Green remediation method for soils polluted with some heavy metals

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Background

- The remediation of heavy metals contaminated soils is still recognized as the most difficult problem to be solved due to its high expenses.
- Soil washing with synthetic chelating agents such as **EDTA** seem to be most popular.
- EDTA is quite **persistent** in the environment due to its **low biodegradability** (Masakazu et al., 2008).
- There is a need for an **eco-friendly** washing material.

OBJECTIVE

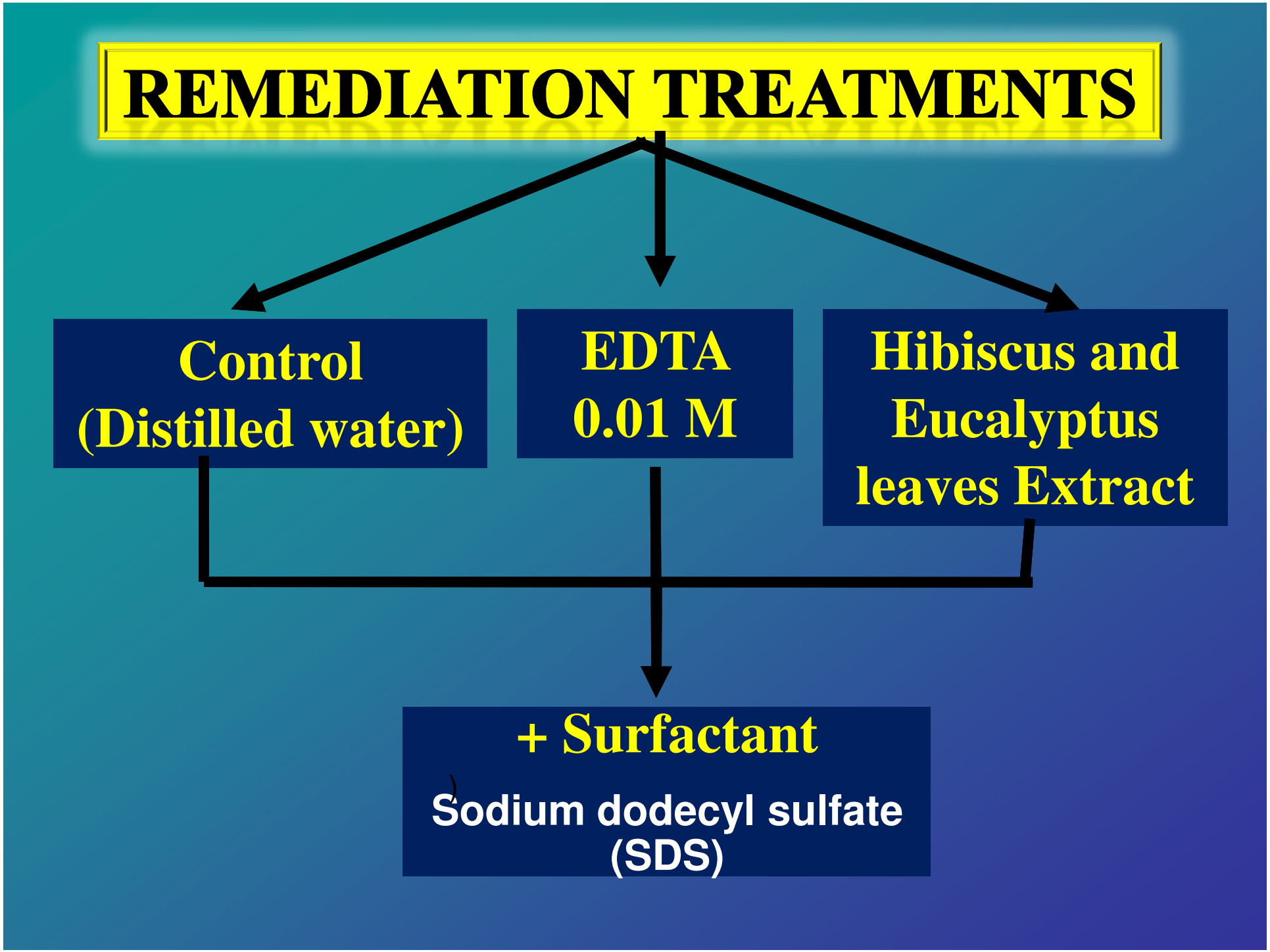
- To evaluate the use of the green leaves extract as an eco-friendly material instead of EDTA in the remediation of the heavy metals polluted soils.

Materials

Three Soil Types

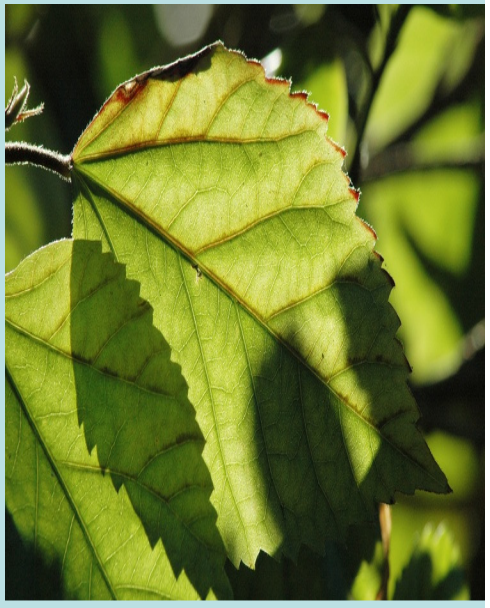
Soil texture	Particle size fraction (g/kg)			pH (1:2.5	EC dS/m	OM g/kg	$CaCO_3$ g/kg	CEC Cmol/kg
	Sand	Silt	Clay					
Sandy	748	144	108	7.79	1.14	1.5	11.6	9.4
Loamy	460	378	162	7.83	1.94	11.3	22.0	33.6
Clay	424	90	486	7.55	3.66	26.6	3.26	48.1

Soil Type	pH (1:1)	EC dS/m (1:1)	Pb (mg/kg)		Cd (mg/kg)		Co (mg/kg)		Cr(mg/kg)	
			Aqua-Regia	DTPA	Aqua-Regia	DTPA	Aqua-Regia	DTPA	Aqua-Regia	DTPA
Sandy	8.0	10.4	1134	1027	44.53	34.65	165.7	23.97	854.4	189.1
Loamy	8.2	15.0	1421	1008	52.71	31.65	229.3	18.62	878.2	153.8
Clay	8.2	16.4	1488	988	54.09	23.13	346.1	7.70	938.0	67.2


REMEDIATION TREATMENTS
Control (Distilled water)
EDTA 0.01 M
Hibiscus and Eucalyptus leaves Extract
+ Surfactant
Sodium dodecyl sulfate (SDS)

Hibiscus

Enriched with phenoles



Eucalyptus

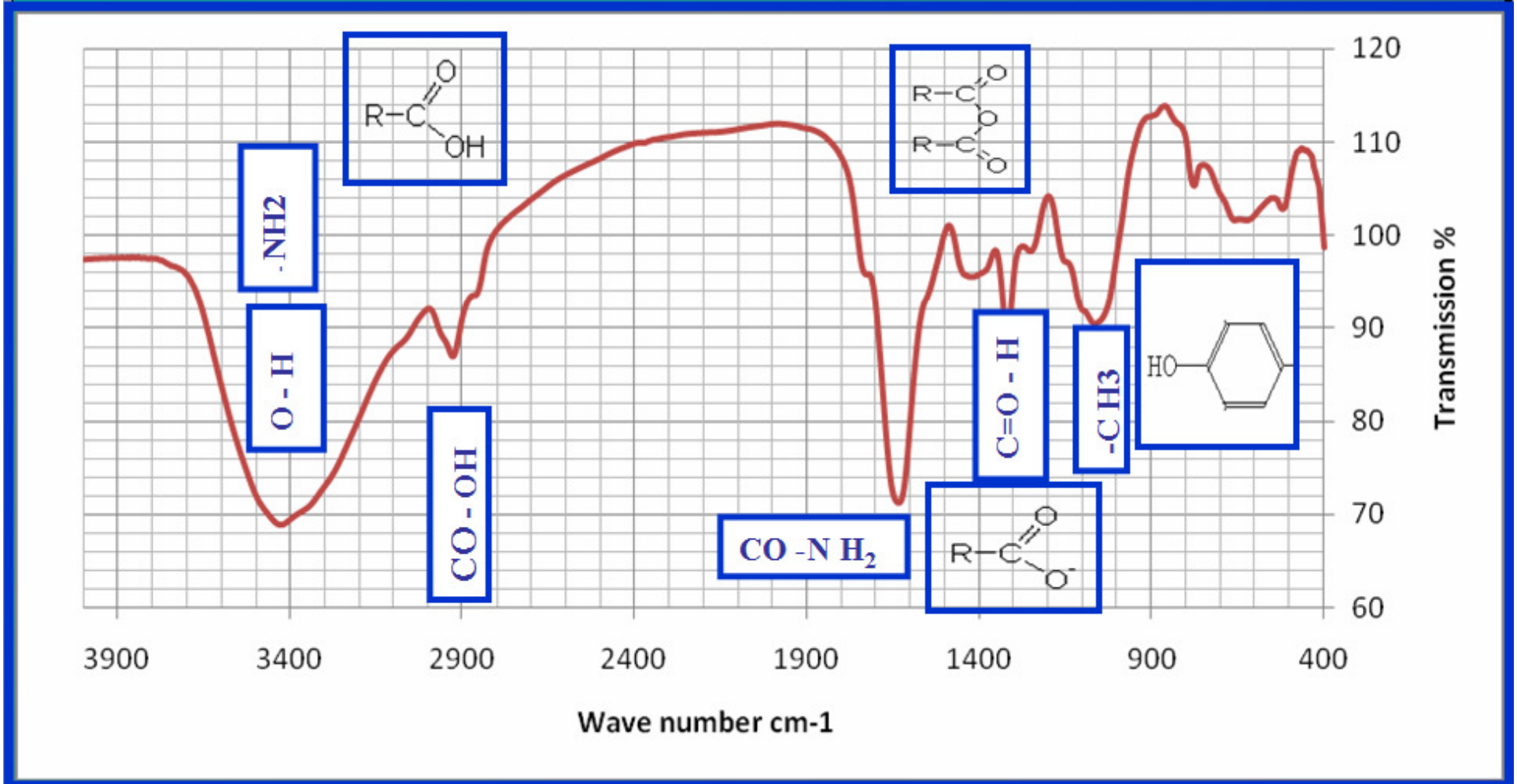
Enriched with aromatics

Green Leaf Extraction

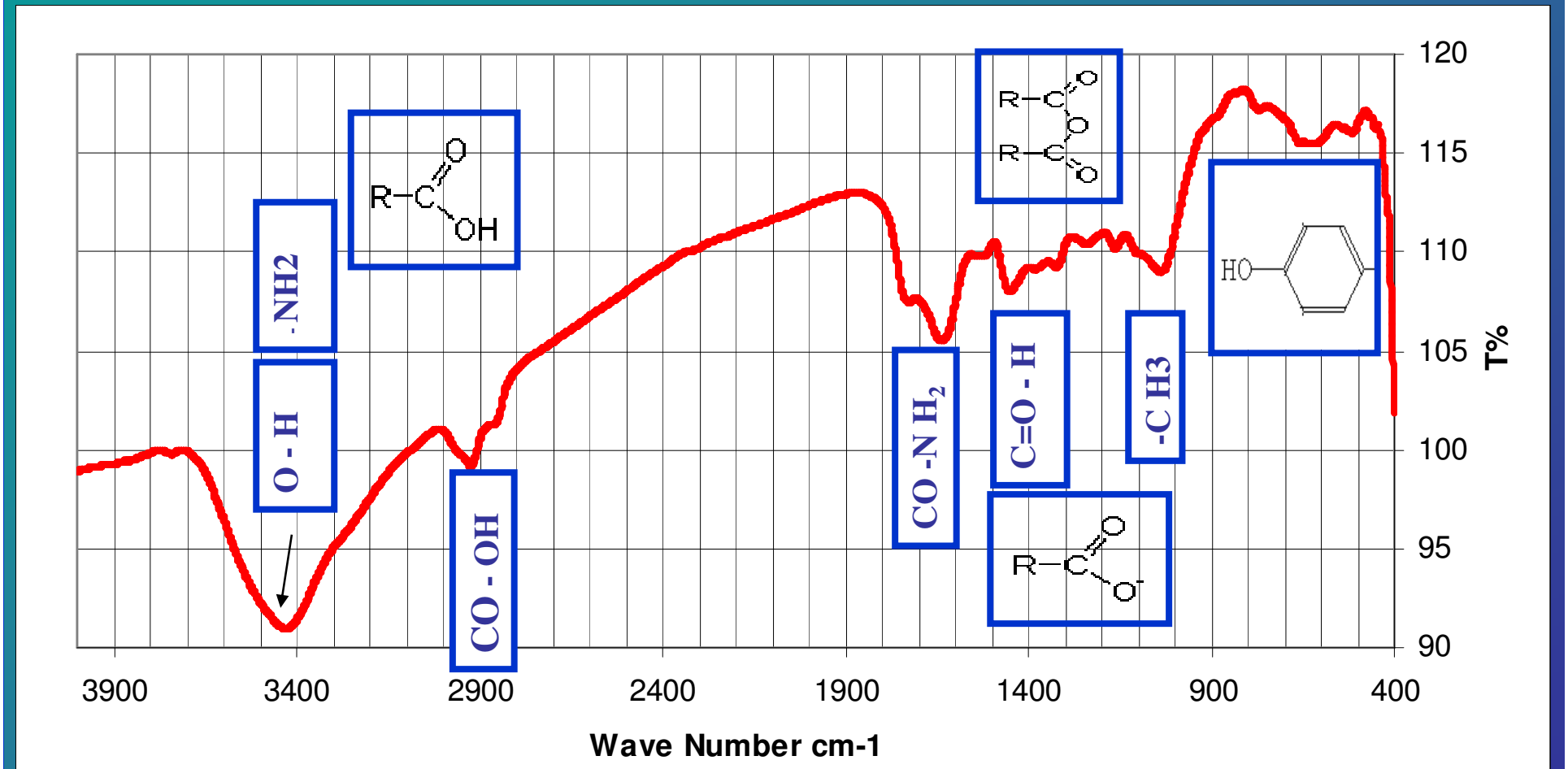
Green Leaf Extraction

Infra-red Examination
Of the Green Leaf Extract

Hibiscus


-NH2
O - H
CO - OH
CO -N H2
C=O - H
-C H3
HO
Transmission %
120
110
100
90
80
70
60
3900
3400
2900
2400
1900
1400
900
400
Wave number cm-1

Eucalyptus


120
115
110
105
100
95
90
T%
3900
3400
2900
2400
1900
1400
900
400
Wave Number cm-1
O - H
NH2
CO - OH
CO -N H2
C=O - H
-C H3
R—C(=O)—OH
R—C(=O)—O—C(=O)—R
R—C(=O)—O⁻
HO

IR -results

Group	Bond type	Frequency Cm-1	Group	Formula	Frequency Cm-1
	C–H bending	985–1472	amides	-NH2	1575
	C–H stretching	2845– 2909	aromatic		754–762
	O–CH3	1475	C–O–C stretching		1164
ketone	C=C,	1575– 1748	phenols		1271– 3627
carboxylic	-COOH	1319–1717			

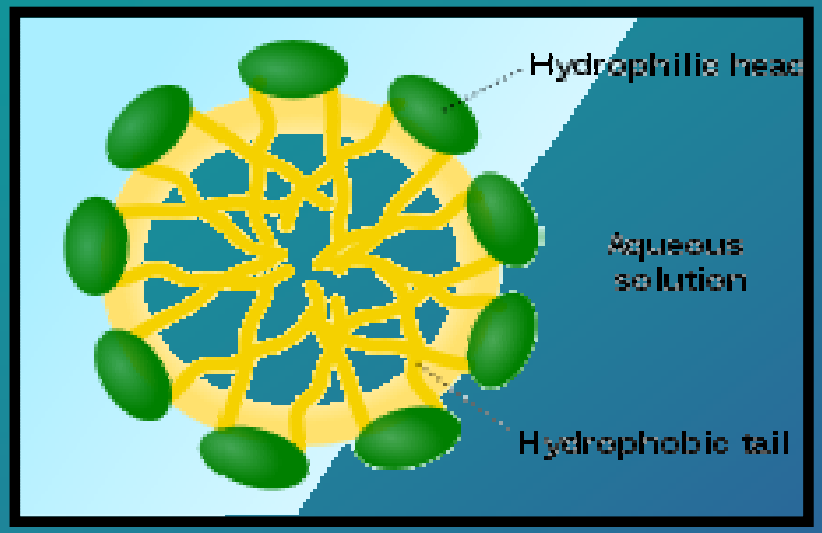
IR -results

- The slurry of the leaves of both Hepescus and Eucalyptus were found to contain high amounts of active groups such as carboxyl, phenol, amino as well as other legends susceptible for metal complexation

Surfactants

Compounds that lower the surface tension of a liquid, the interfacial tension betwee two liquids, or that between a liquid and a solid.

Surfactant Chemical Structure



Organic compounds that are amphiphilic, contain both

*hydrophobic groups (their tails)

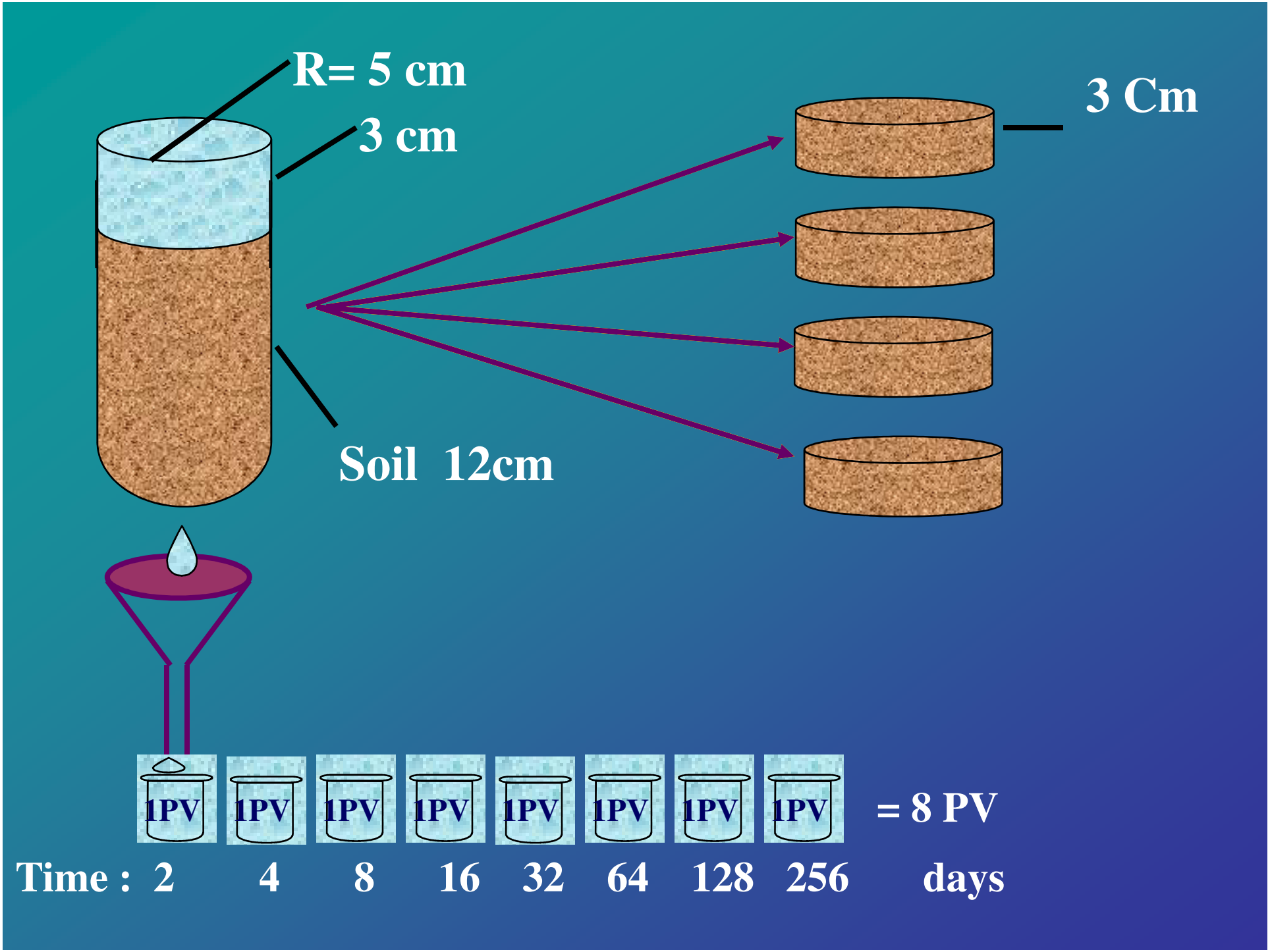
*hydrophilic groups (their heads).

Groupings Allow For Surface Interaction With Many Contaminants

Role of Surfactants

- Surfactants also have a part in removing heavy metals (HMs) from soil surfaces, probably through the formation of complexes, micelles and ion exchange processes (Gao,2007).
- Under acidic or alkalic condition, surfactants have removed heavy metals from soil through direct complexation followed by solubilization (Herman et al,. 1995, Mulligan et al., 1999, Abidin and Yeliz, 2005 and Mulligan, 2005).

Leaching Columns and sampling


R= 5 cm
3 cm
3 Cm
Soil 12cm
1PV
1PV
1PV
1PV
1PV
1PV
1PV
1PV
= 8 PV
Time : 2 4 8 16 32 64 128 256 days

Results

Soil-pH changes

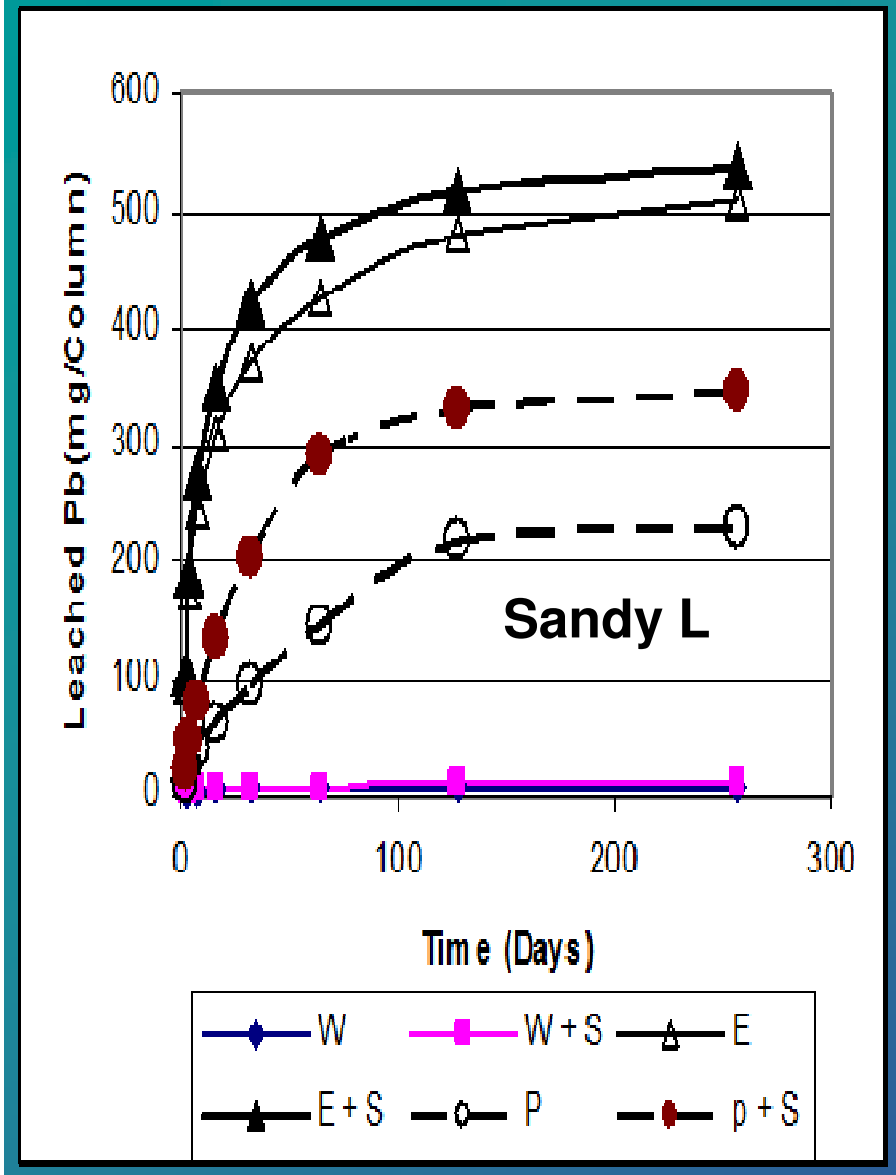
PV	Sandy (1:2.5) = 8.00					
	Cont.	W + S	E	E + S	P	p + S
1	7.44	7.16	7.32	7.28	6.28	6.13
8	7.39	7.15	7.31	7.25	5.31	5.11

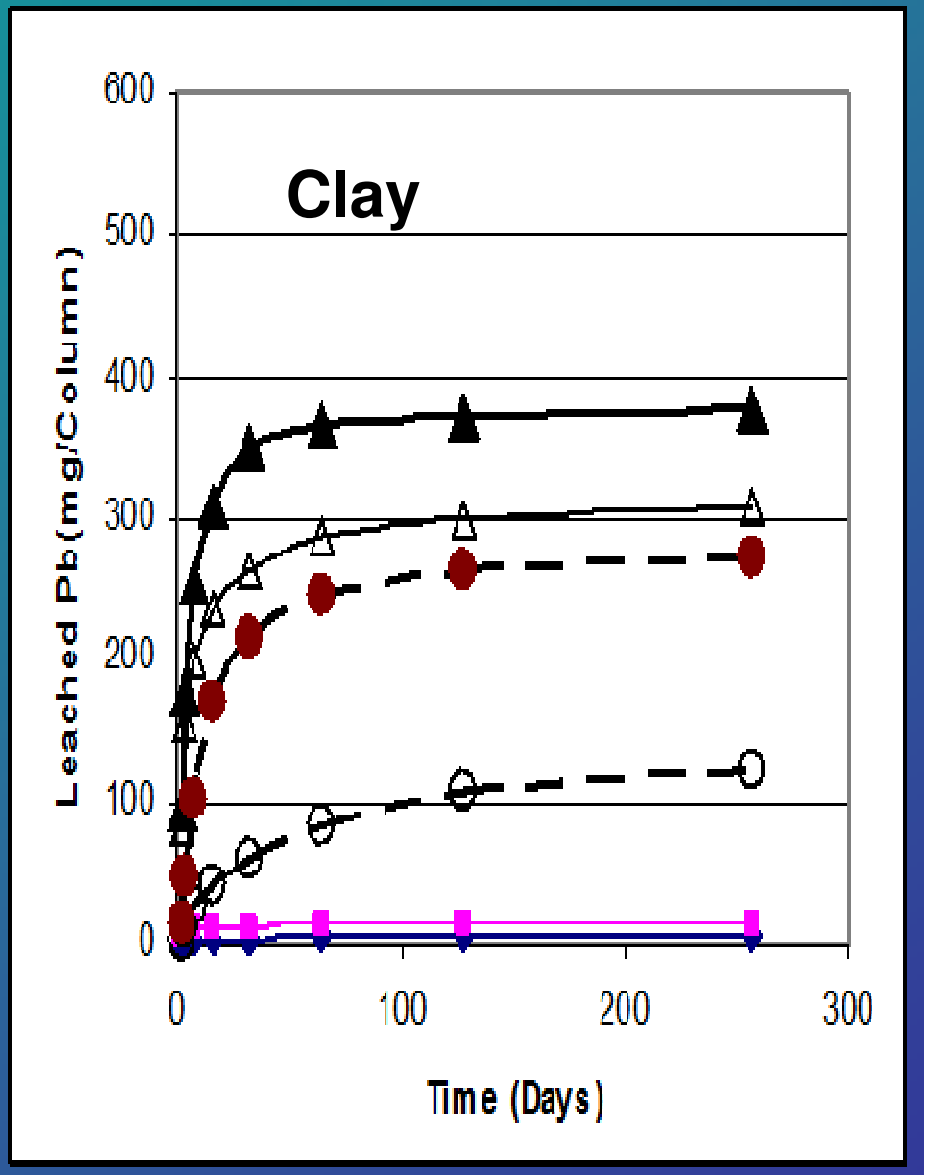
PV	Clay (1:2.5) = 8.44					
	Cont.	W + S	E	E + S	P	p + S
1	8.42	8.11	8.01	7.89	7.44	7.16
8	7.65	7.39	7.15	7.01	5.48	5.54

Soil Salinity Changes

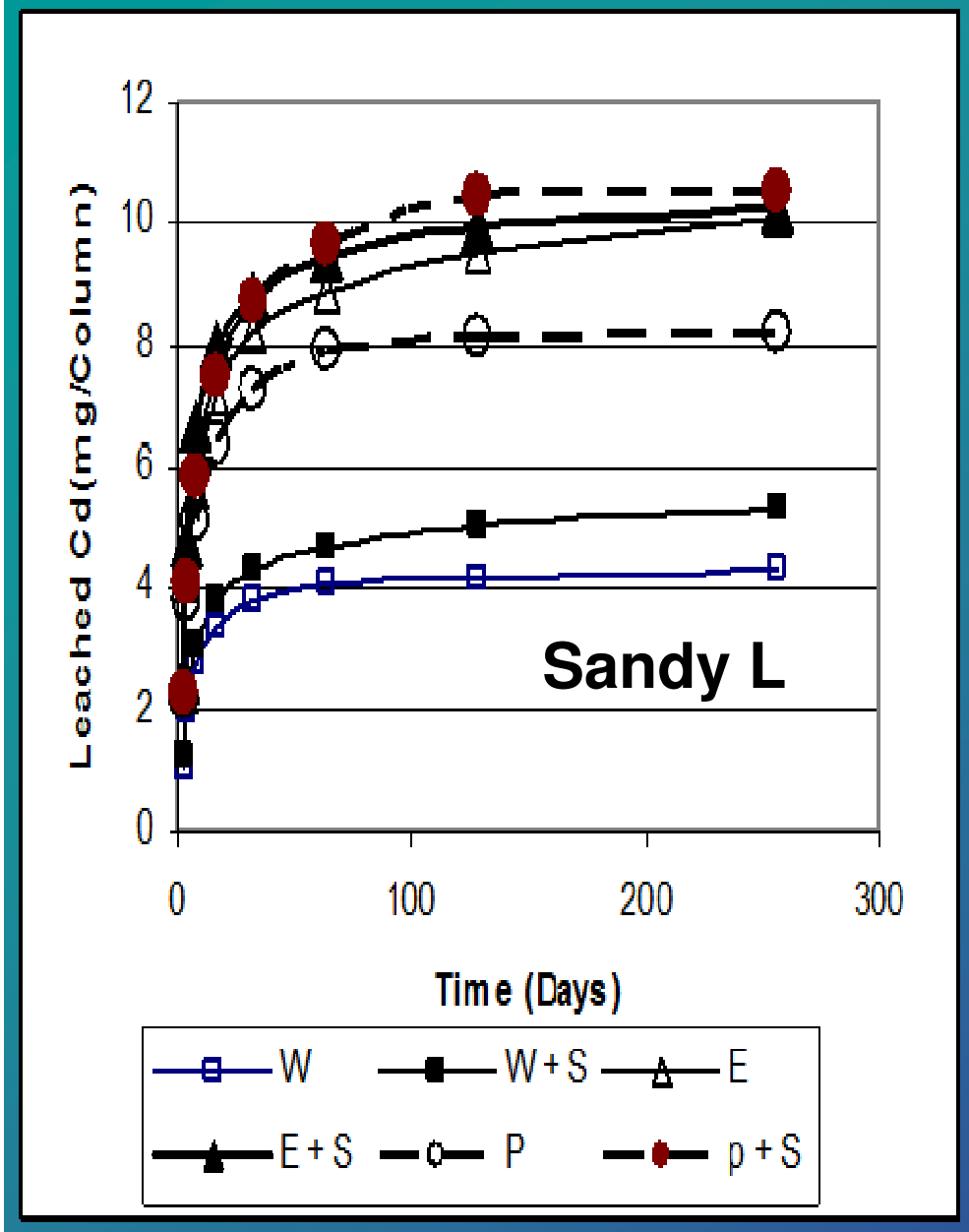
PV	Sandy (1:2.5) =10.4 dS/m					
	Cont.	W + S	E	E + S	P	p + S
1	11.0	10.6	10.0	9.9	9.8	9.7
8	2.61	2.83	2.11	2.51	2.88	2.81

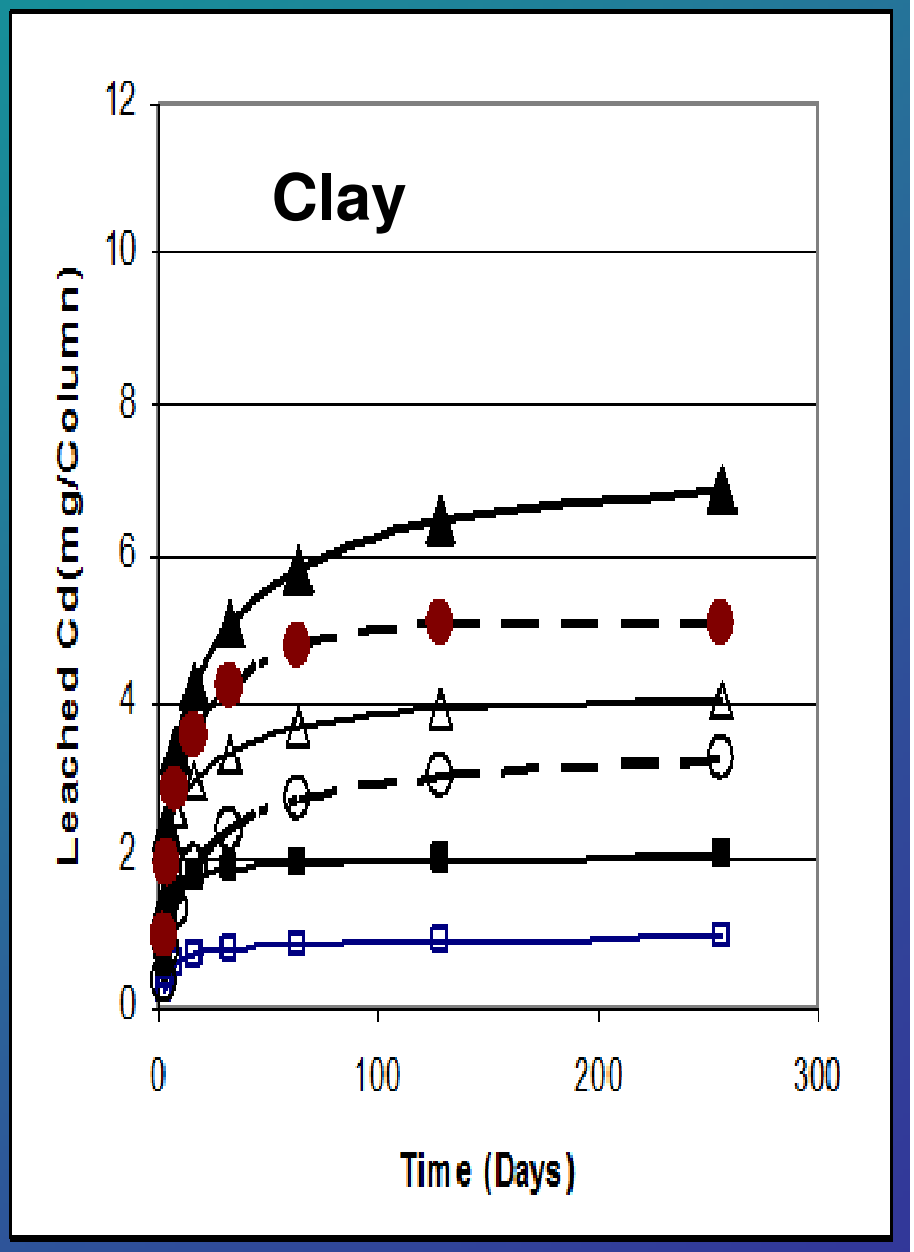
PV	Clay (1:2.5) =26.4 dS/m					
	Cont.	W + S	E	E + S	P	p + S
1	26.4	25.6	24.4	24.0	23.5	22.9
8	2.53	2.32	3.90	2.17	2.00	3.09



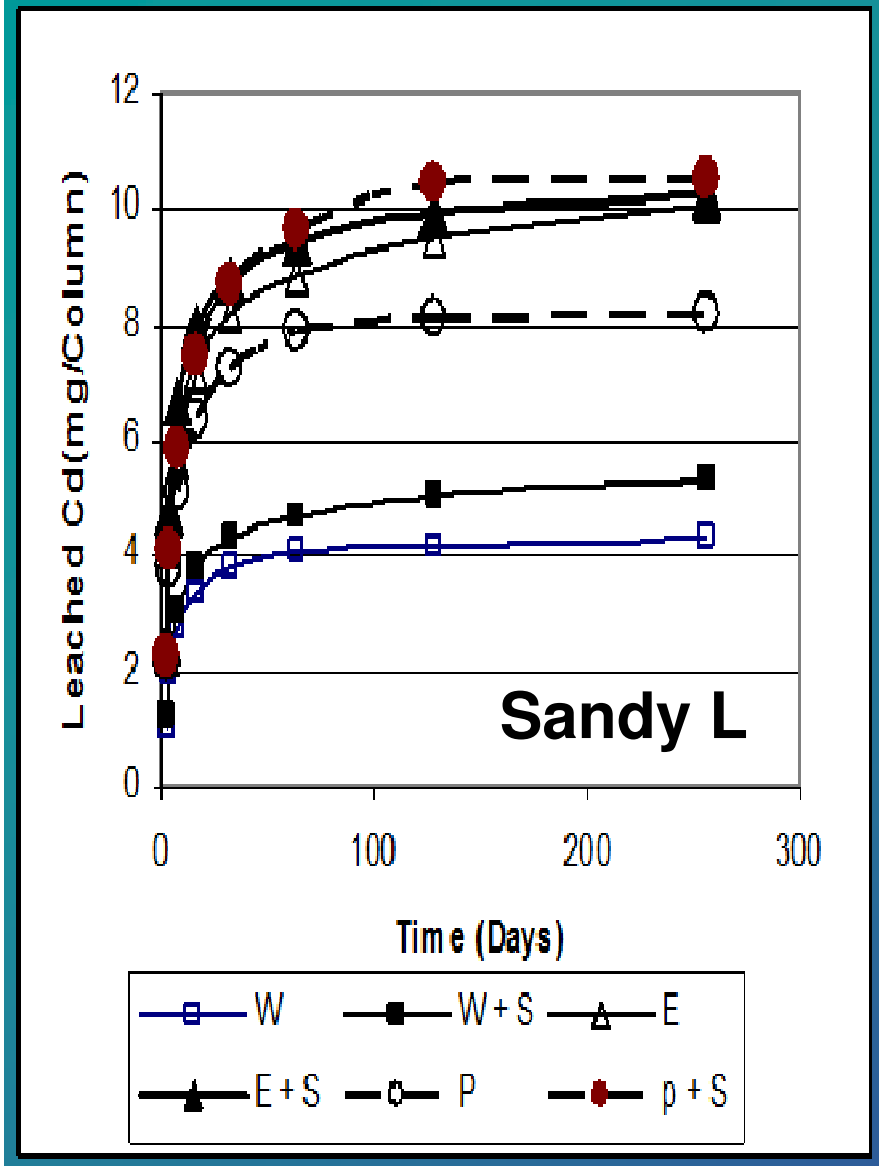


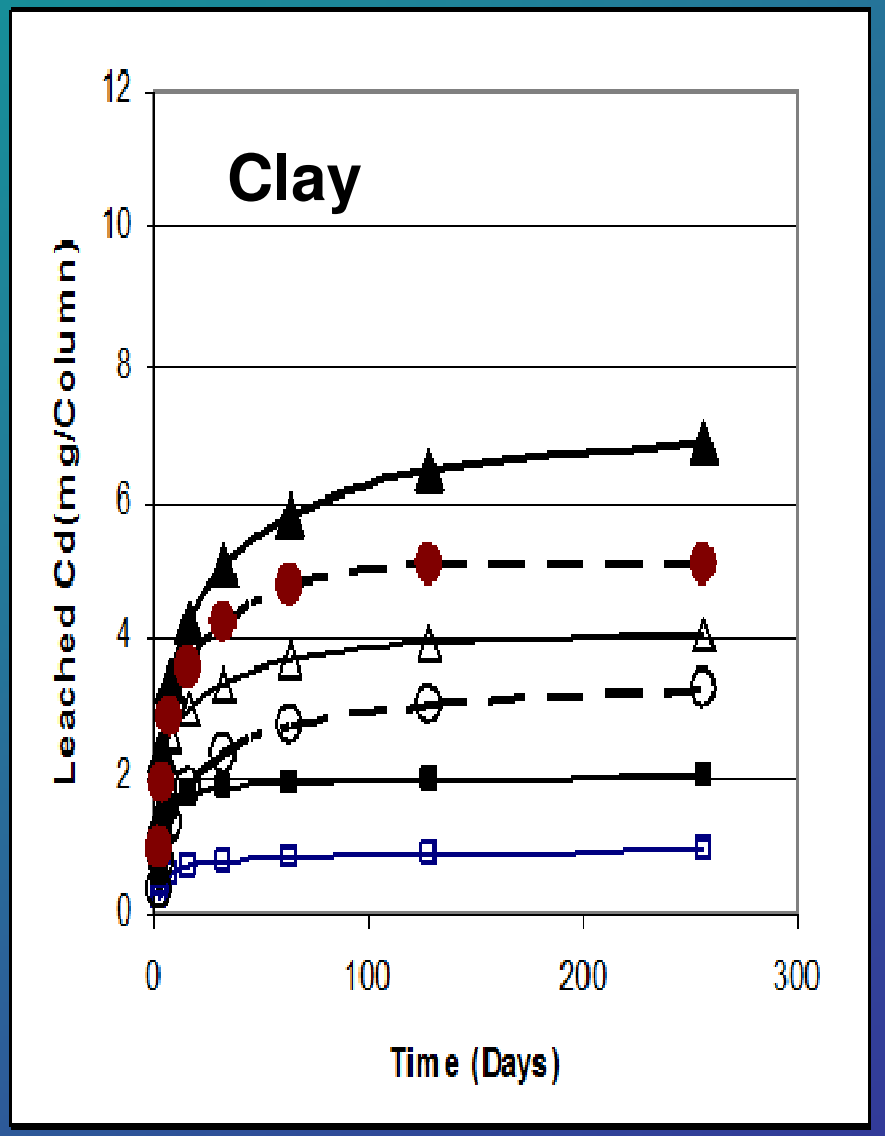
The cumulative curves of the leached amounts of Pb (mg/column)



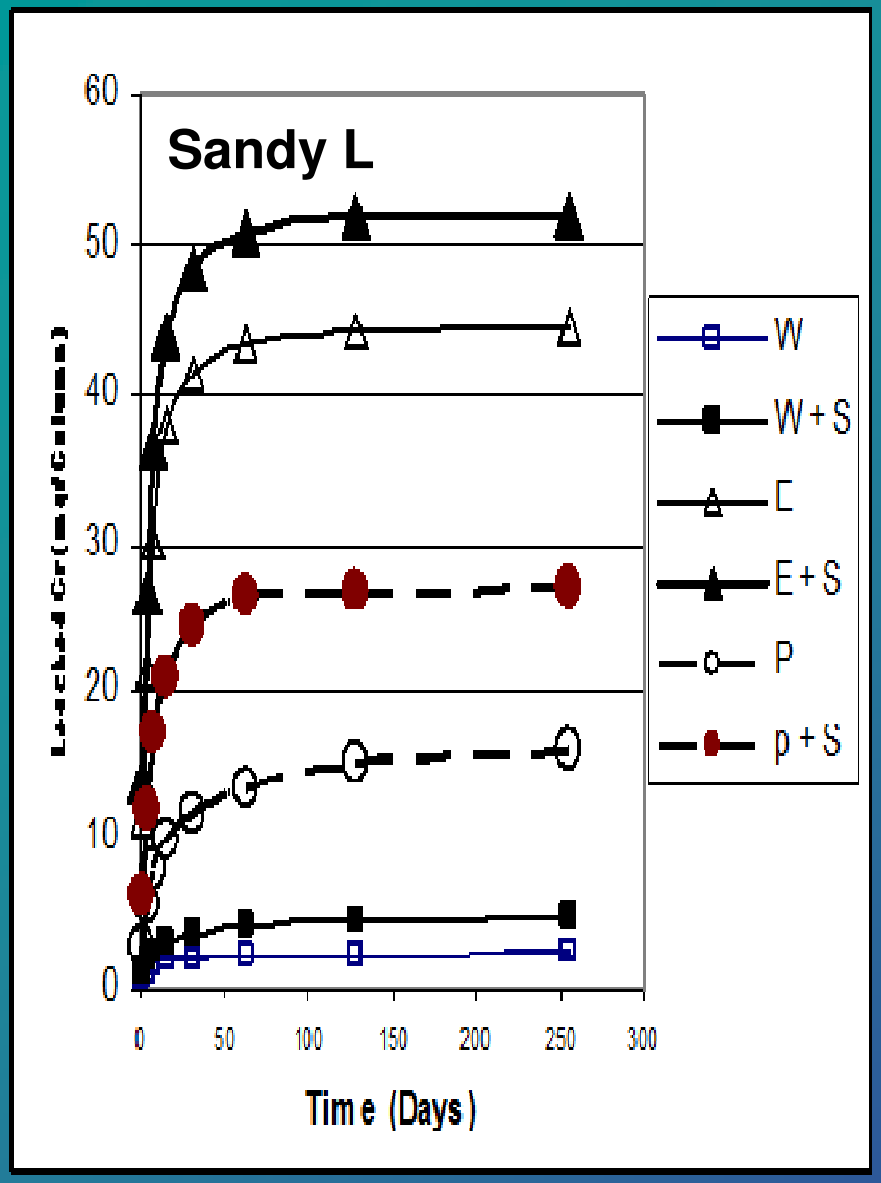


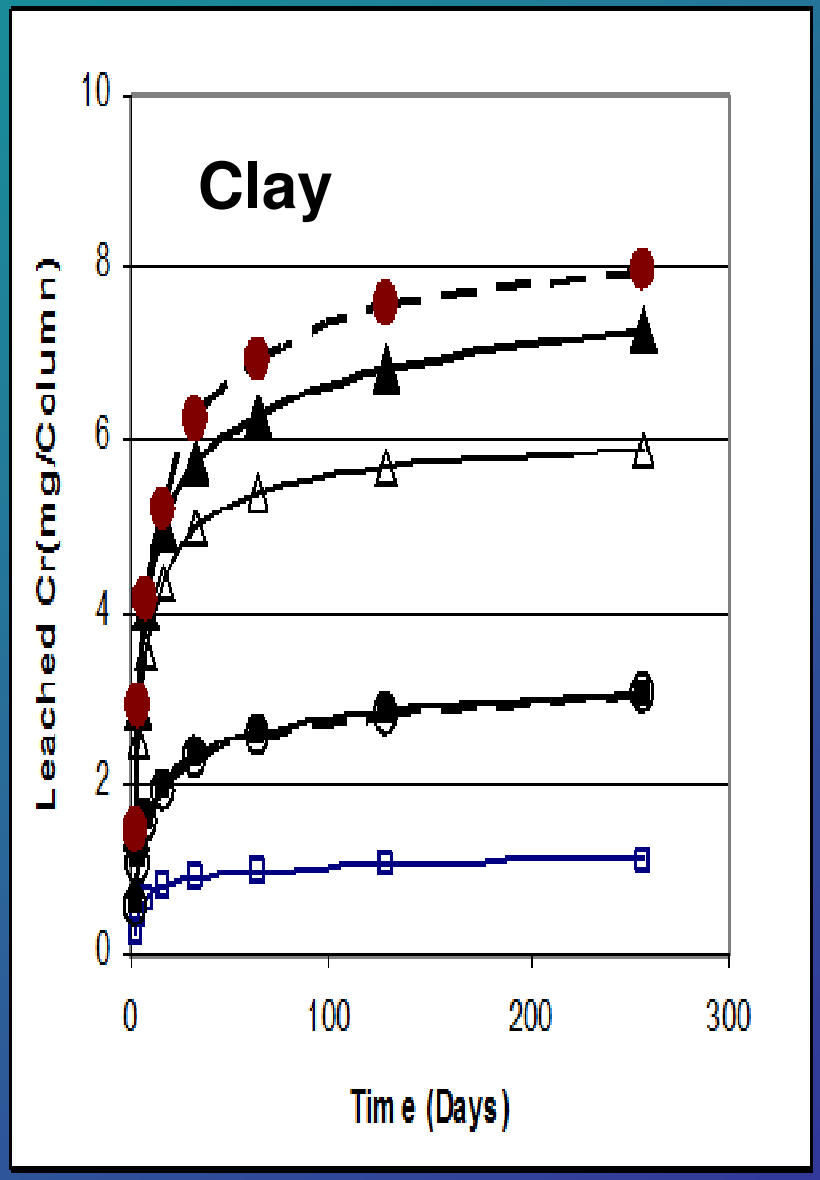
The cumulative curves of the leached amounts of Cd (mg/column)





The cumulative curves of the leached amounts of Co (mg/column)



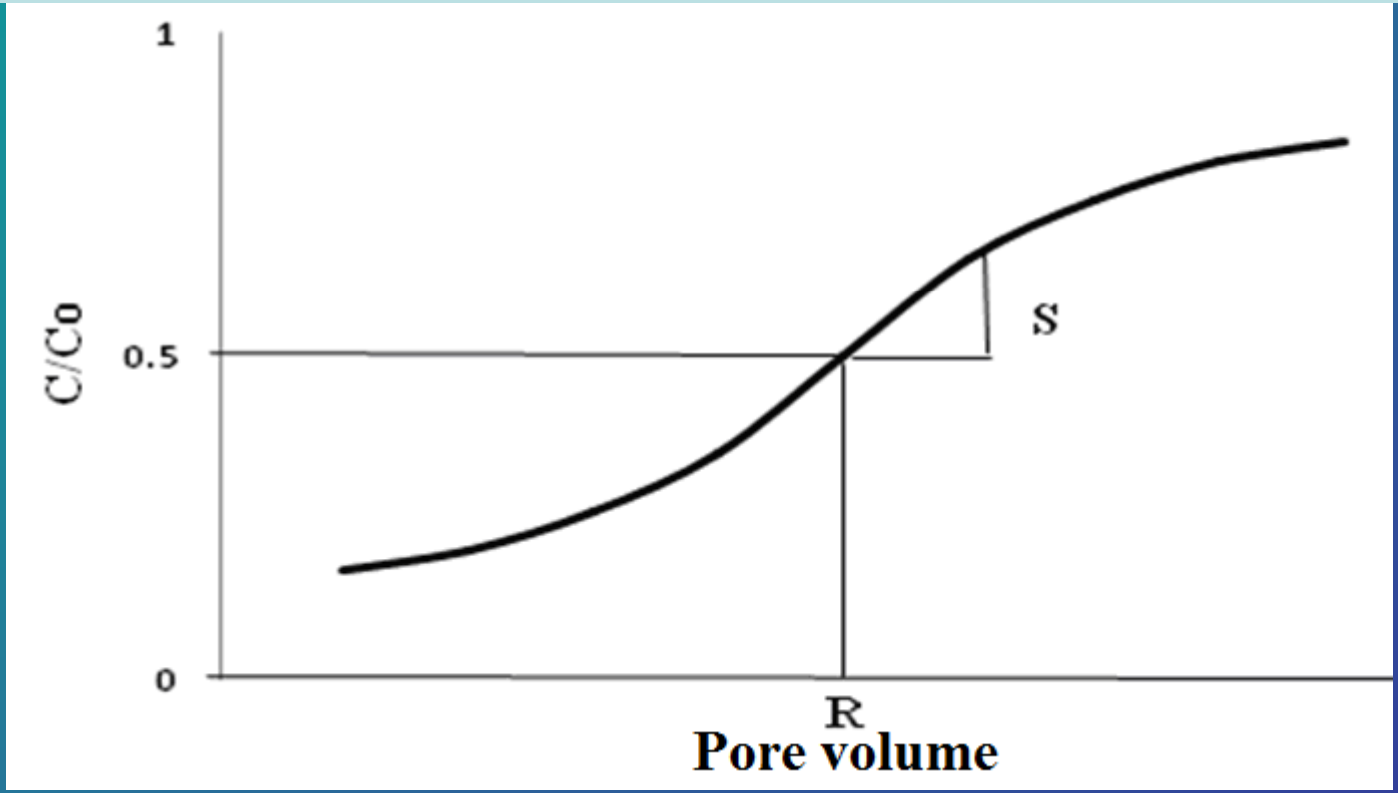


The cumulative curves of the leached amounts of Cr (mg/column)

Conclusions

- **Sandy loam** showed the **highest amounts** of the leachable metals while the **lowest amount** was recorded for the **clay** one.
- The washing with EDTA extracted higher amounts of Pb and Cd as compared to the plant slurry in sandy loam or clay soils.
- The **surfactant** enhanced leaching of all the studied metals and soils.
- In Cobalt, **plant slurry (P and P+S)** was superior or equal to EDTA (E and E+S)

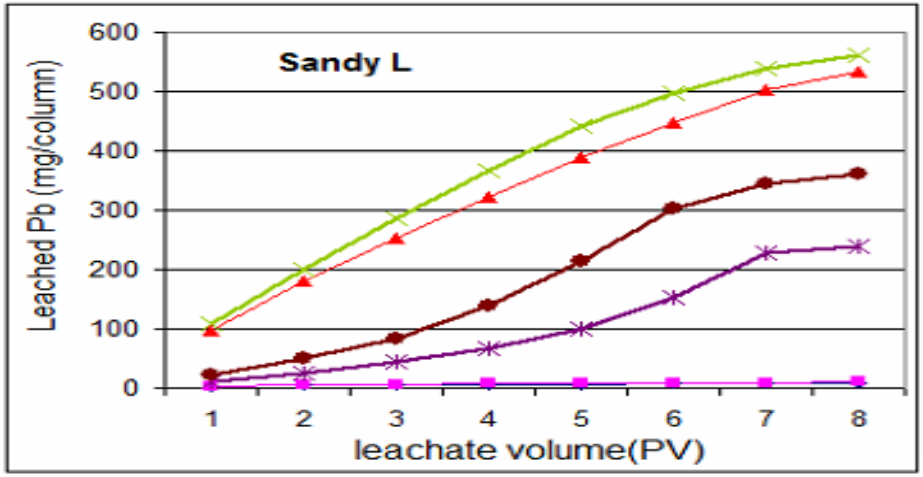
Calculating Retardation (R) from the model breakthrough curve (BTC)

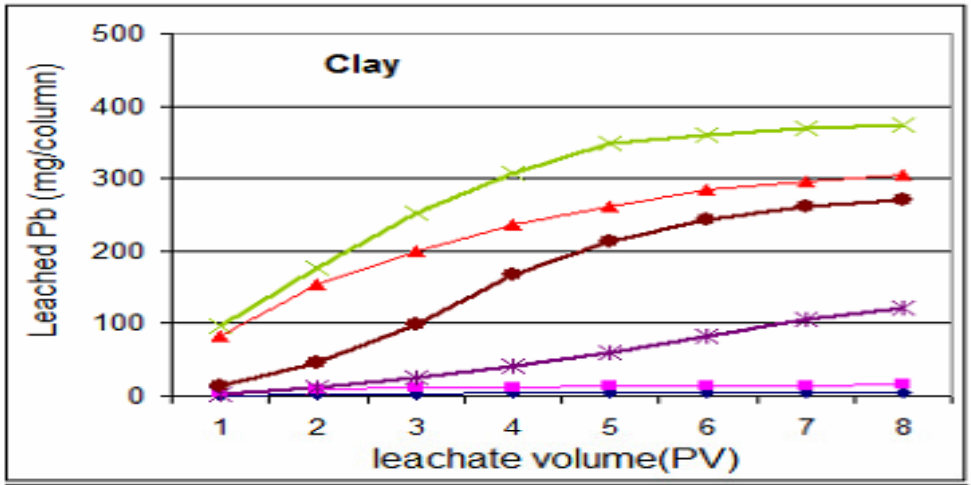


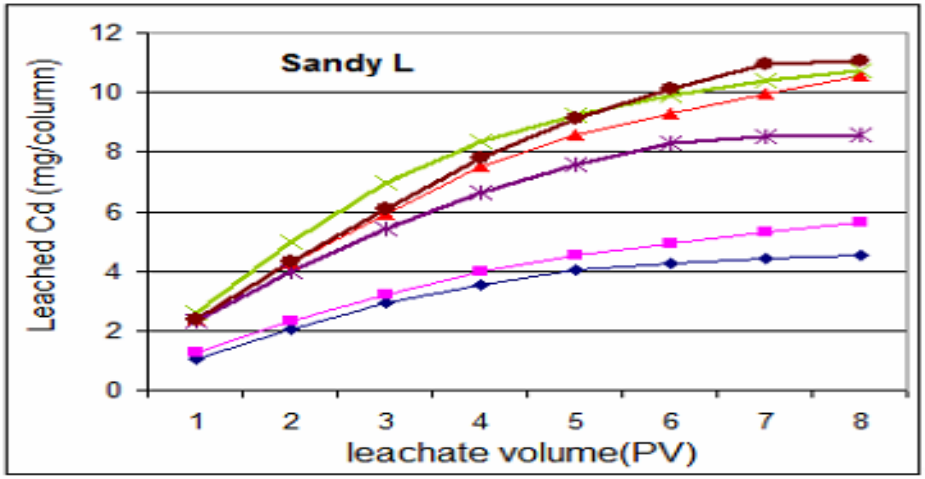
Retardation factor (R)

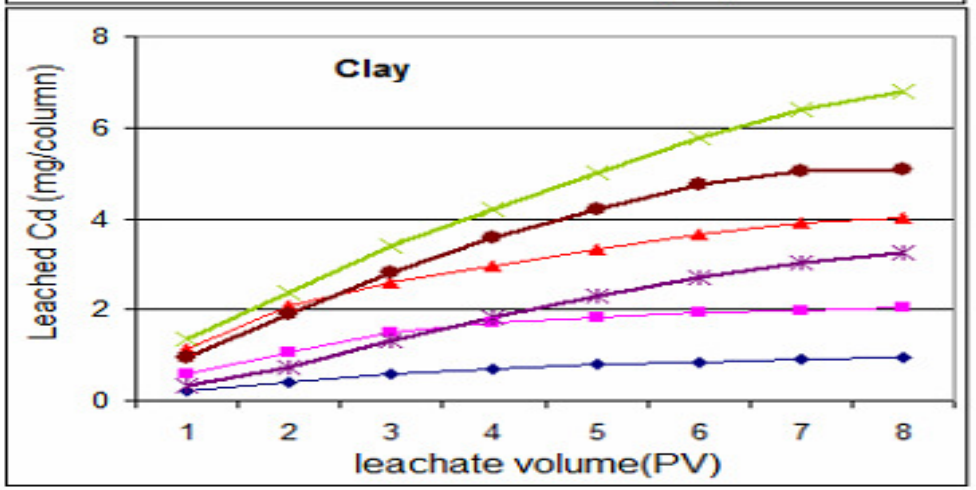
- **Retardation factor (R)** which represent the number of pore volumes which leached (Mn) 50% of the total leached amounts (Mt) of each metal (Mn/Mt = 0.5)

The cumulative amounts of the leached Pb and Cd (mg/column)



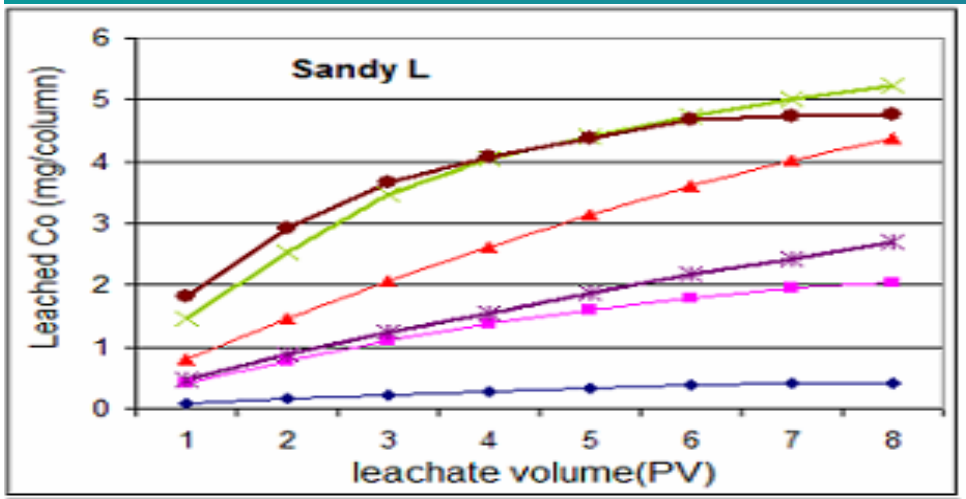


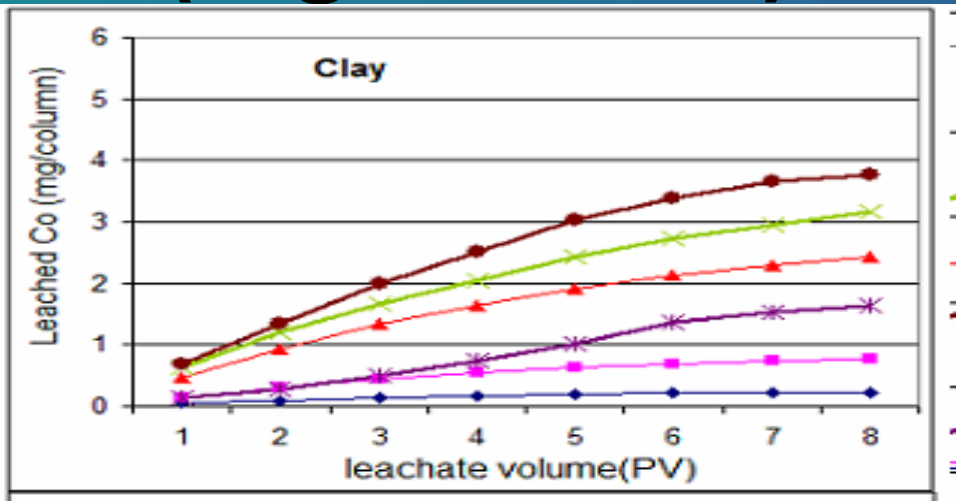


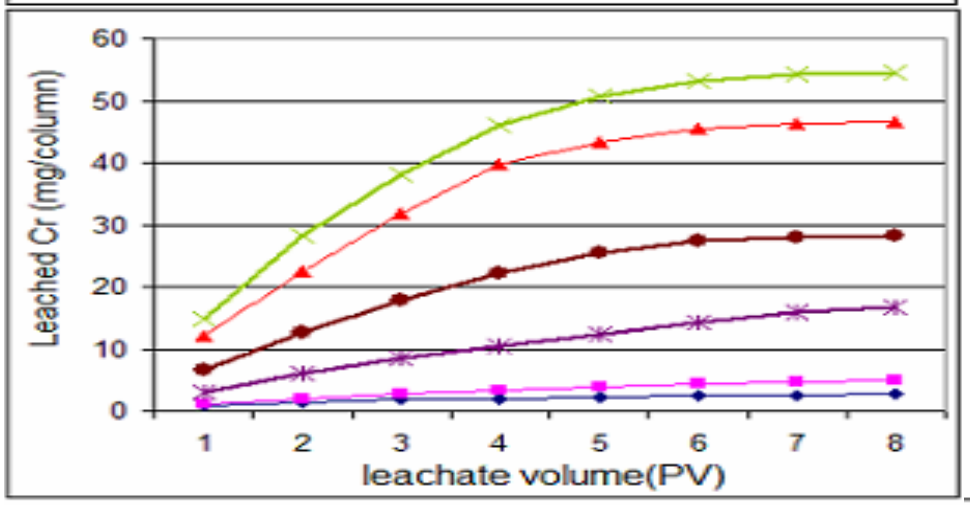


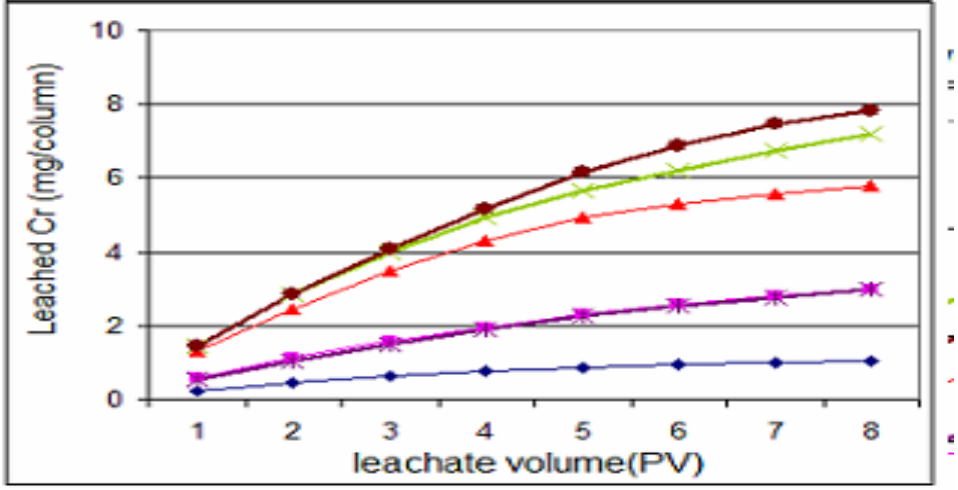
Cont. W + S E E + S P p + S

The cumulative amounts of the leached Co and Cr (mg/column)









Cont. W + S E E + S P p + S

Breakthrough (BTC) Retardation of Pb, Cd, Co and Cr ions in the investigated soils using different leaching solutions.

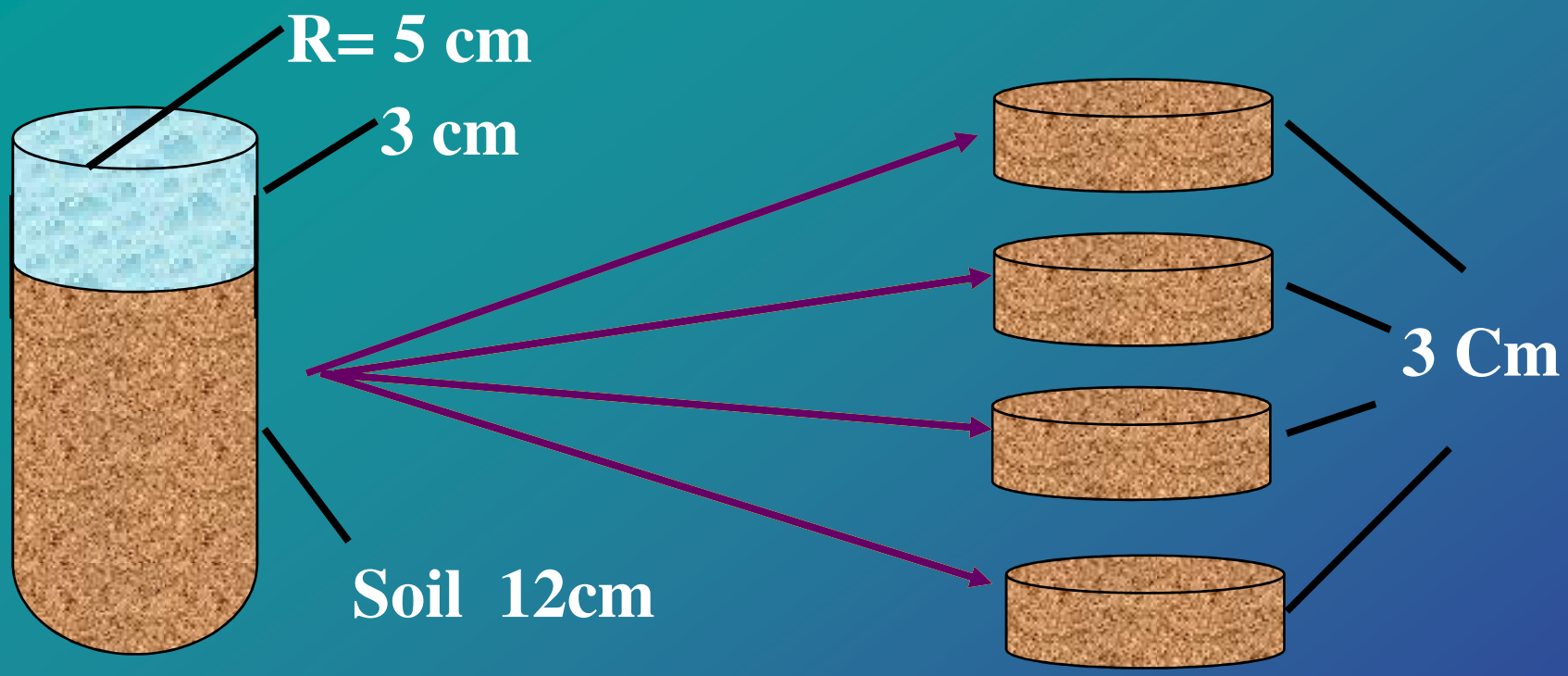
Soil	Metal	E	E+S	P	P+S
Sandy	Pb	3.100	3.000	3.400	3.200
	Cd	1.600	1.200	1.560	1.600
	Co	2.200	2.100	3.350	2.250
	Cr	2.100	1.900	3.000	2.300
Clay	Pb	6.200	6.100	6.800	6.600
	Cd	3.200	3.100	3.500	3.400
	Co	4.200	4.100	4.400	4.250
	Cr	3.100	2.900	3.300	3.100

Retardation Brief

- Pb > Co > Cd >Cr

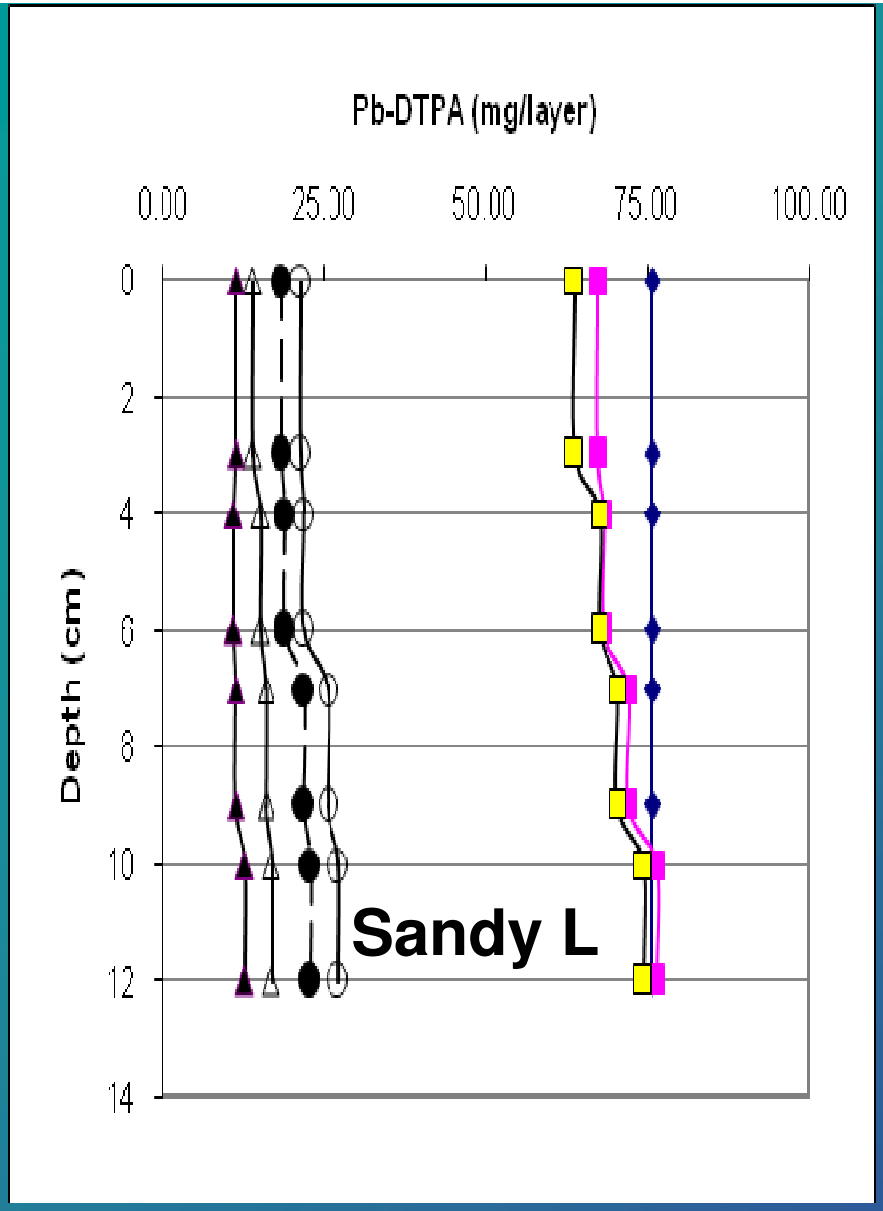
- Clay >> Sandy
- For all the leached metals

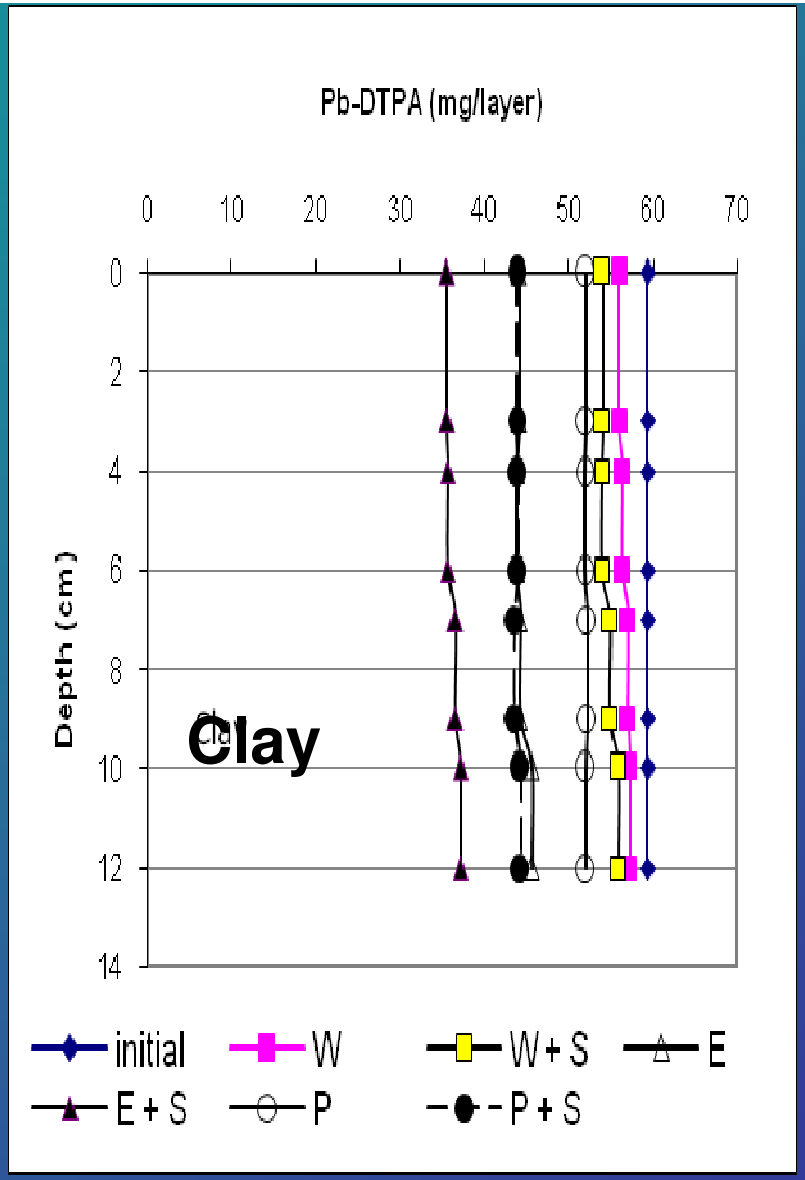
Downward Metal Distribution



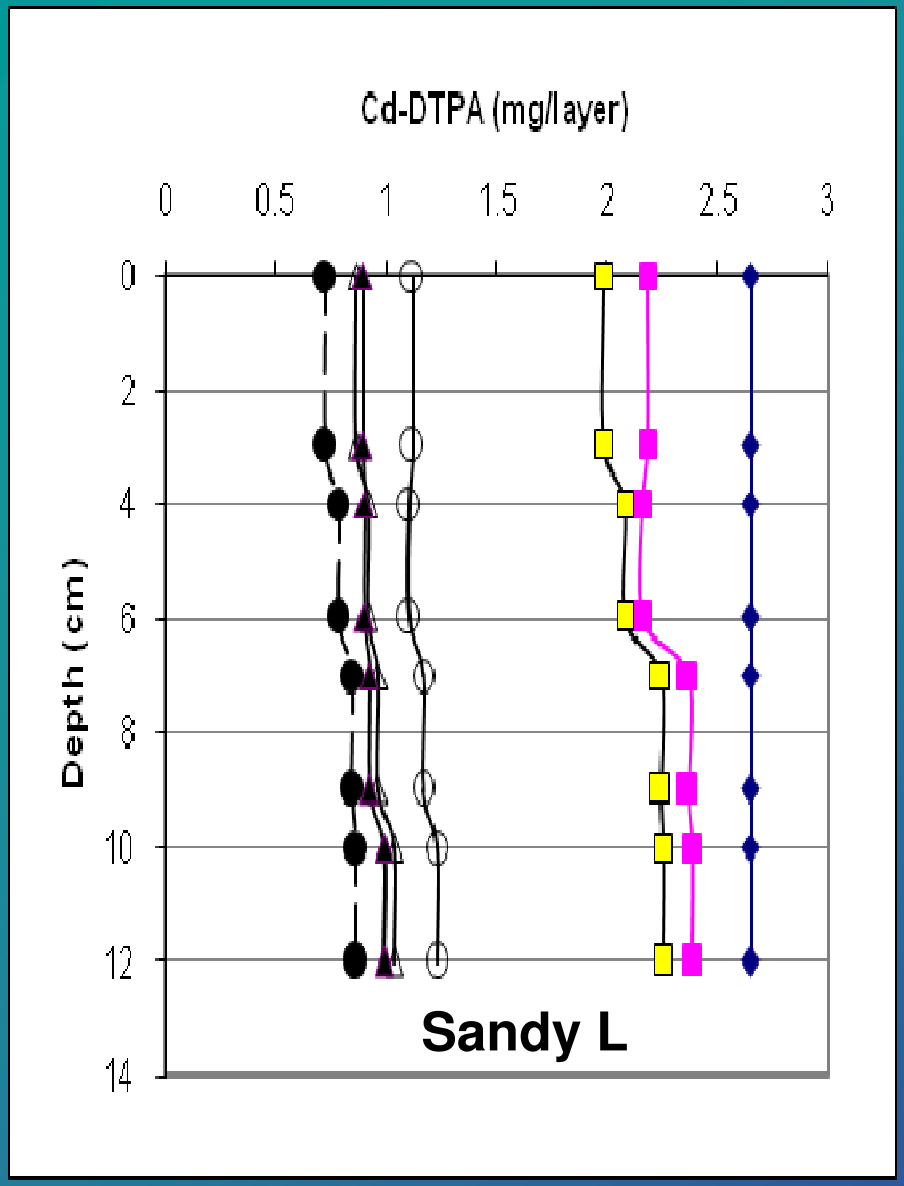
At the end of leaching, soil column was sectioned every 3 cm and DTPA extracted metal was measured

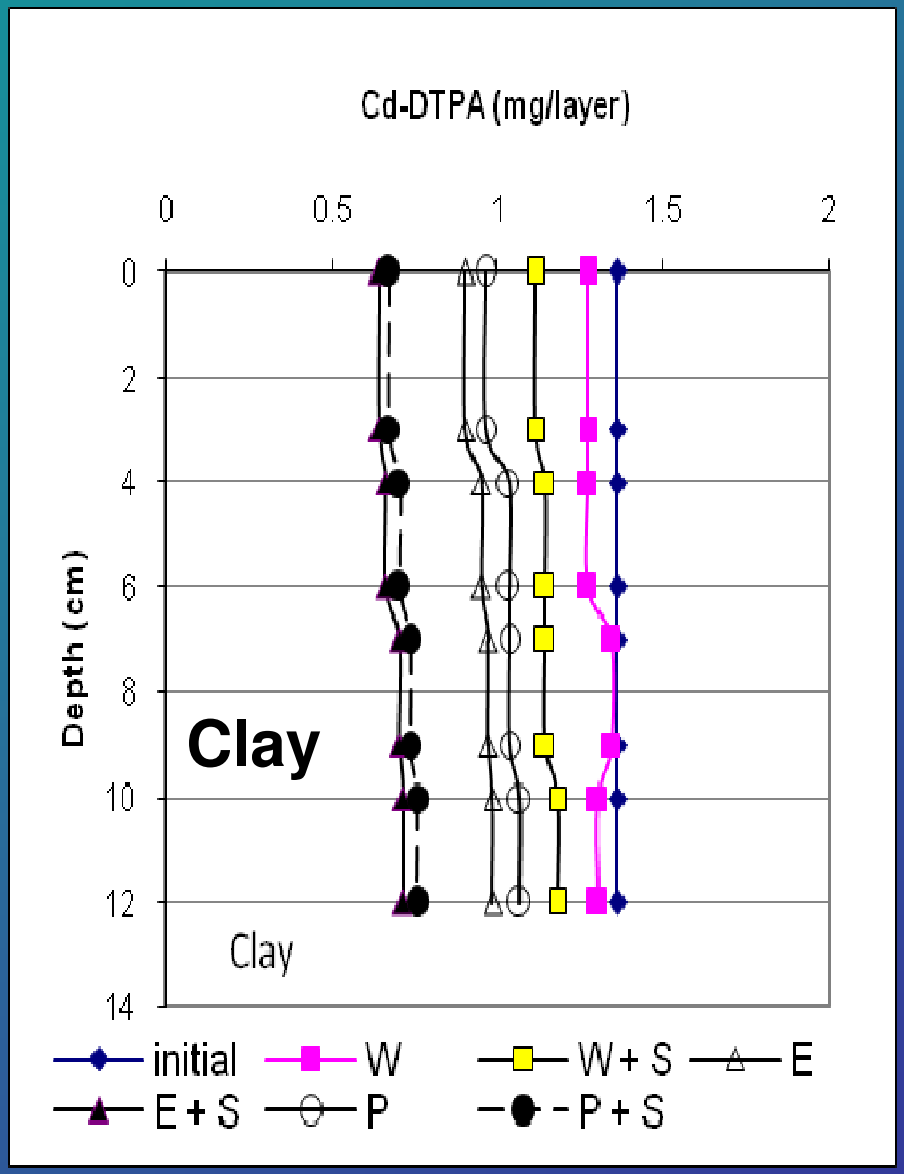
Total pore volumes = 8 PV



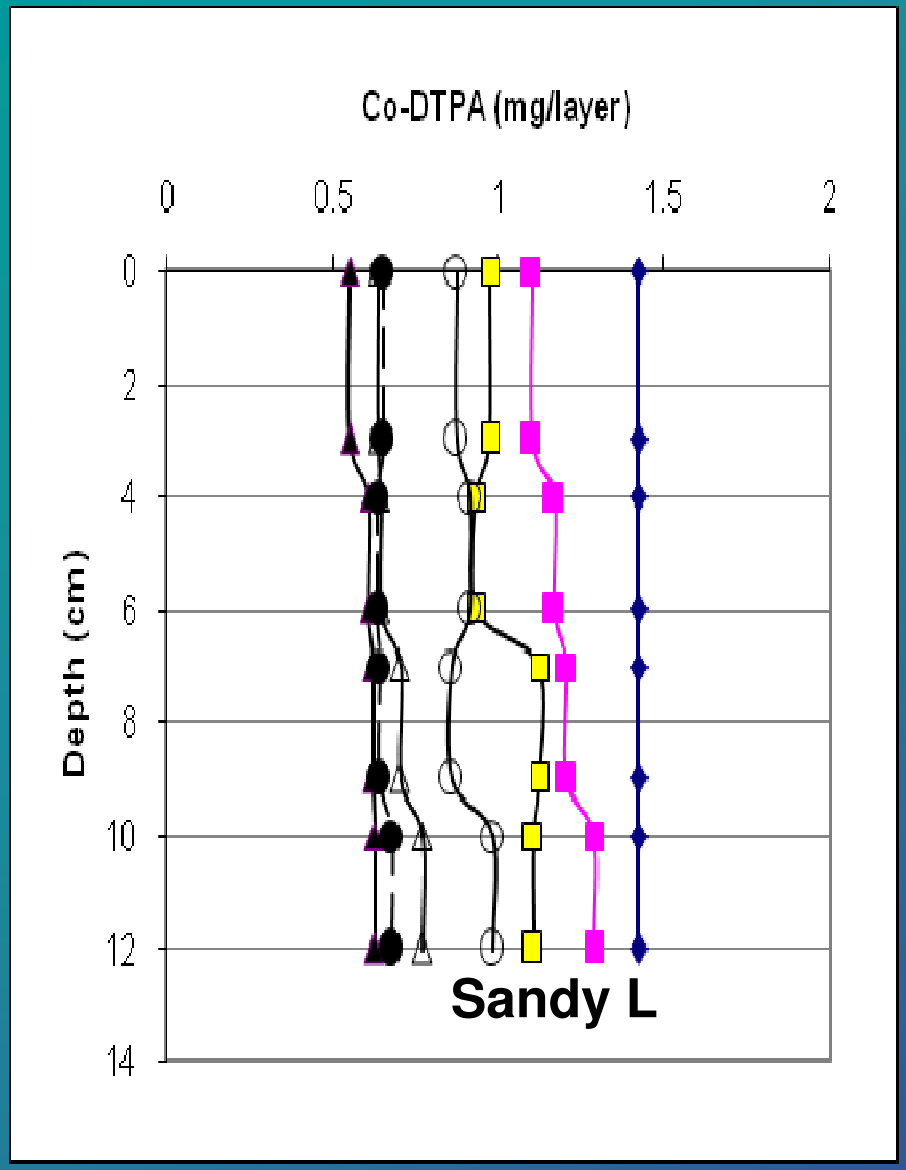


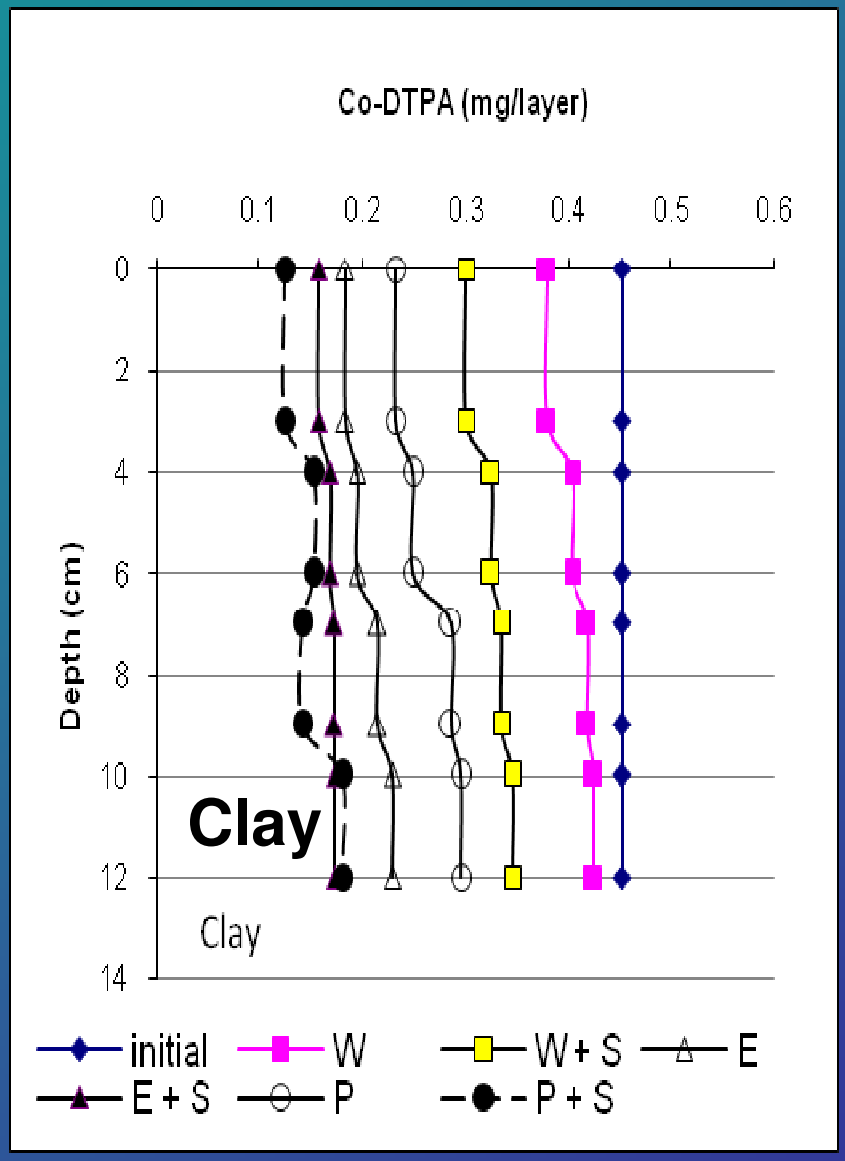
Downward distribution of DTPA extractable Pb in the soil columns at the end of the leaching experiment



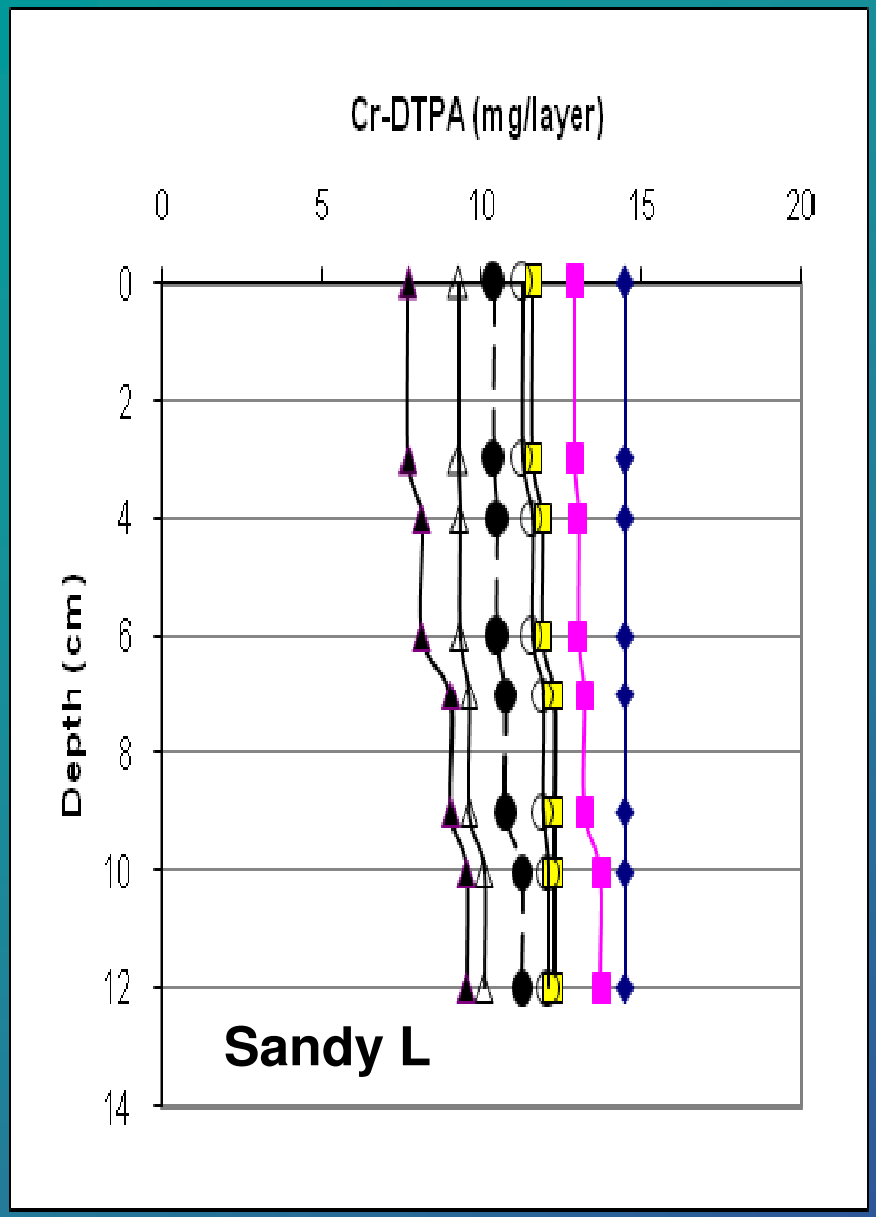


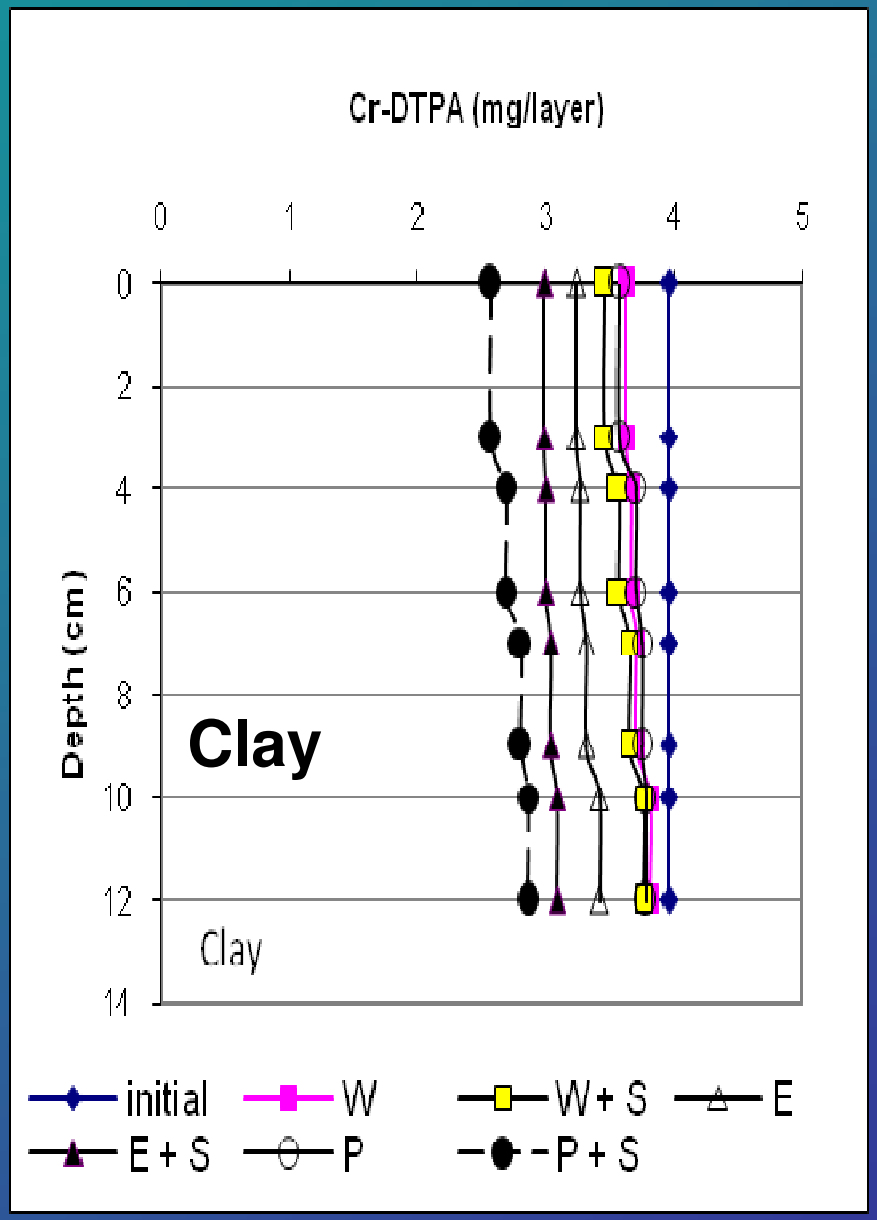
Downward distribution of DTPA extractable Cd in the soil columns at the end of the leaching experiment





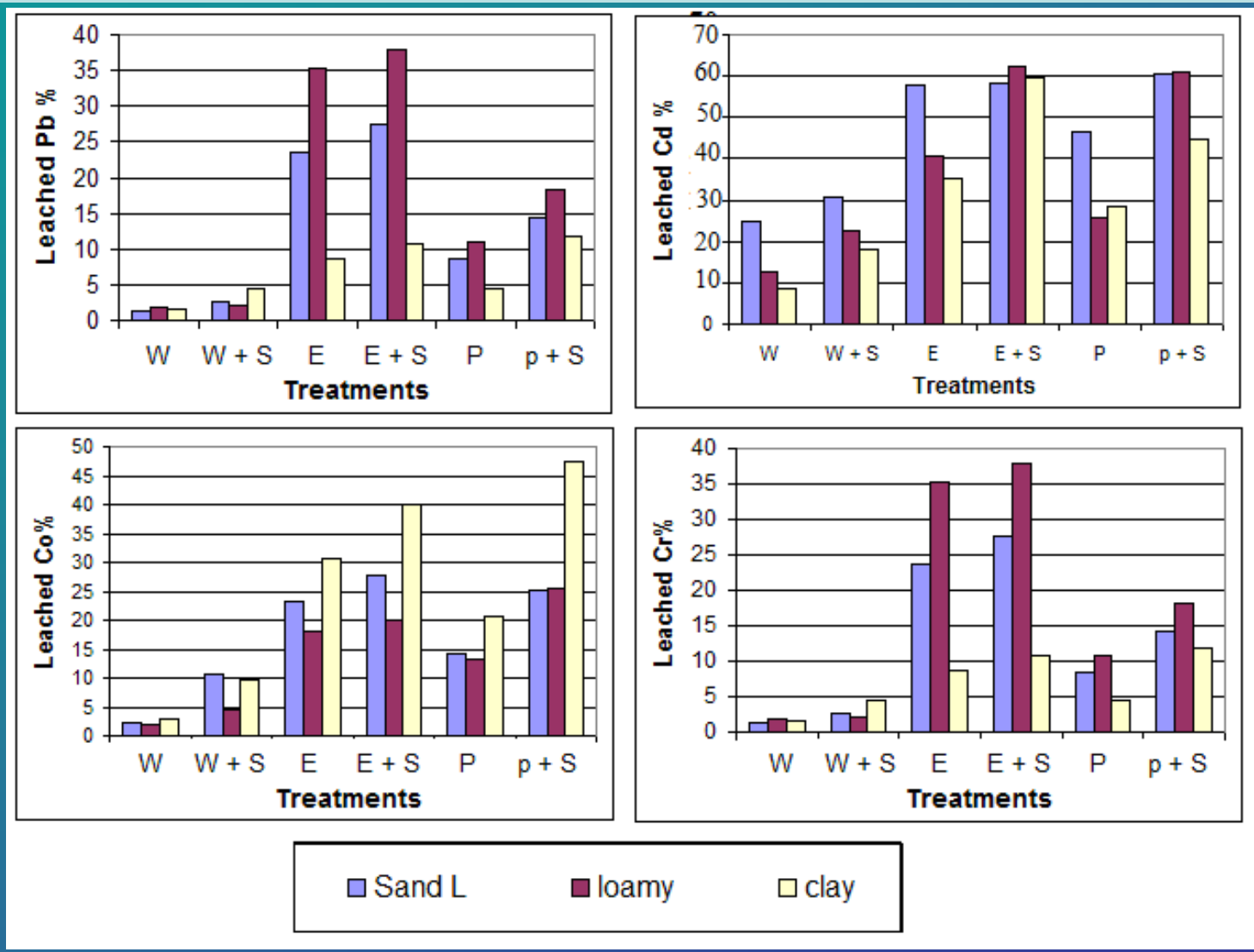
Downward distribution of DTPA extractable Co in the soil columns at the end of the leaching experiment





Downward distribution of DTPA extractable Cr in the soil columns at the end of the leaching experiment

Remediation Efficiency



Conclusion

- In conclusion, the slurry of the leaves of both Hepescus and Eucalyptus were found to contain high amounts of active groups such as carboxyl, phenol, amino as well as other legends susceptible for metal complexation.
- The enormous amount of the active ligands with the slightly acidic reaction (pH= 6.5) may facilitate the metals washing from the polluted soil columns even more efficiently than EDTA in some cases.

Thank you