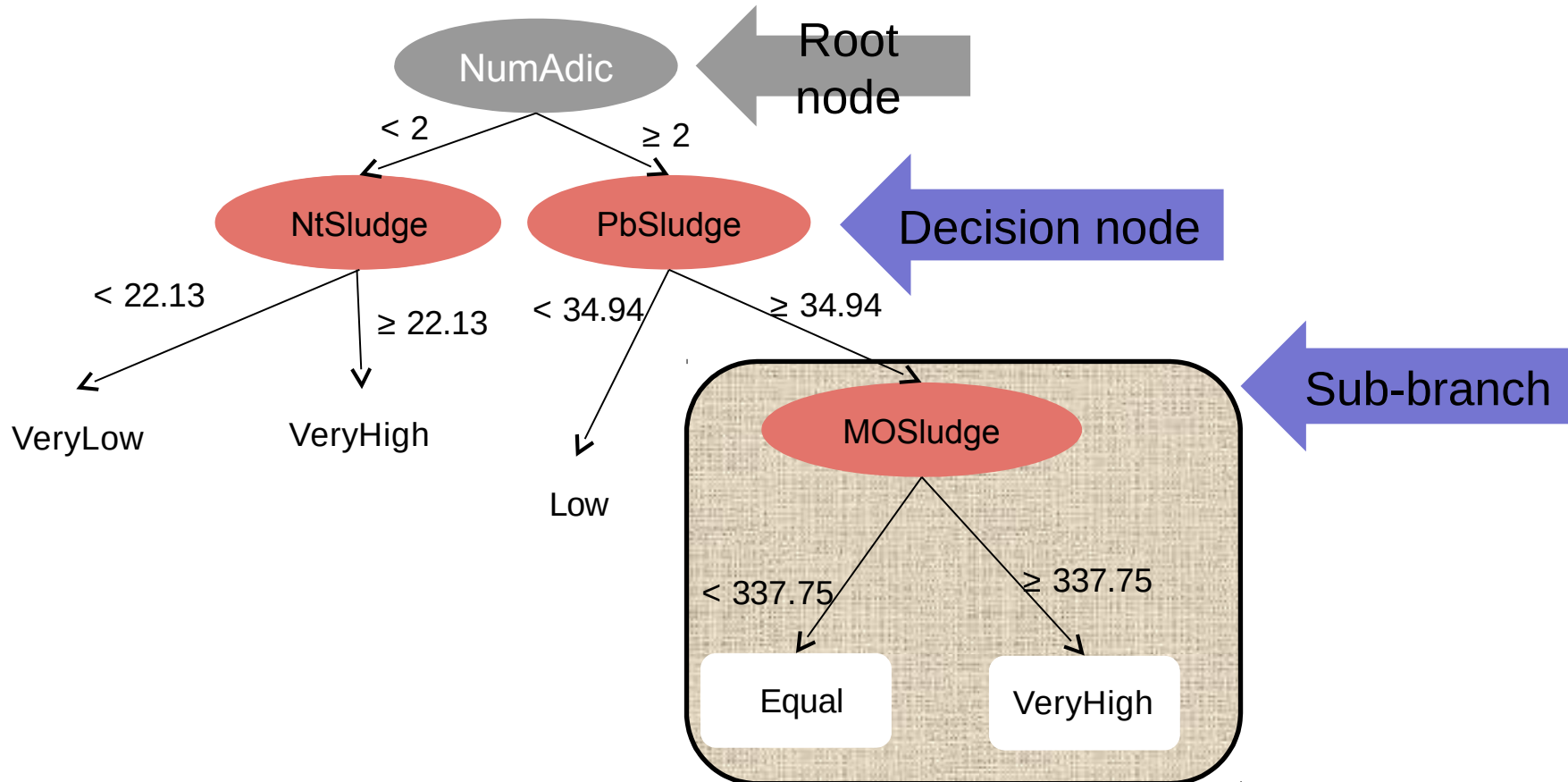
Models used in Data Mining

	Supervised Predictive		Non Supervised Descriptive	
	<i>Classification</i>	<i>Regression</i>	<i>Grouping</i>	<i>Association</i>
<i>Neural Networks</i>	X	X	X	
<i>Decision Trees</i>	X	X	X	X
<i>Linear and Log Regression</i>		X		
<i>Logistic Regression</i>	X		X	

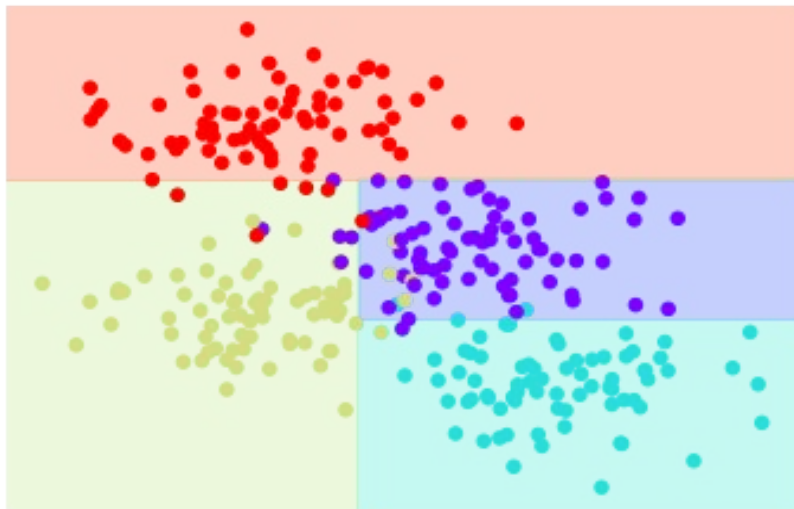


Decision trees

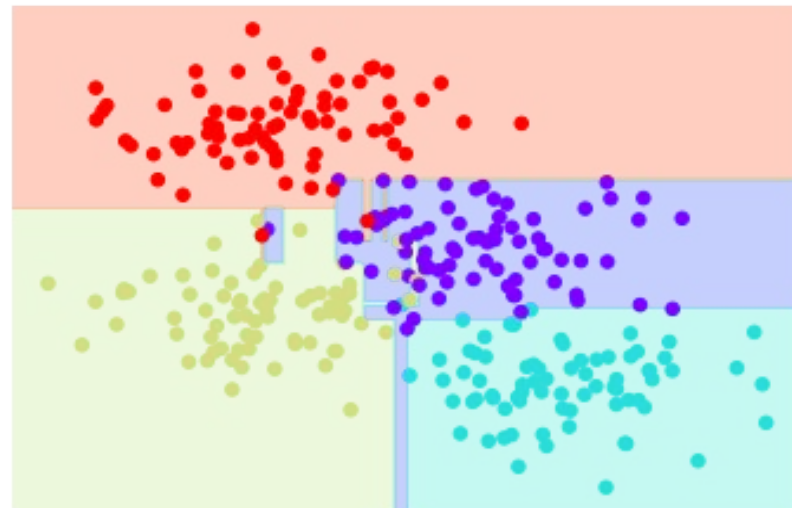
- Supervised models which can be used both for classification and regression
- Decision trees recursively split a dataset in two or more subsets until a stop criterion is reached (homogeneity)
- During training, labeled instances (cases) are used in the construction of the tree. These instances are divided according to the value of some attribute using a criterion of uniformity
- **The algorithm REPTree** uses information gain as splitting criterion when building classification trees, and variance gain for regression trees.



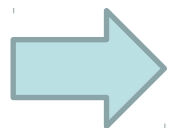
Complexity of the tree



4 LEVELS



8 LEVELS

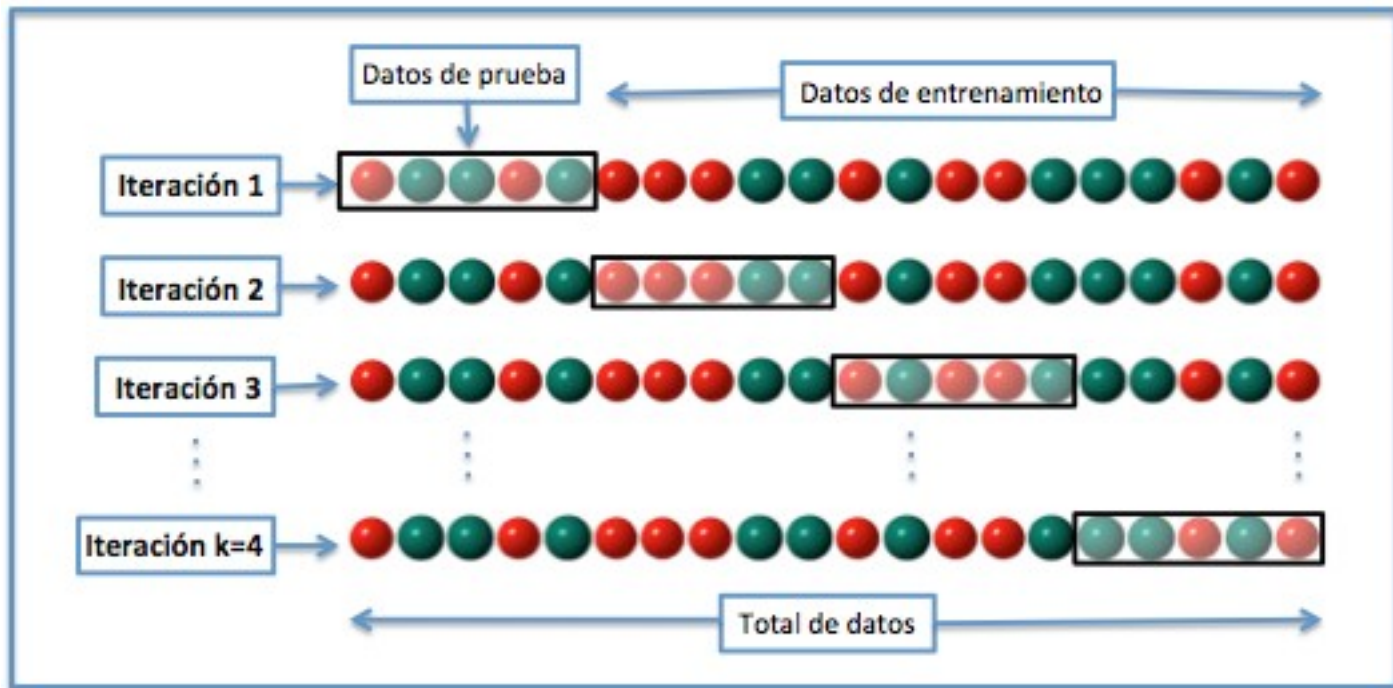


Pruning criteria

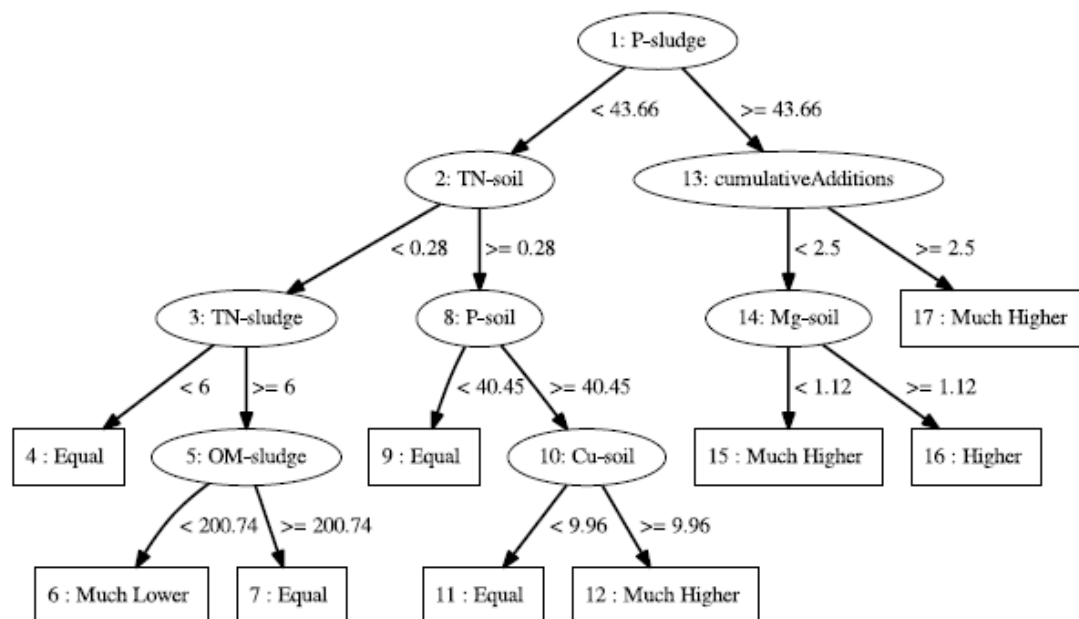
Parameter	Values
Maximum depth	1, 2, 3 and 4
Minimum weight of instances per fold	8, 16, 24 and 32
Data for pruning (In terms of total number of instances. Denominator of the fraction)	3, 5, 7, 9 and 11

Cross-validation

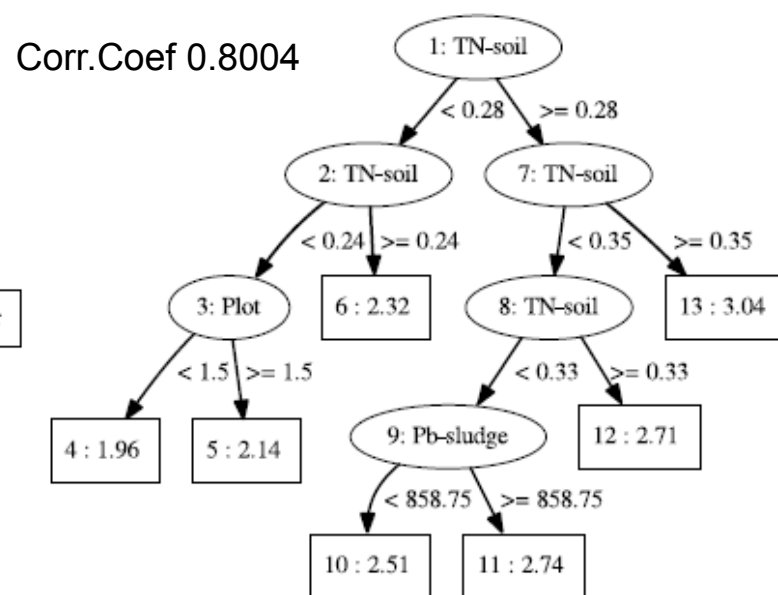
- The models are validated and the correlation is computed using 10-fold cross validation
- The initial dataset is divided into 10 sub-sets: 9 sub-sets are used to train the model, leaving the tenth to calculate the error of the sample
- This process is repeated 10 times, using each of the available sub-sets.
- Correlation coefficient was calculated as the arithmetical mean of the 10 correlation coefficient that were obtained from the partial samples



ID	Description	Enumeration	#
SP	Soil properties	pH-soil, EC-soil, OM-soil, TN-soil, P-soil, Na-soil, K-soil, Mg-soil, Ca-soil	9
SHM	Soil heavy metals	Cd-soil, Cu-soil, Cr-soil, Fe-soil, Mn-soil, Ni-soil, Pb-soil, Zn-soil	8
Root	Root heavy metals	Cd-root, Cu-root, Cr-root, Fe-root, Mn-root, Ni-root, Pb-root, Zn-root	8
Grain	Grain heavy metals and nutrients	Cd-grain, Cu-grain, Cr-grain, Fe-grain, Mn-grain, Ni-grain, Pb-grain, Zn-grain, OM-grain, TN-grain	10
CSS	compost of sewage sludge properties and heavy metals	pH-CSS, EC-CSS, OM-CSS, TN-CSS, P-CSS, Na-CSS, K-CSS, Mg-CSS, Ca-CSS, Cd-CSS, Cu-CSS, Cr-CSS, Fe-CSS, Mn-CSS, Ni-CSS, Pb-CSS, Zn-CSS	17
Other1	Other parameters	LastAddition, cumulativeAdditions, Addition, Plot	4
Other2	Other parameters 2	Current, Previous, Previous2, Fertilizer, Season	29



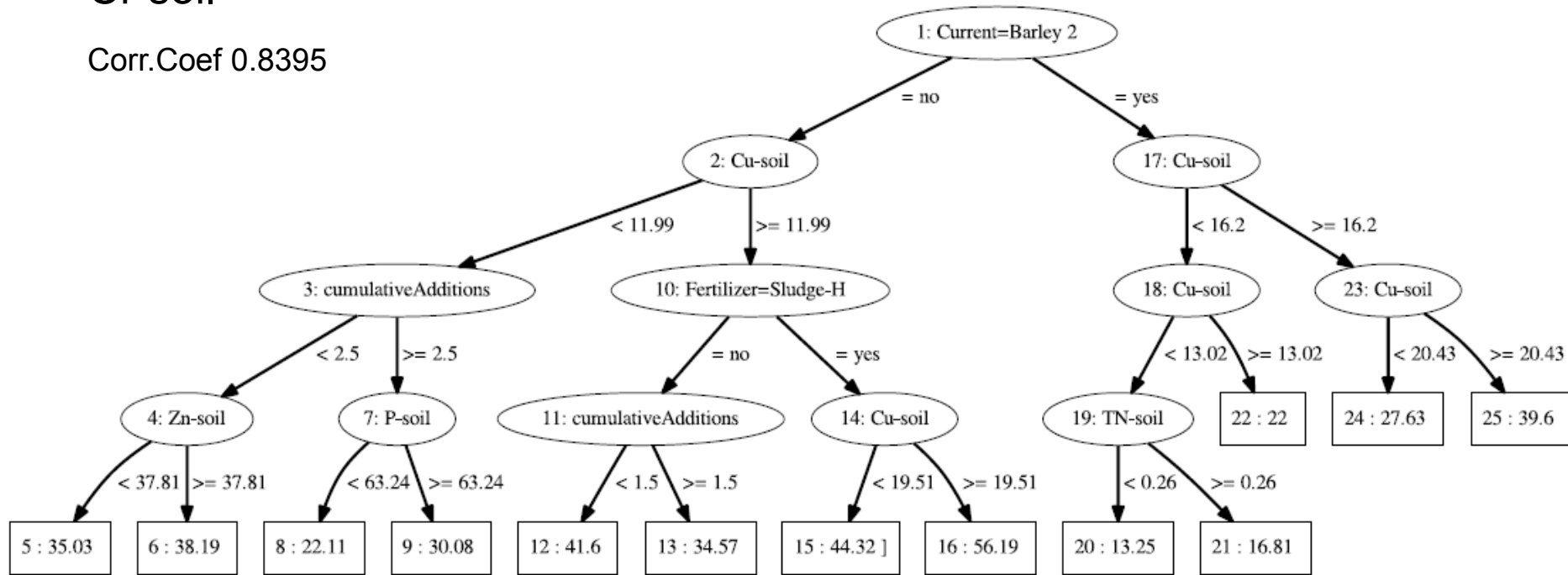
Crop production



Soil Organic Matter

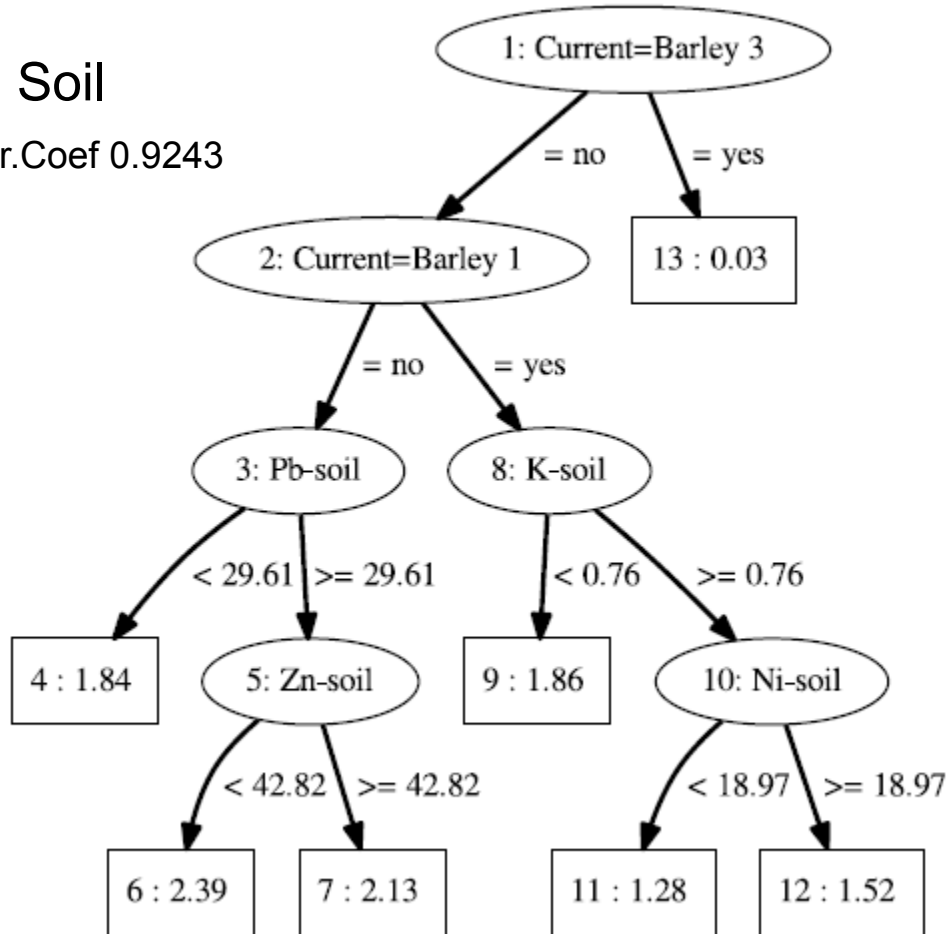
Cr soil

Corr.Coeff 0.8395



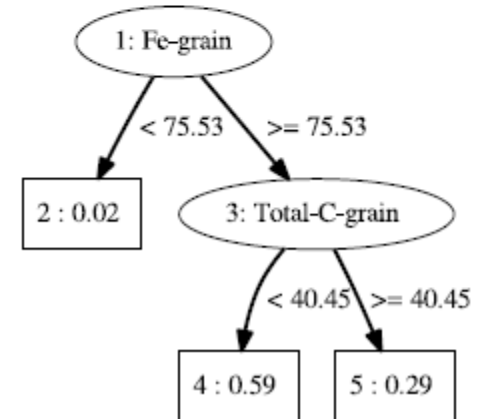
Cd Soil

Corr.Coeff 0.9243



Cd Grain

Corr.Coeff 0.7969



Model validation

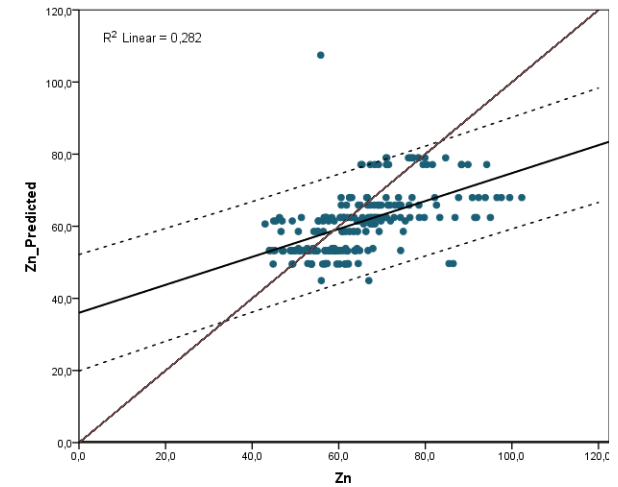
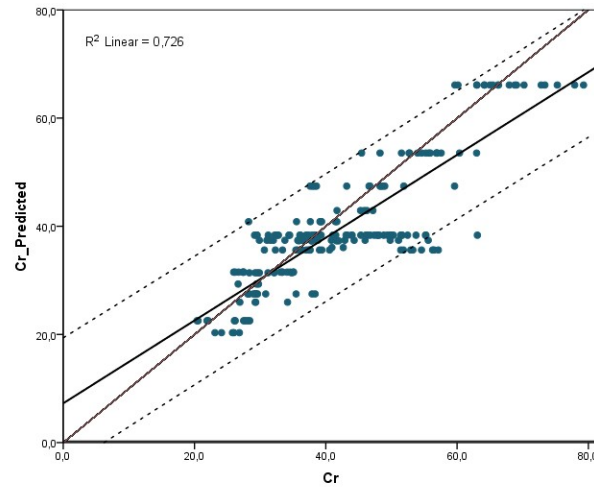
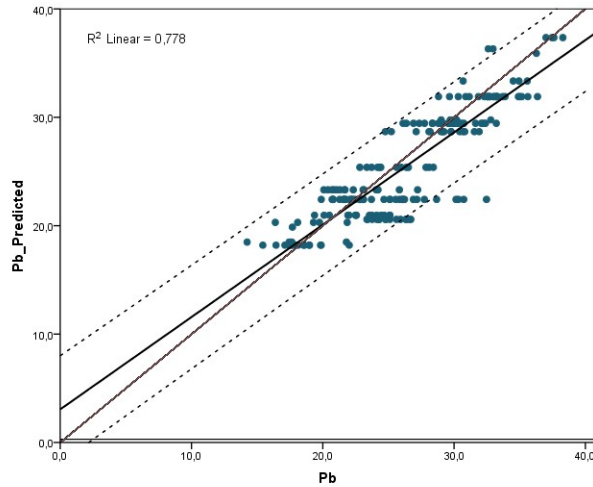
➤ *Training set*

- Three experimental plots with similar crop rotation: cereal, sunflower, legumes
- Similar soil: Calcaric cambisol
- Compost of Sewage Sludge CSS, same dosis
- Bi-yearly addition
- Properties = 52
- N = 1350
- 10-fold cross validation

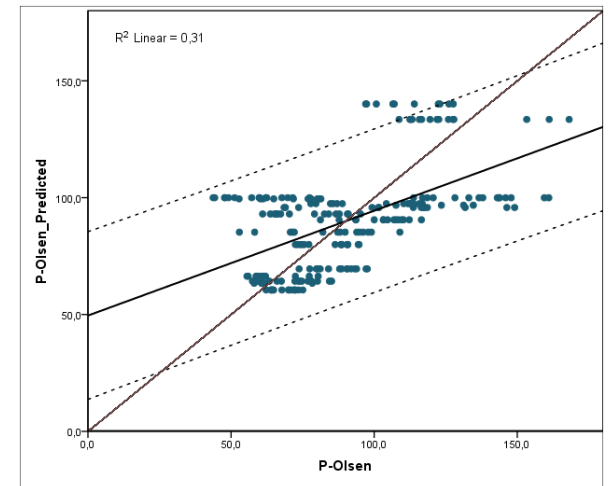
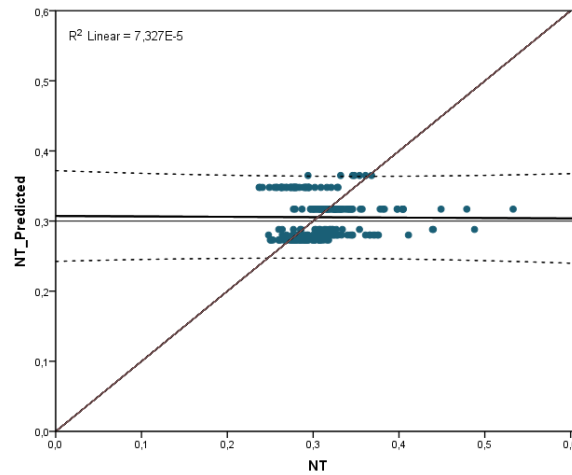
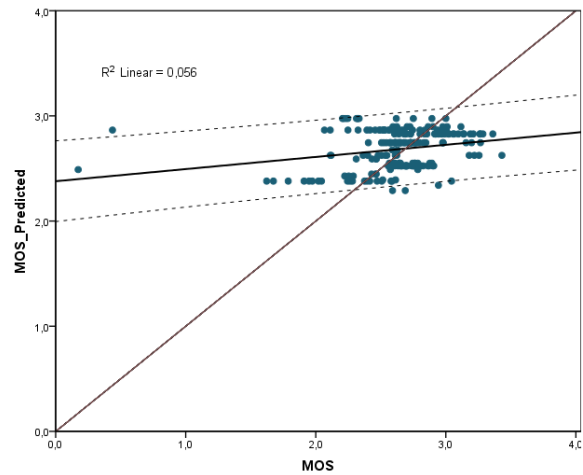
➤ *Validation set*

- Subplots of one experience
- Yearly addition
- Properties = 52
- N = 225
- 10-fold cross validation

Good prediction for Heavy Metals



Lack of prediction for other soil parameters

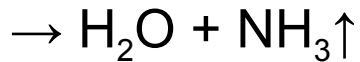
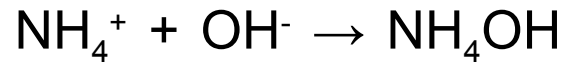


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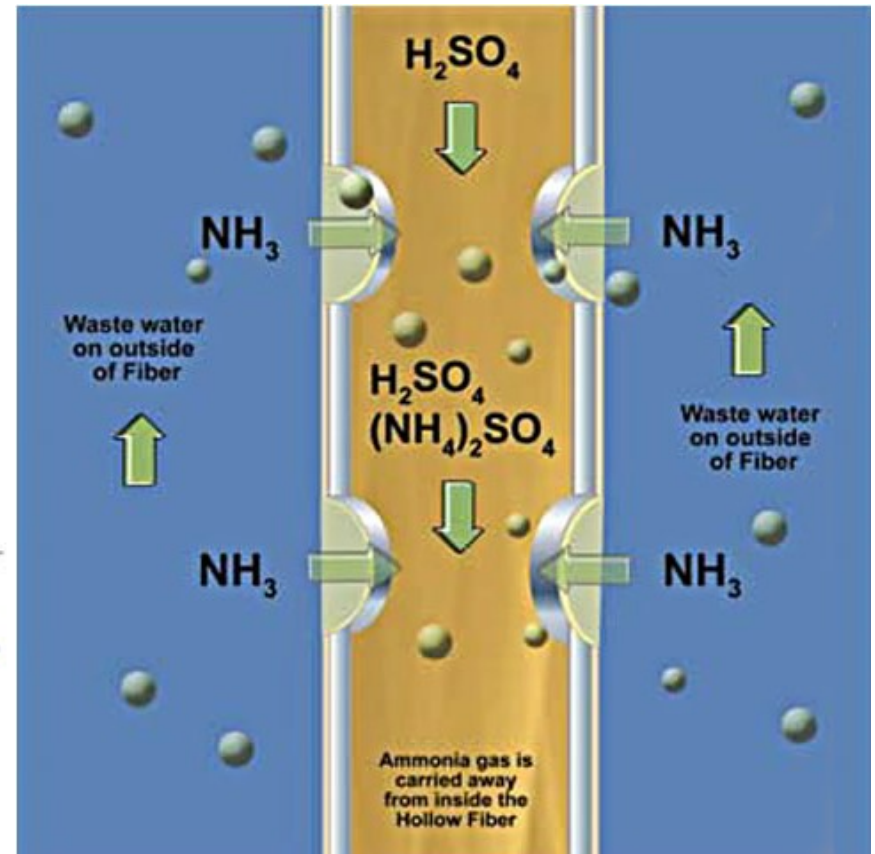
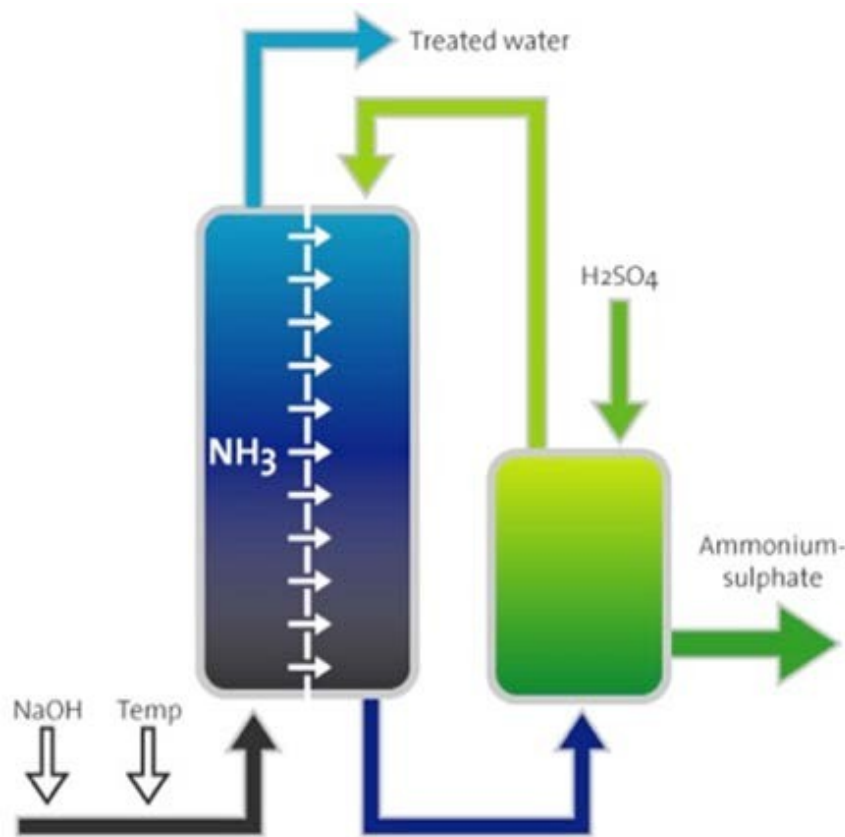
- ◆ Definition and origin of heavy metals in soils
- ◆ Ecotoxicological considerations of heavy metals in soils
- ◆ Environmental risk of the agronomic use of organic wastes
- ◆ Data mining in the prediction of heavy metal accumulation in soils
- ◆ **New processes in the treatment of organic wastes**

Nutrient recovery from effluents: sewage sludges, animal slurries

- Ammonia stripping:

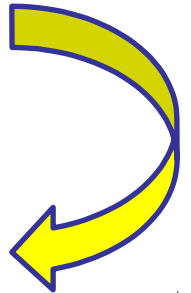
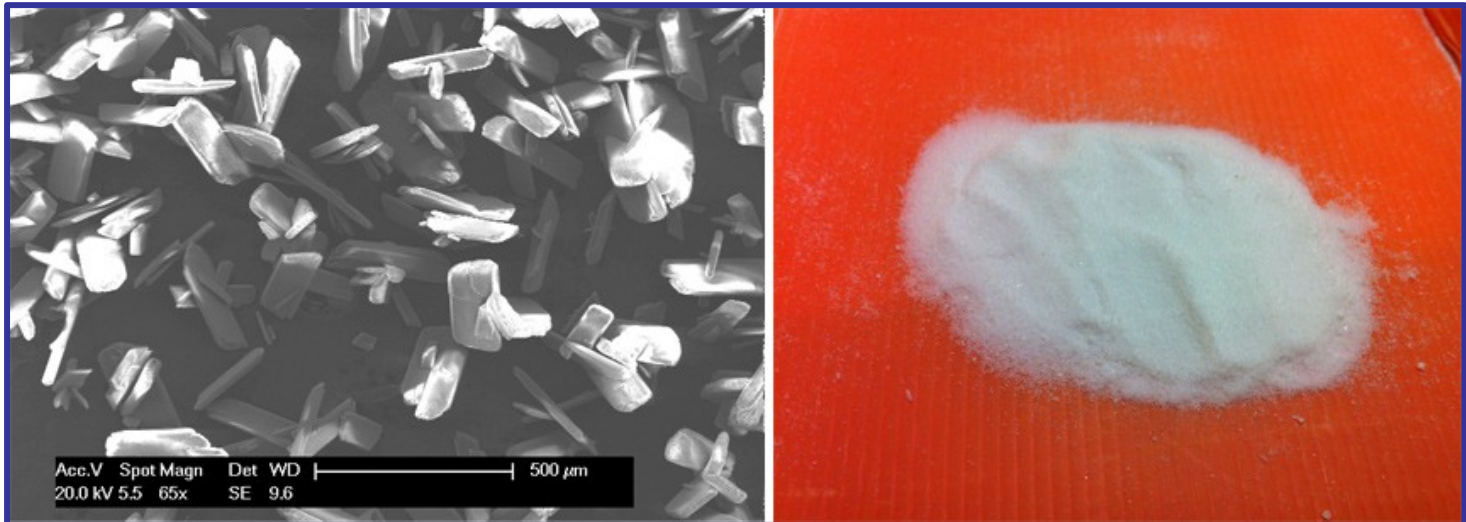


Polypropylene hollow fibers: Porosity 40%, OD/ID 300/220 μm

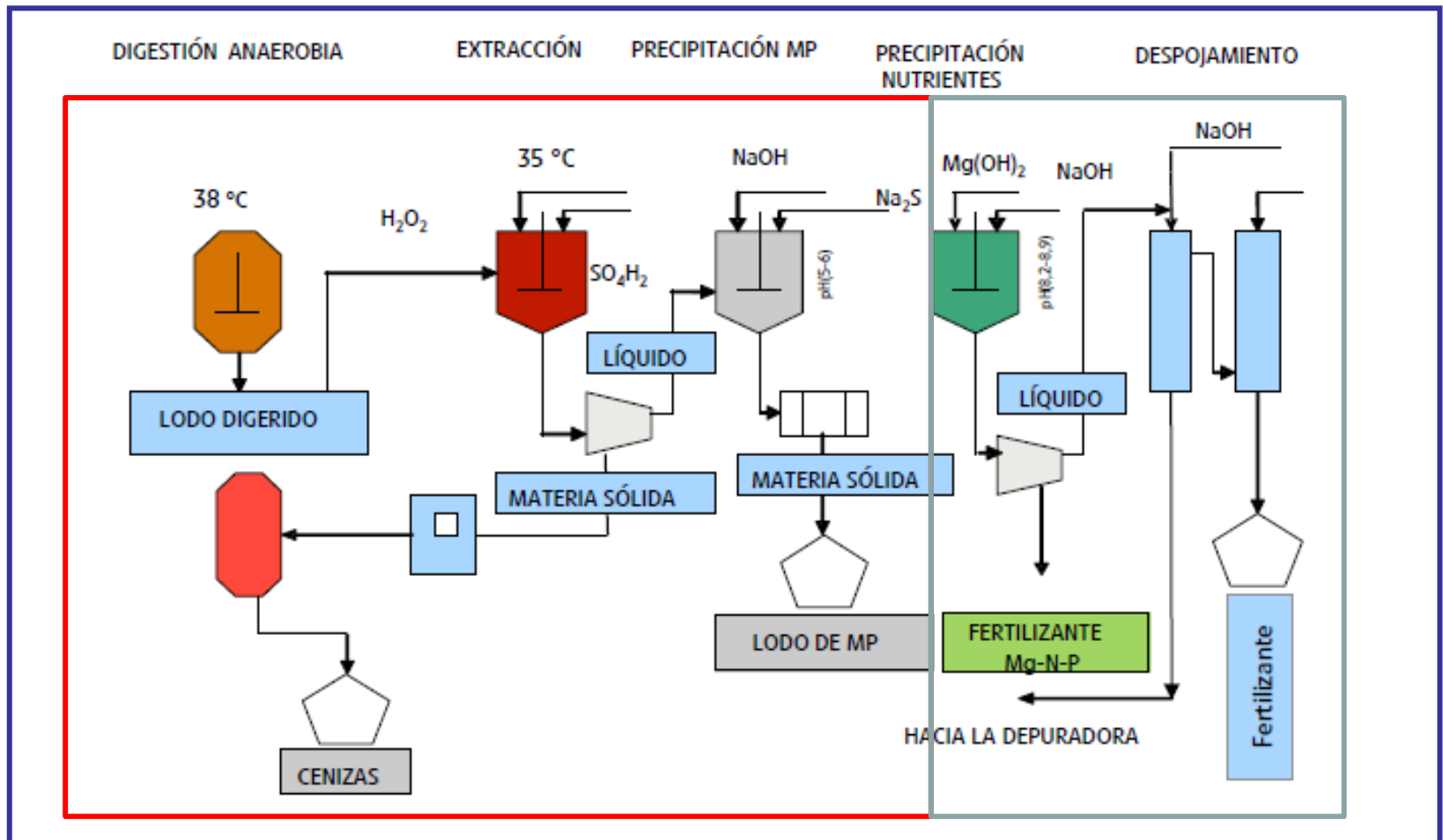


Nutrient recovery from effluents: sewage sludges, animal slurries

- Struvite precipitation: $\text{Mg}^{+2} + \text{NH}_4^+ + \text{PO}_4^{3-} \rightarrow \text{MgNH}_4\text{PO}_3 \downarrow$



Combined processes: demetalization-nutrient recovery

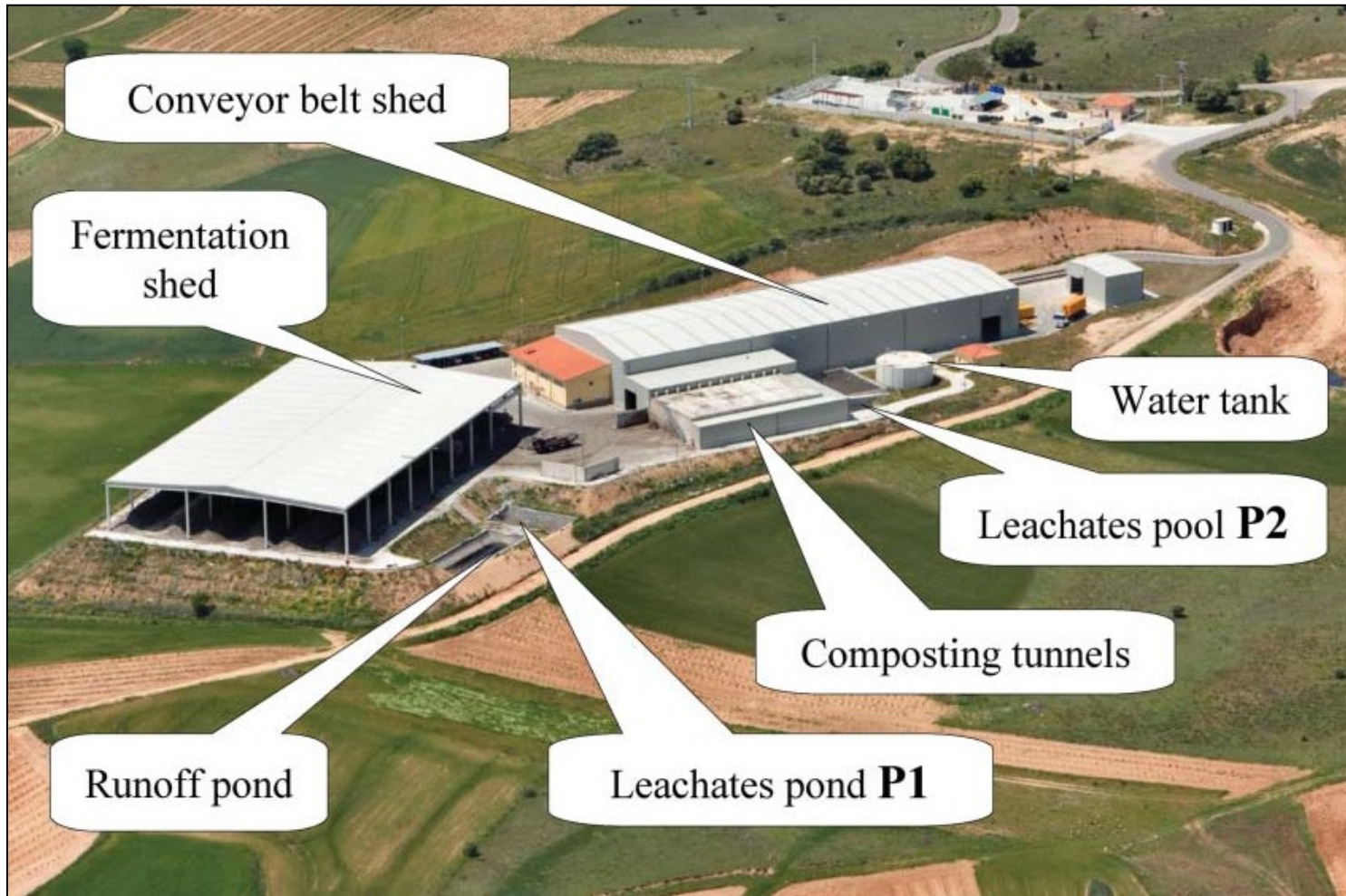


Properties of recovered products

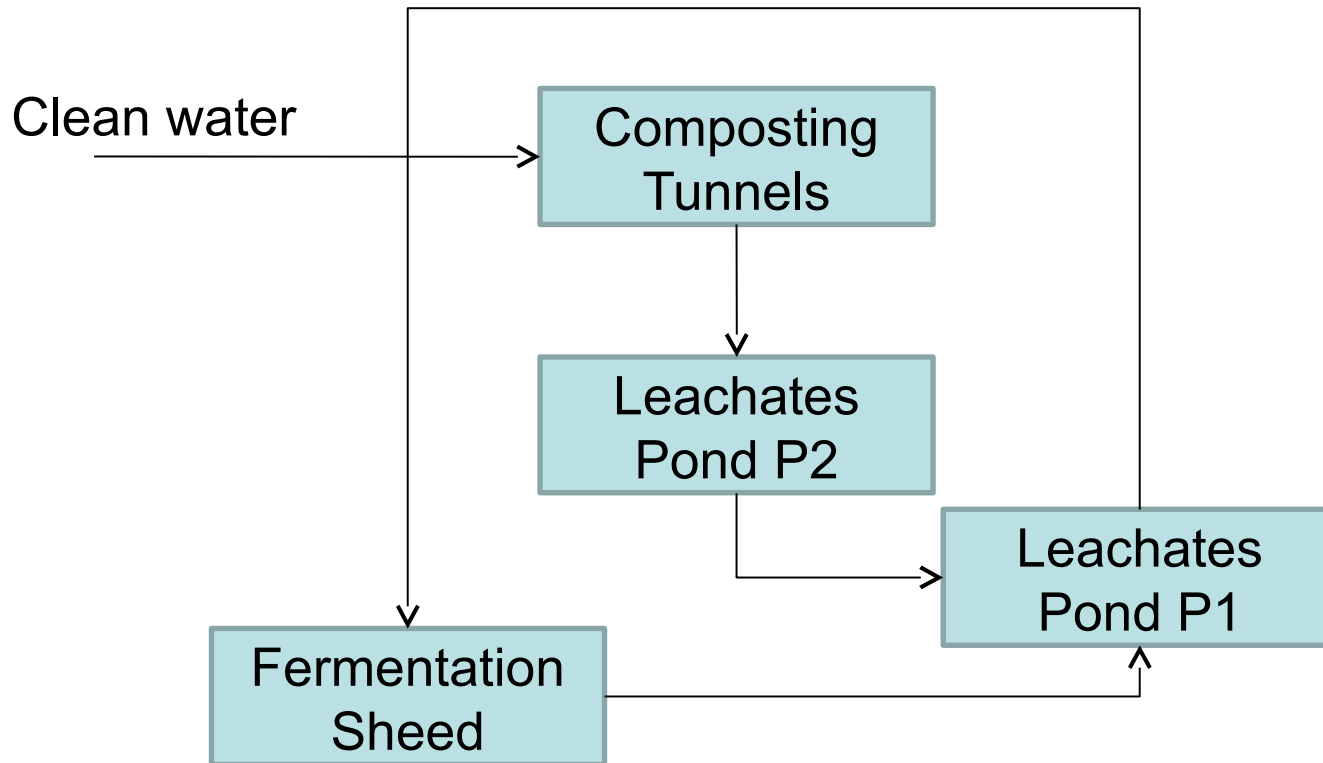
mg kg ⁻¹	STPI	STLb	ASPI
P	85762,10± 1892,87	93132,18± 1401,85	nd± nd
K	108,40± nd	2154,21± 145,54	21997,13± 992,34
S	1529,57± 36,59	1544,14± 2,16	19703,13± 369,09
Ca	13065,85± 320,59	11275,14± 321,67	822,92± 143,40
Mg	30268,06± 493,05	30544,70± 46,12	95,33± 22,36
Na	4423,99± 211,69	8225,17± 694,75	15088,94± 970,34
mg kg ⁻¹	STP	STLb	ASPI
Al	1626,84± 17,34	808,72± 18,24	nd± nd
Fe	3036,05± 73,16	2201,13± 34,46	4568,24± 78,92
Cd	3,78± nd	0,62± 0,18	1,36± 0,53
Co	3,03± 0,88	0,62± 0,18	11,04± 0,17
Cr	9,59± 1,13	4,97± 0,01	nd± nd
Cu	29,99± 1,19	72,37± 4,31	24,81± 2,79
Mn	46,60± 1,76	33,78± 3,38	324,41± 3,28
Ni	nd± nd	nd± nd	nd± nd
Pb	nd± nd	nd± nd	nd± nd
Zn	128,28± 11,10	50,49± 2,16	nd± nd

STPI, Struvite from pilot plant; **STLb**, Struvite from laboratory; **ASPI**, Ammonium sulfate from plant

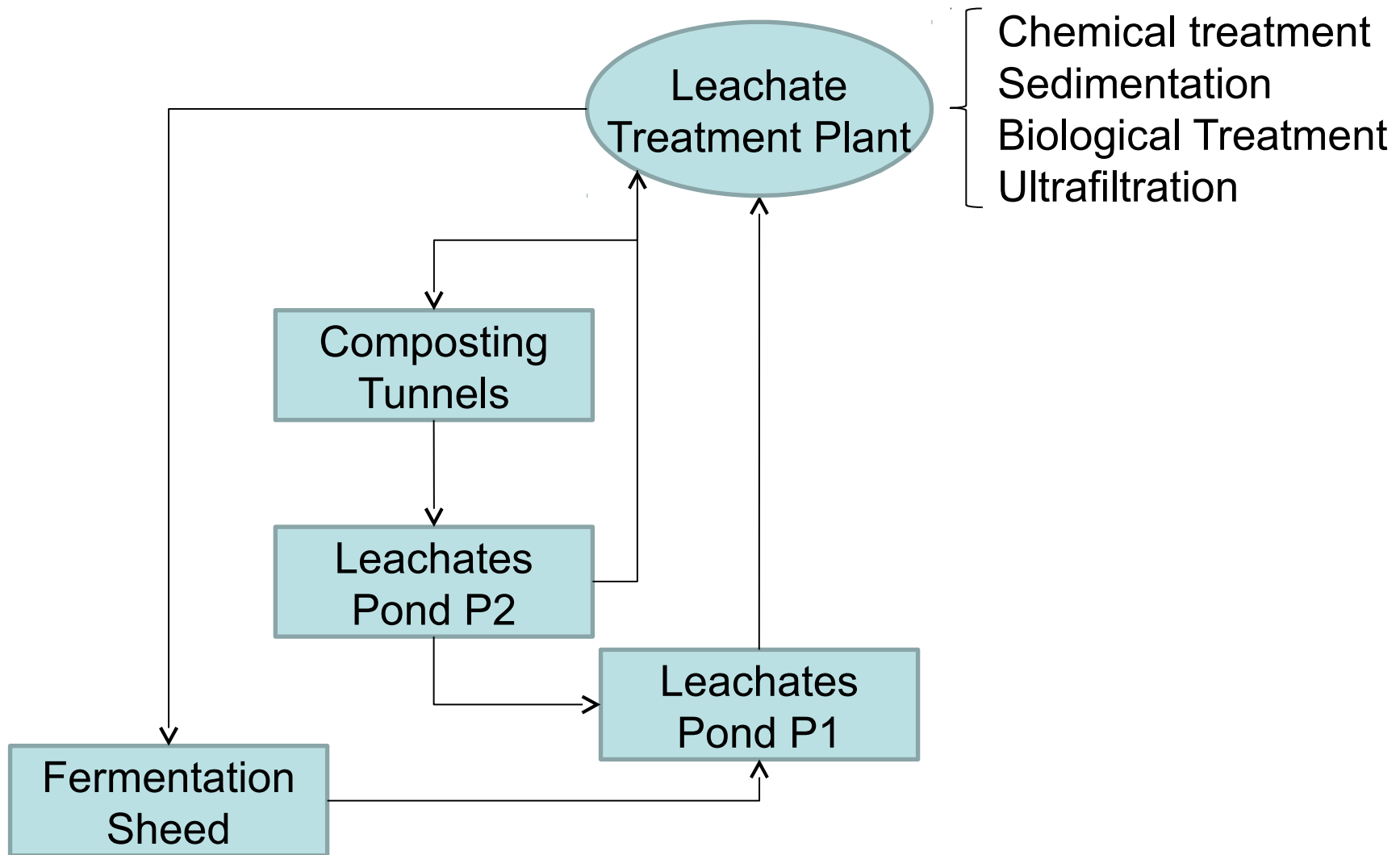
Treatment plant of Municipal Wastes, Aranda de Duero (Burgos)



Current procedure: recycling leachates in compost fermentation



Alternative procedure: treating leachates for compost fermentation



Biological treatment

Leachate mixtures	Parameters			Heavy metals							Elements				
	TOC	N total	N-NH ₄ ⁺	Cd	Cu	Ni	Pb	Zn	Cr	Mn	Fe	Na	K	Ca	Mg
LE100P2-LP100P2	80%	51%	30%	58%	58%	98%	46%	97%	81%	98%	93%	18%	29%	91%	21%
LE75P2P3-LP75P2P3	91%	57%	35%	52%	40%	92%	71%	96%	94%	96%	95%	27%	16%	94%	42%
LE50P2P3-LP50P2P3	79%	11%	13%	42%	21%	26%	21%	88%	70%	88%	83%	20%	19%	84%	36%
LE100P1-LP100P1	98%	38%	8%	23%	28%	42%	13%	77%	69%	77%	96%	0%	23%	78%	23%
LE50P1P3-LP50P1P3	100%	82%	83%	45%	47%	86%	59%	88%	98%	68%	99%	78%	58%	73%	13%

Ultrafiltration

Leachate mixtures	Parameters			Heavy metals							Elements				
	TOC	N total	N-NH ₄ ⁺	Cd	Cu	Ni	Pb	Zn	Cr	Mn	Fe	Na	K	Ca	Mg
LE100P2-LP100P2	81%	49%	19%	57%	66%	99%	42%	97%	86%	97%	93%	3%	13%	92%	37%
LE75P2P3-LP75P2P3	83%	33%	4%	36%	15%	86%	57%	92%	87%	92%	98%	5%	19%	87%	28%
LE50P2P3-LP50P2P3	71%	22%	3%	45%	95%	19%	39%	87%	82%	86%	97%	15%	31%	73%	33%
LE100P1-LP100P1	97%	40%	21%	37%	75%	72%	23%	90%	89%	94%	99%	4%	9%	88%	34%
LE50P1P3-LP50P1P3	100%	39%	28%	85%	51%	76%	55%	93%	78%	95%	100%	4%	11%	93%	37%

Mixtures

- 100% P2 without decanting
- mixture of 75% P2 and 25% P3 leachates without settling
- mixture at 50% of P2 and P3 leachates without settling
- 100% leachate P1 and decantation
- mixture at 50% of P1 and P3 with decantation

Thanks you for your attention!

¡Gracias por su atención!