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# Soil Washing: a Promising Technique for Heavy Metals Removal from Contaminated Soils

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# Overview of the presentation

- Keywords suggestion
  - What I'm not going to tell you
    - What I'm going to tell you
  - Keywords analysis
    - What you are going to tell me
    - What you are not going to tell me





# Unsaid things

- Heavy metals (HMs)
  - HMs toxicity
  - HMs sources
  - Techniques for HMs removal
  - Physical washing

# Heavy metals definition

Periodic Table of the Elements

1	2											3	4	5	6	7	8	9	10
1	2											3	4	5	6	7	8	9	10
3	4											5	6	7	8	9	10		
11	12											13	14	15	16	17	18		
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36		
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54		
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86		
87	88	89	104	105	106	107	108	109	110	111	112								

Naming conventions of new elements

\* Lanthanide Series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

+ Actinide Series

90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

*metals with density higher than 5000 kg/mc*

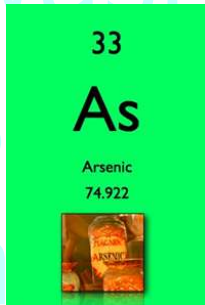
# Heavy metals toxicity

## Top 10 Hazardous Substances (Agency for Toxic Substances and Disease Registry)



- **As** = # 1. Target organs are the blood, kidneys, and central nervous, digestive, and skin systems.
- **Pb** = # 2. Target organs are the bones, brain, blood, kidneys, and thyroid gland
- **Hg** = # 3. Target organs are the brain and kidneys
- **Cd** = # 7 Target organs are the liver, placenta, kidneys, lungs, brain, and bones.

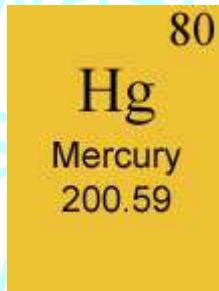
# Main sources of heavy metals in the soil



- As: paints, rat poisoning, fungicides, and wood preservatives



- Pb: batteries, cable coverings, plumbing, fuel additives, crystal glass, pesticides



- Hg: almost banned, but still persistent (natural)



- Cd: insecticides, fungicides, sludge, and commercial fertilizers

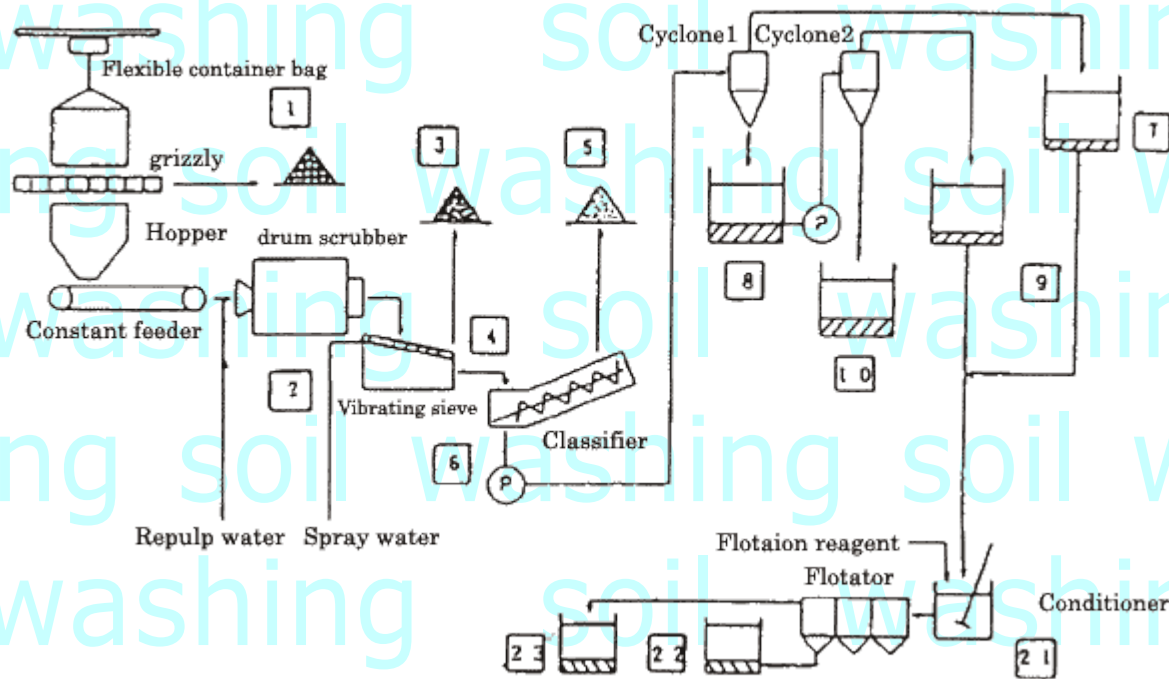


# Remediation of heavy metals polluted soils

- Phytoremediation
- Electrokinetic remediation
- Stabilisation/solidification
- Soil washing

# Physical washing

- Granulometric classification





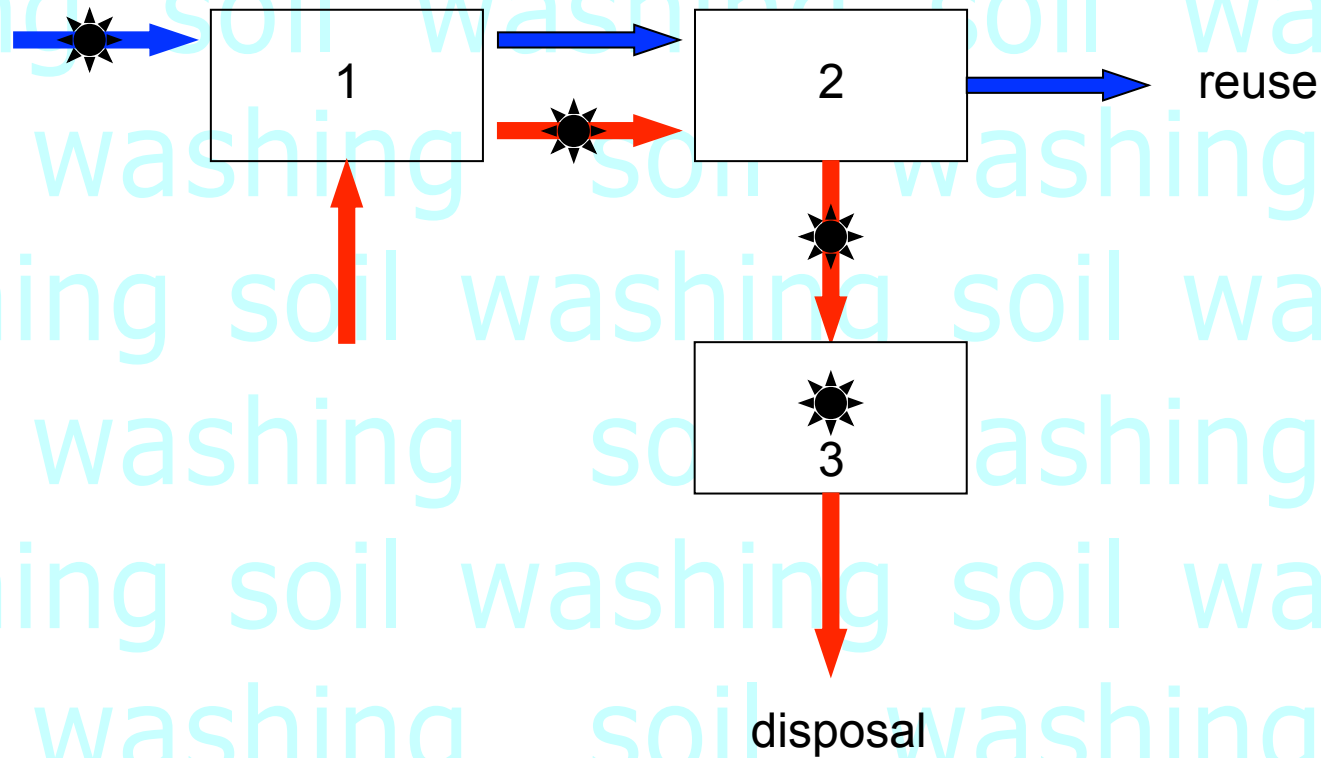
# Soil washing

- Definition
- Heavy metals mobility
- Washing agent
- Kinetics
- Examples
- Soil reuse
- Washing solution disposal

# Soil washing?

- Washing of the contaminated soils with an appropriate solution
- Transfer of the contaminant from the soil to the solution
- Separation of the decontaminated soil from the contaminated solution

# Washing process



# Parameters affecting process performances

- Soil characteristics
- HMs characteristics (including mobility and concentration)
- Age of the contamination
- Washing agent characteristics (including concentration)
- Other treatment process operative parameters (T, pH, mixing, S/L)

# Mobility

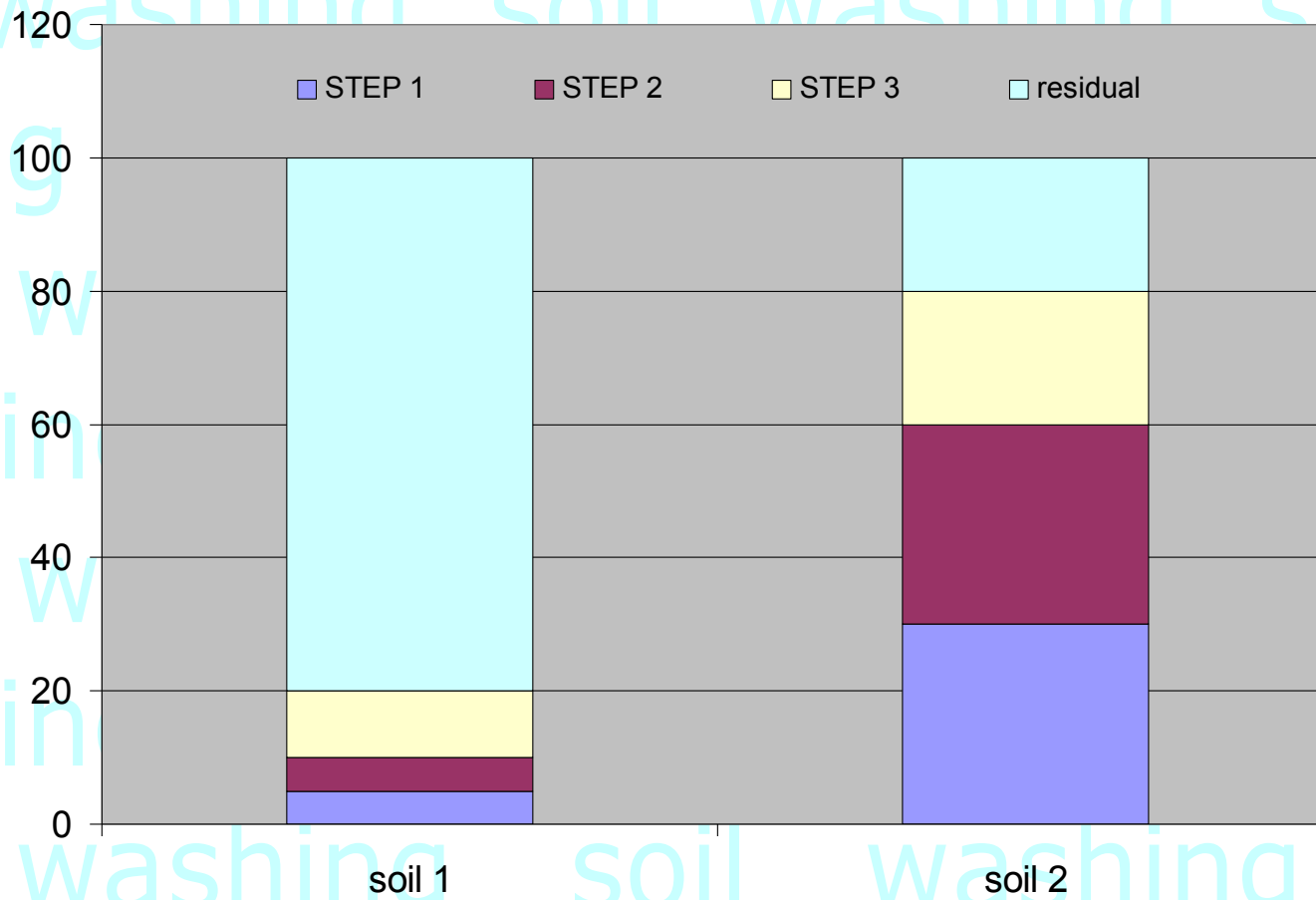
- Soil-plant transfer
- Migration in a soil profile, reaching groundwater
- Potential efficiency of washing, real required performances
  - Unpolluted soils: silicates and primary minerals = immobile
  - Polluted soils: exchangeable, carbonates, Fe-Mn oxides, organic, residual = mobile/immobile



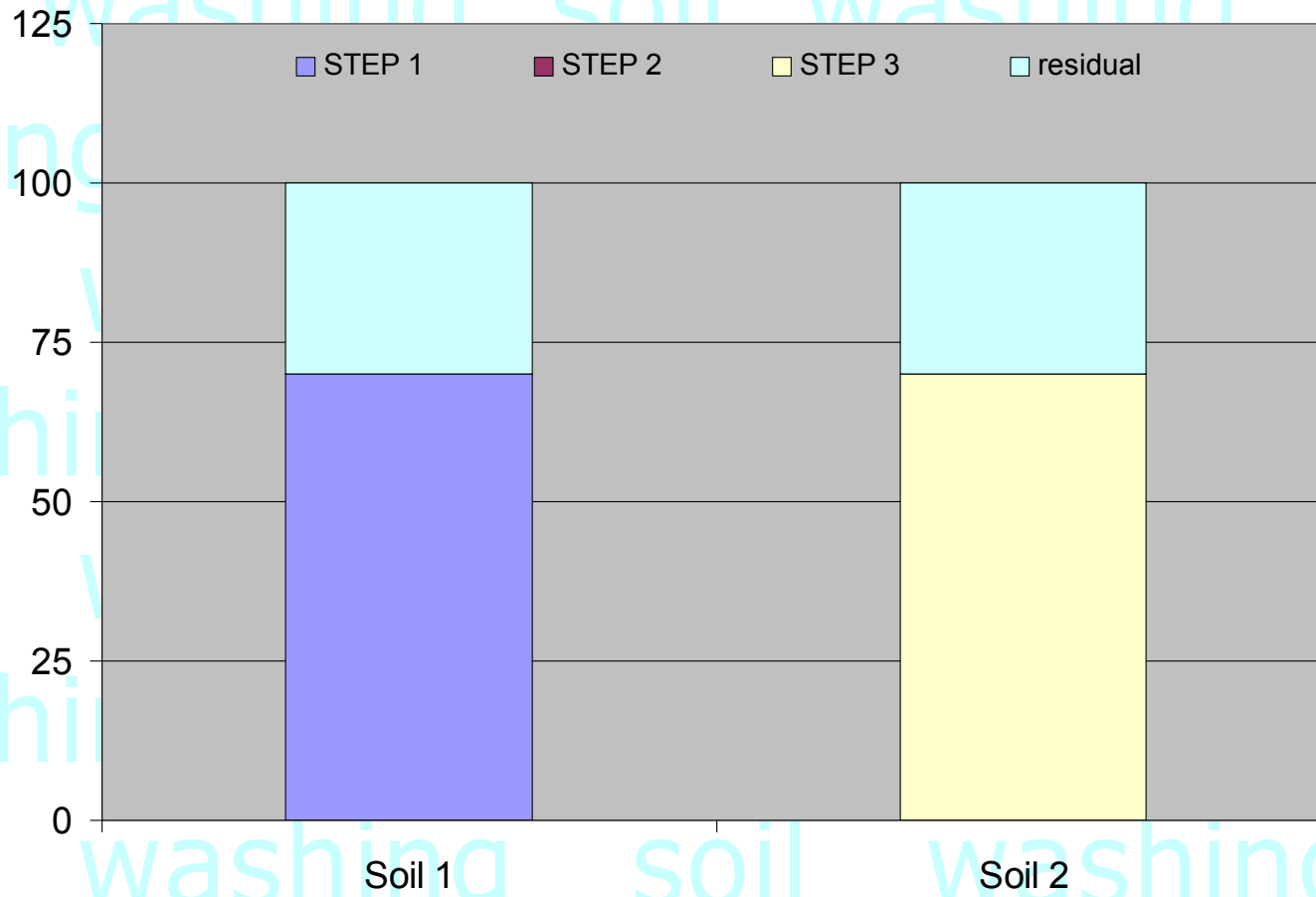
# Sequential extraction

- BCR three steps, largely used (modified to avoid effect of soil pH in Step 2)
  - Sample treated with acetic acid to liberate exchangeable/acid extractable metals (STEP 1)
  - Use of hydroxylamine hydrochloride to solubilise the reducible phase (STEP 2)
  - Oxidation with hydrogen peroxide and isolation in ammonium acetate solution to obtain the fraction bound to the organic matter (STEP 3)

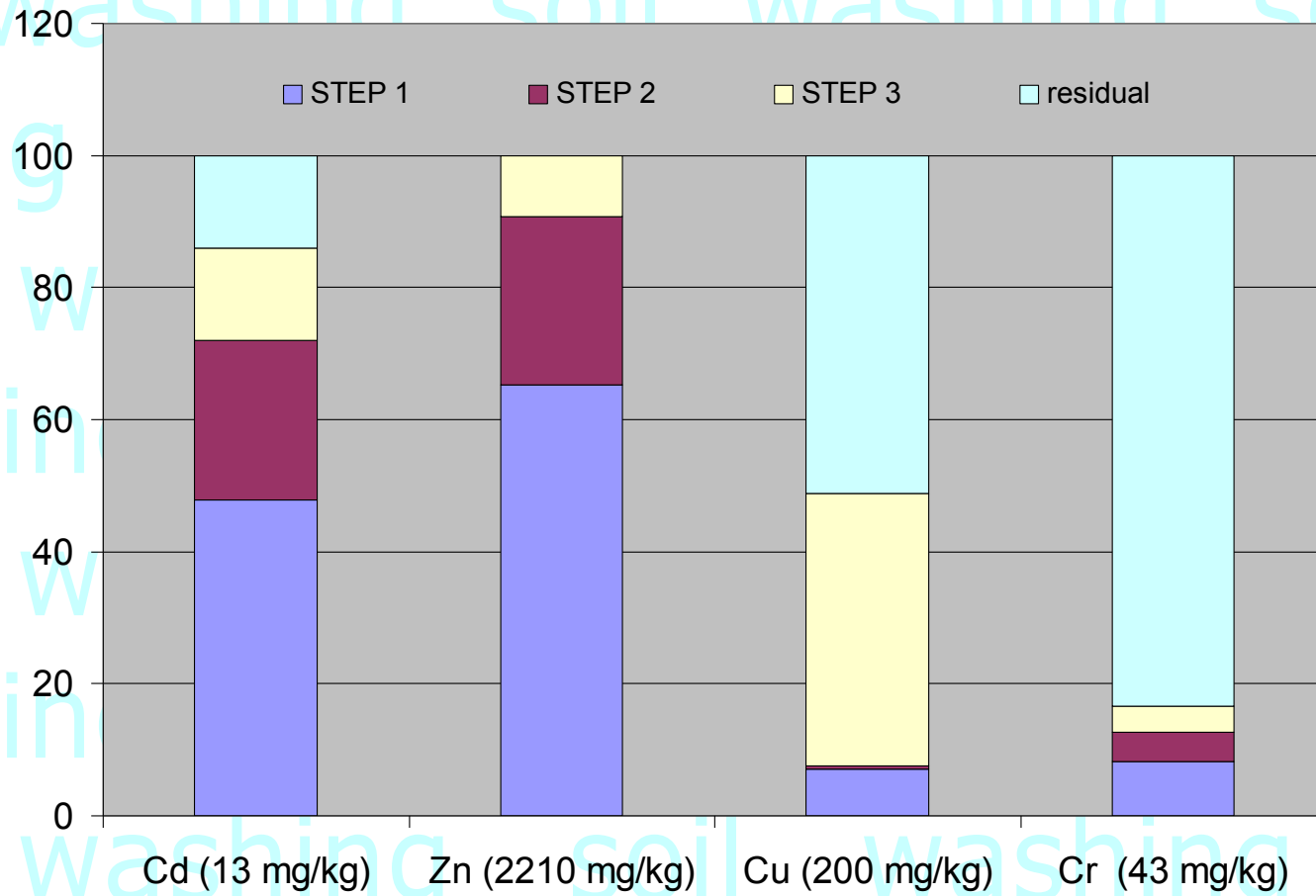
# EXAMPLES



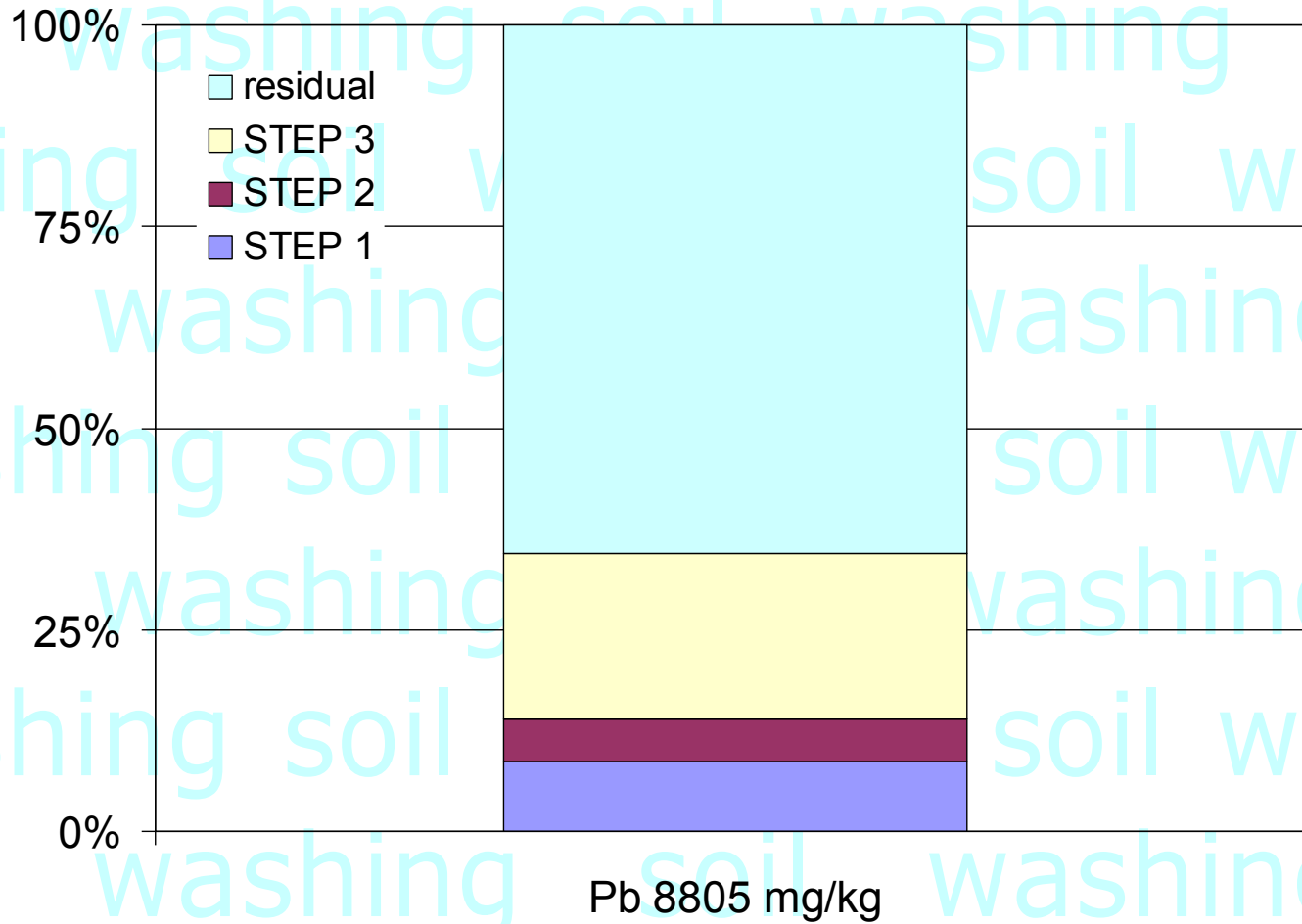
# EXAMPLES



# EXAMPLES



# EXAMPLES



# Procedure

- Mix: 1 g soil + 40 mL 0.11 mol/L acetic acid
  - Shake at 30 rpm at 22°C for 16 h
  - Separate the extract (centrifugation at 3000 g, 20 minutes)
  - Wash the residue for 15 minutes with 20 mL double deionised water, centrifuge and discard the supernatant
- Add: 40 mL 0.5 mol/L hydroxylammonium chloride
  - Shake (acidification with 2.5% v/v 2 mol/L nitric acid)
  - Separate the extract and wash
- Add: 10 mL 8.8 mol/L hydrogen peroxide.
  - Digest 1 h at 22°C + 1 h at 85°C, reduce the volume to less than 3 mL
  - Add 10 mL hydrogen peroxide
  - Digest 1 h at 85°C, reduce the volume to 1 mL
  - Add 50 mL 1 mol/L ammonium acetate (adjust pH at 2.0)
  - Shake at 30 rpm at 22°C for 16 h.
  - Separate the extract and wash
- Digest with aqua regia

# Pitfalls of sequential extraction

- Not yet standardised
  - dissolution of non target phase
  - incomplete dissolution of target phase
  - readsorption or reprecipitation of dissolved species
  - modification of the original oxidation state of the metal
  - deficiency of reagent dose (high polluted soils)

Extended X-ray fine structure spectroscopy by-pass  
over mentioned problems

# Washing agent

- Required characteristics
  - Good selectivity
  - High saturation capacity
  - Low interaction with soil components
  - Low cost
  - Absence of toxicity
- Acid, Base, Salt, Chelant, Oxidizing agent, Reducing agent



# Acid extraction

- Reduced affinity between  $M^{n+}$  and soil particles (positively charged) - repulsion or competition with  $H^+$
- Solubilisation of salts
  - OK: protonated metals
    - Chloridic, acetic, citric, tartaric, piruvic acid (0.05-1 N)
    - NOT OK: distruction of solid matrix
      - Reduced reuse of treated soil
      - Washing solution treatment

# Basic extraction

- Reduced affinity between  $\text{MO}^{n-}$  and soil particles (negatively charged) - repulsion or competition with  $\text{OH}^-$
- Solubilisation of NOM
- OK: negatively charged metal species
  - Sodium hydroxide (0.1-1 N)
  - NOT OK: dissolution of NOM
    - Reduced reuse of treated soil
    - Washing solution treatment

# Extraction with salts

- Ionic exchange with adsorbed HMs
- Sodium and magnesium chloride; Sodium and calcium nitrate (0.1-1 M)
- OK: adsorbed HMs
- NOT OK: nitrates and chlorides released in the washing solution
  - Washing solution treatment

# Extraction with chelants

- Chelants increase metal solubility (fast ligand adsorption onto surface functional groups of solid particles + slow mineral metal detachment + fast protonation restoring the original surface functional groups)
  - OK: selectivity
  - EDTA, NTA, EDDS ..... (0.01M - 0.1 M)
  - NOT OK: costs, toxicity
    - Washing solution treatment

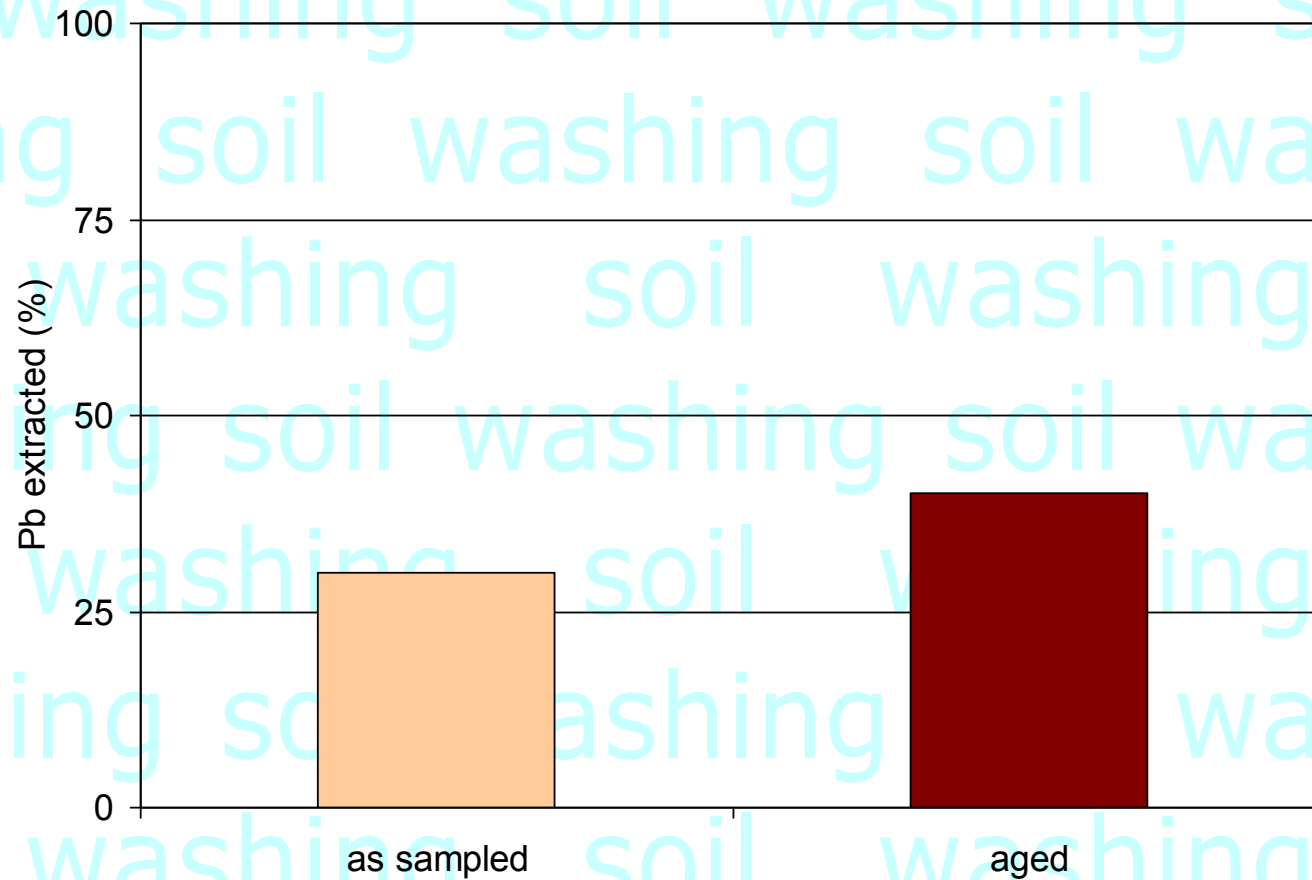
# Extraction with oxidizing agents

- Oxidation of certain metals increase their solubility
- Oxidation of NOM
- OK: function of solubility; NOM bound HMs
- $\text{H}_2\text{O}_2$  (30%)
- NOT OK: dissolution of NOM
  - Reduced reuse of treated soil
  - Washing solution treatment

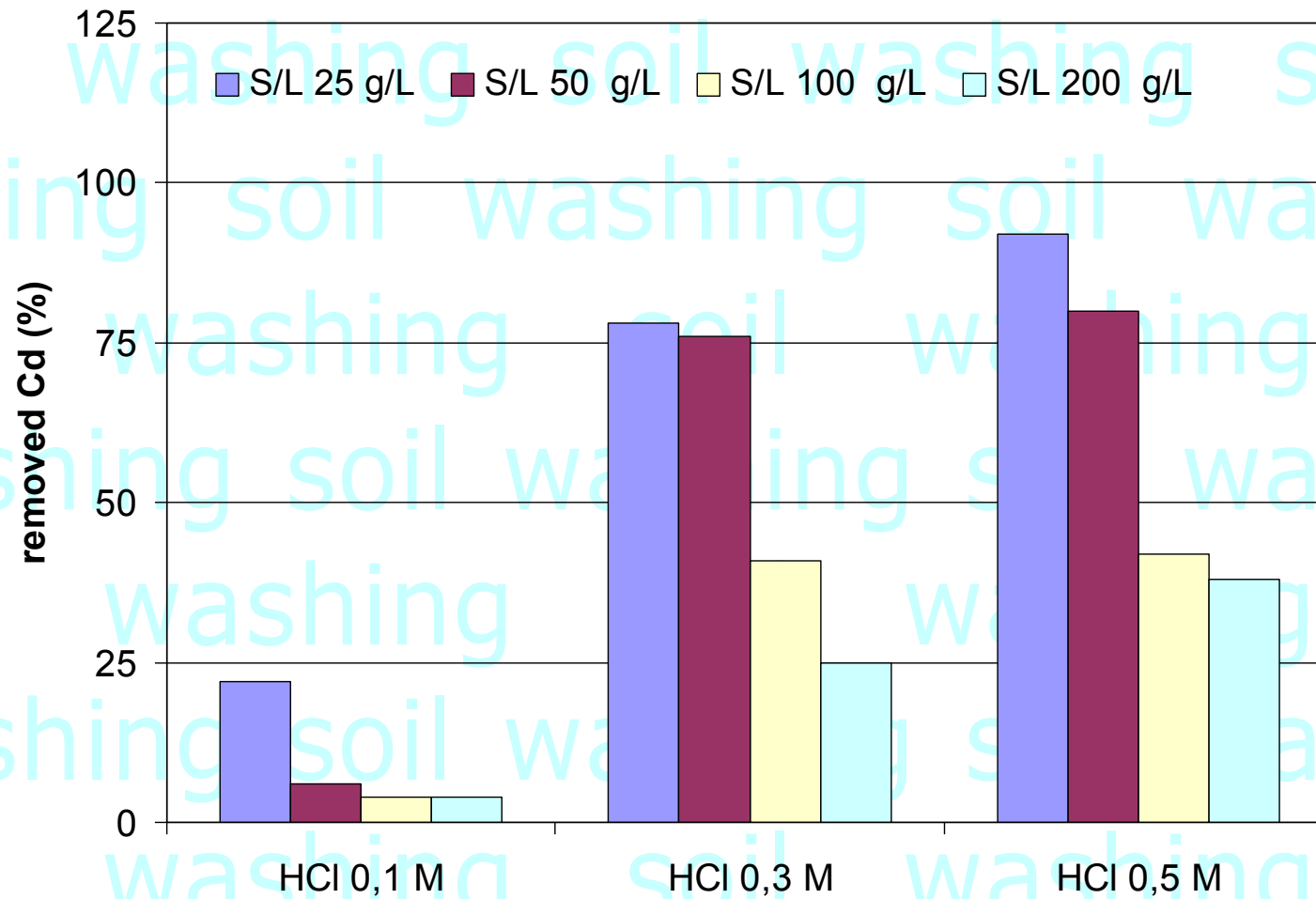
# Extraction with reducing agents

- Reduction of Iron and Manganese increase their solubility
  - OK: HMs bound to Fe and Mn
  - Sodium tiosulphate (0.1 – 1 M)
  - NOT OK: destruction of solid matrix
    - Reduced reuse of treated soil
    - Washing solution treatment

# Process parameters

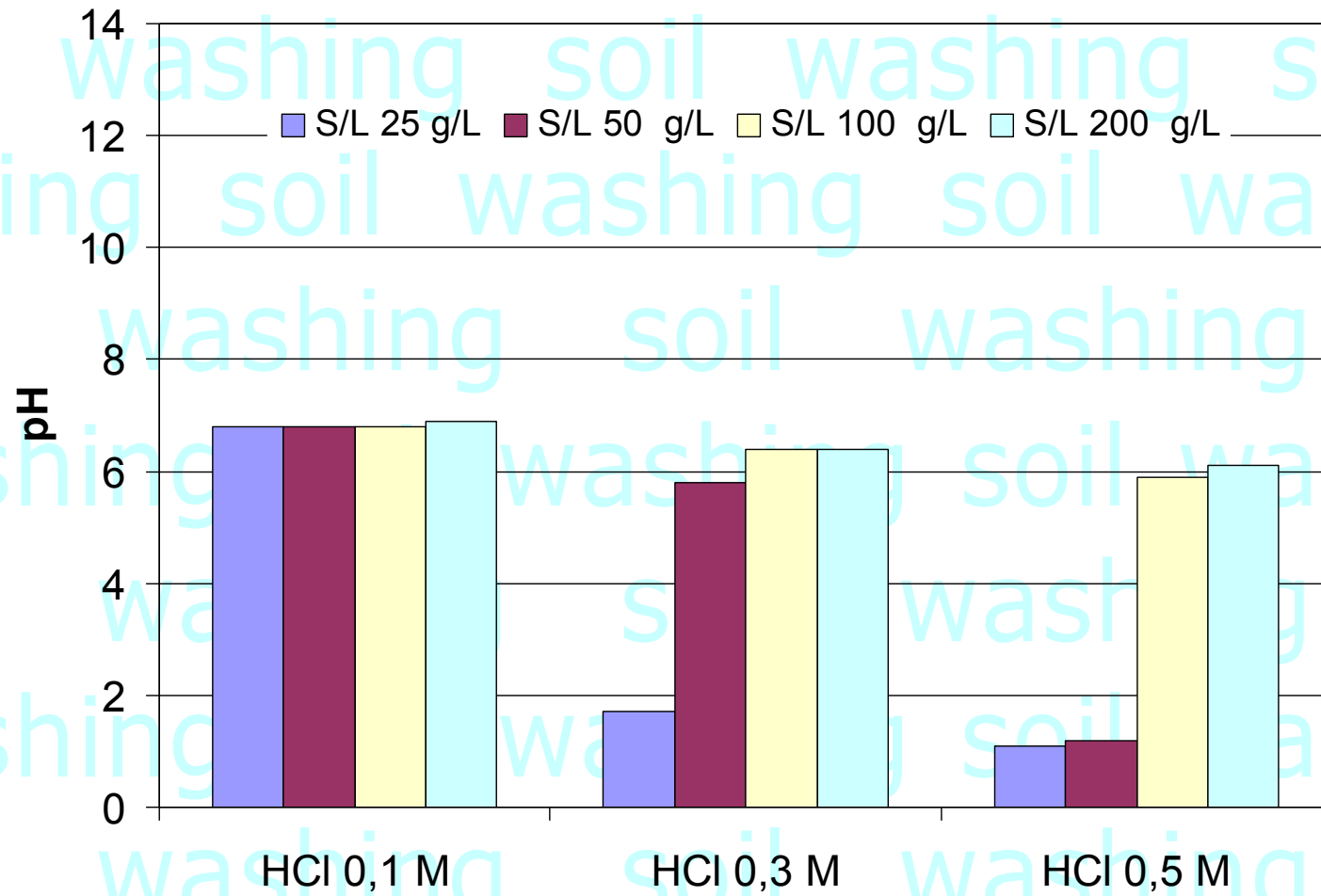


# Process parameters

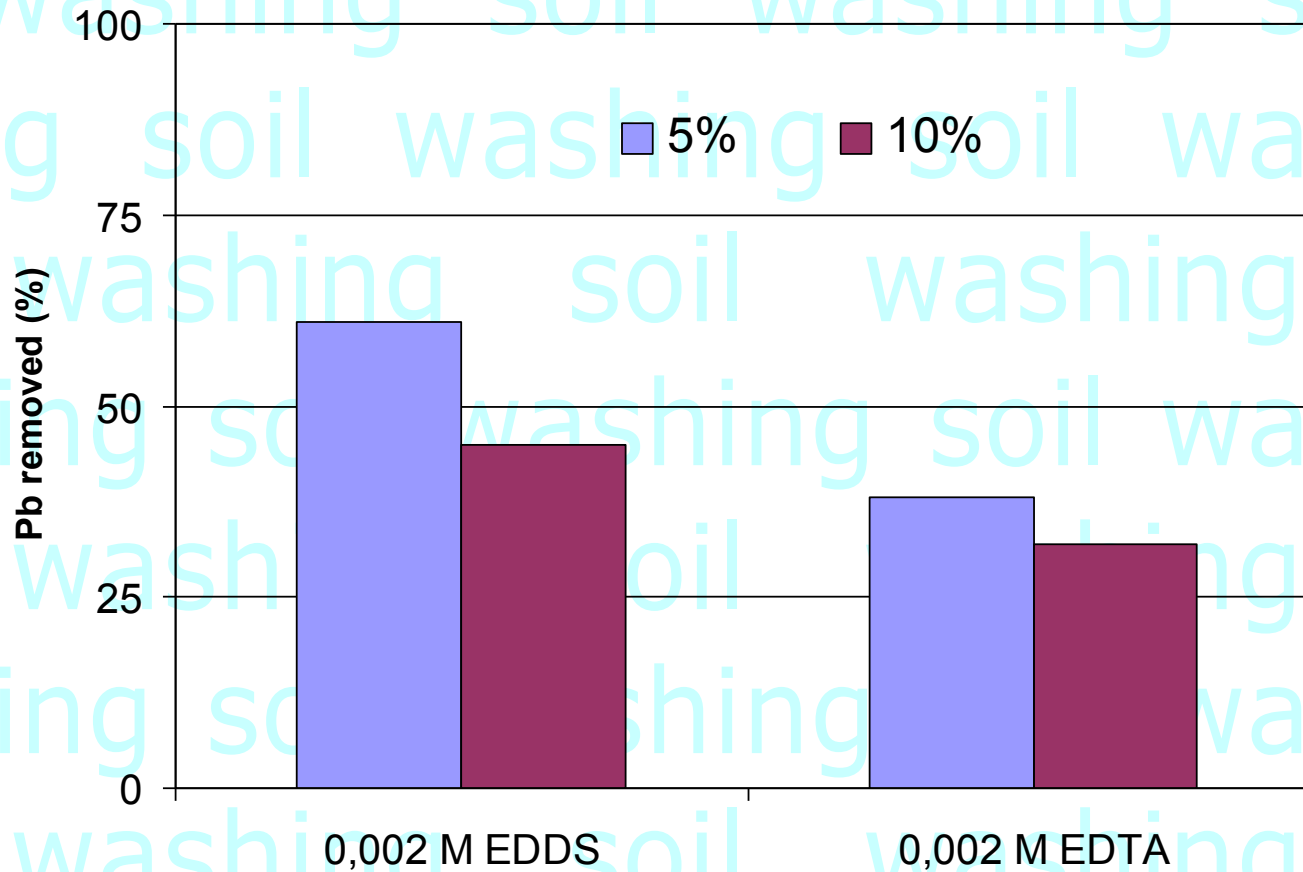




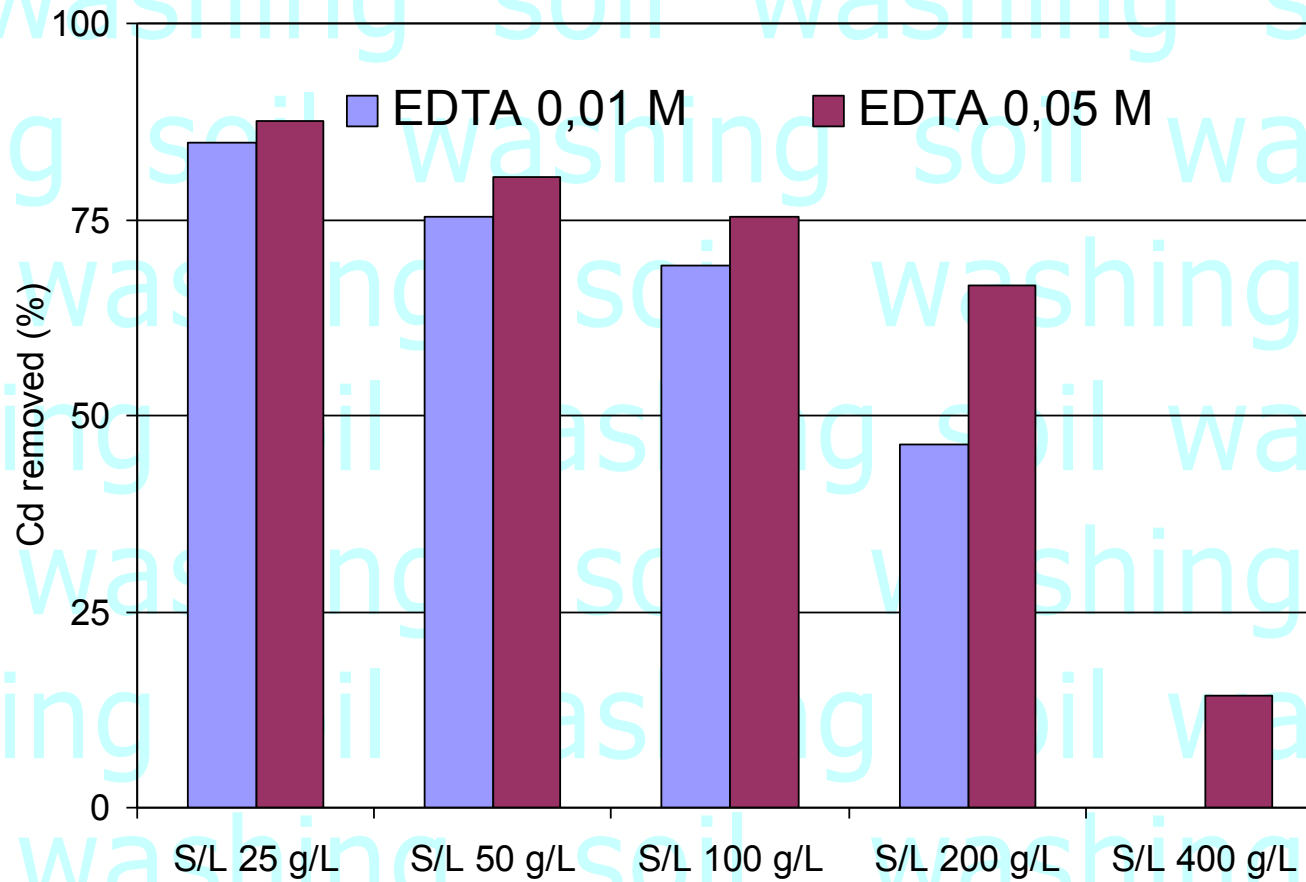
# Process parameters



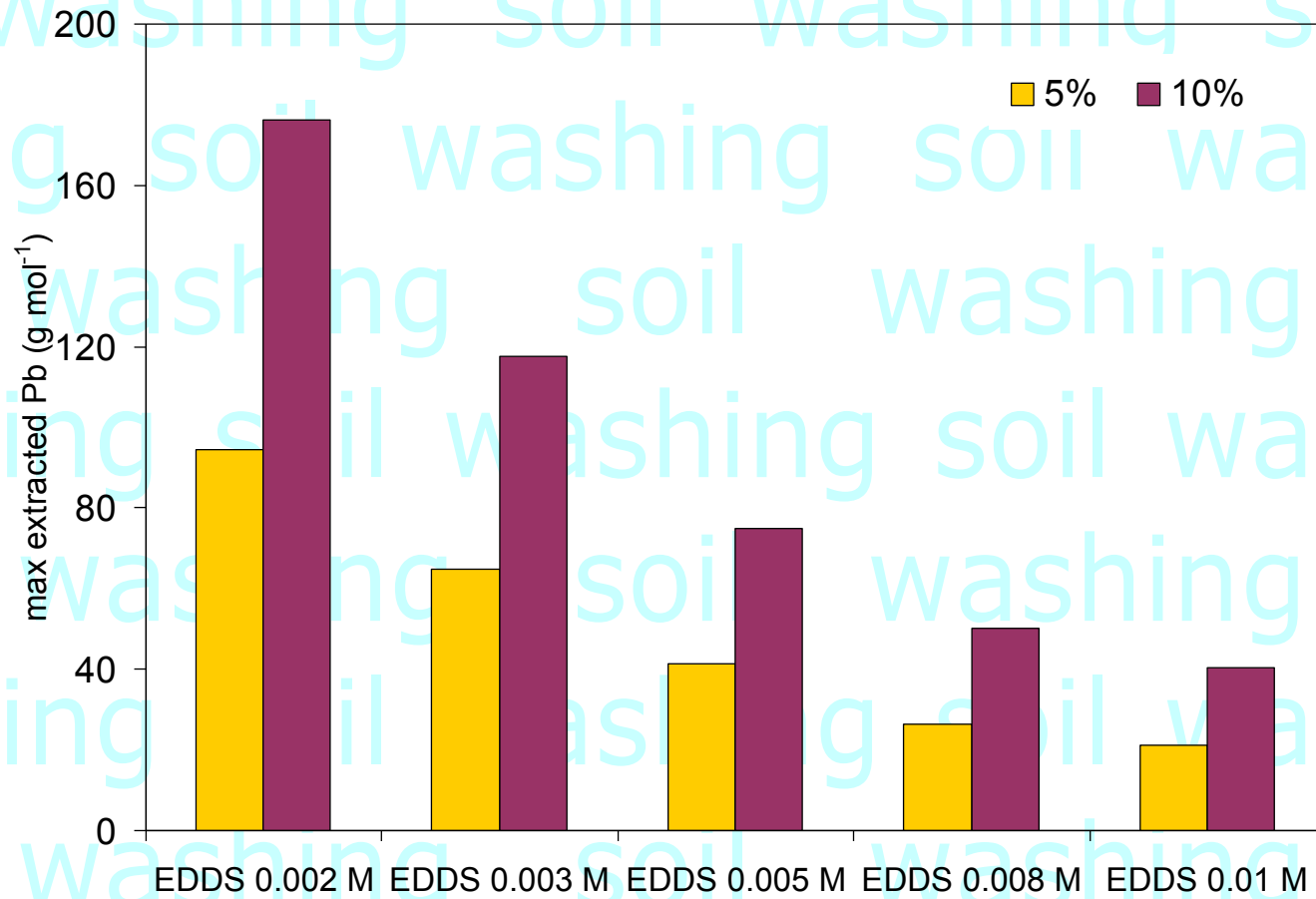
# Process parameters



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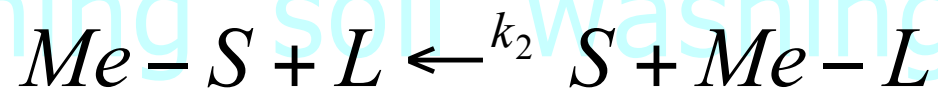
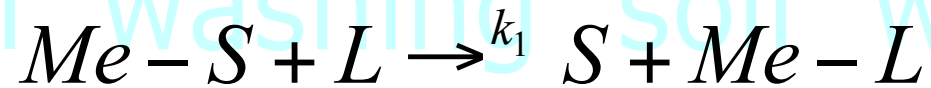
# Process parameters



## Kinetics

- Very fast in case of pH variation (oxidation and reduction)
- Time dependent in case of chelants

## Kinetics - chelants

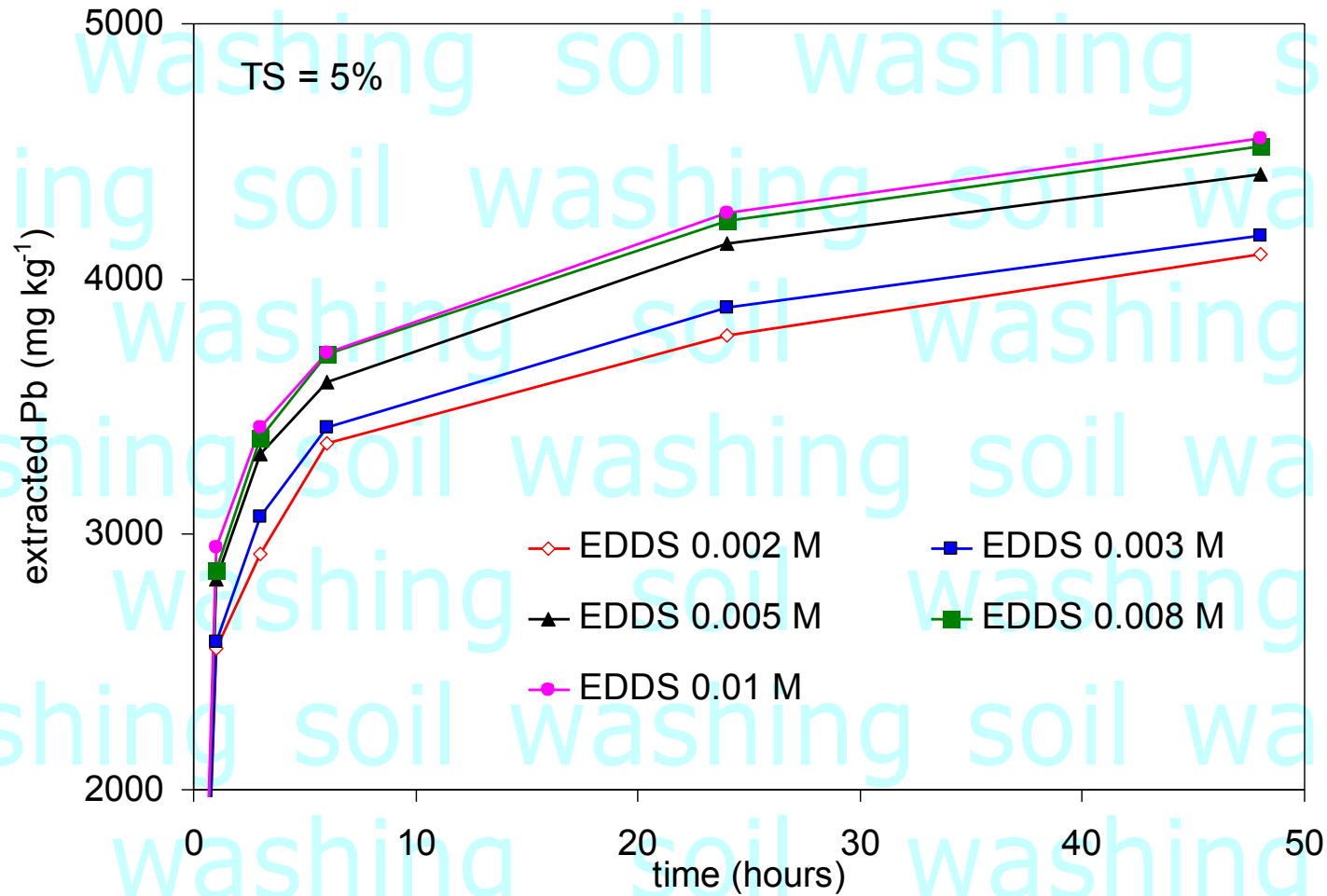


$$\frac{d[Me - L]}{dt} = k_1[Me - S] - k_2[Me - L]$$

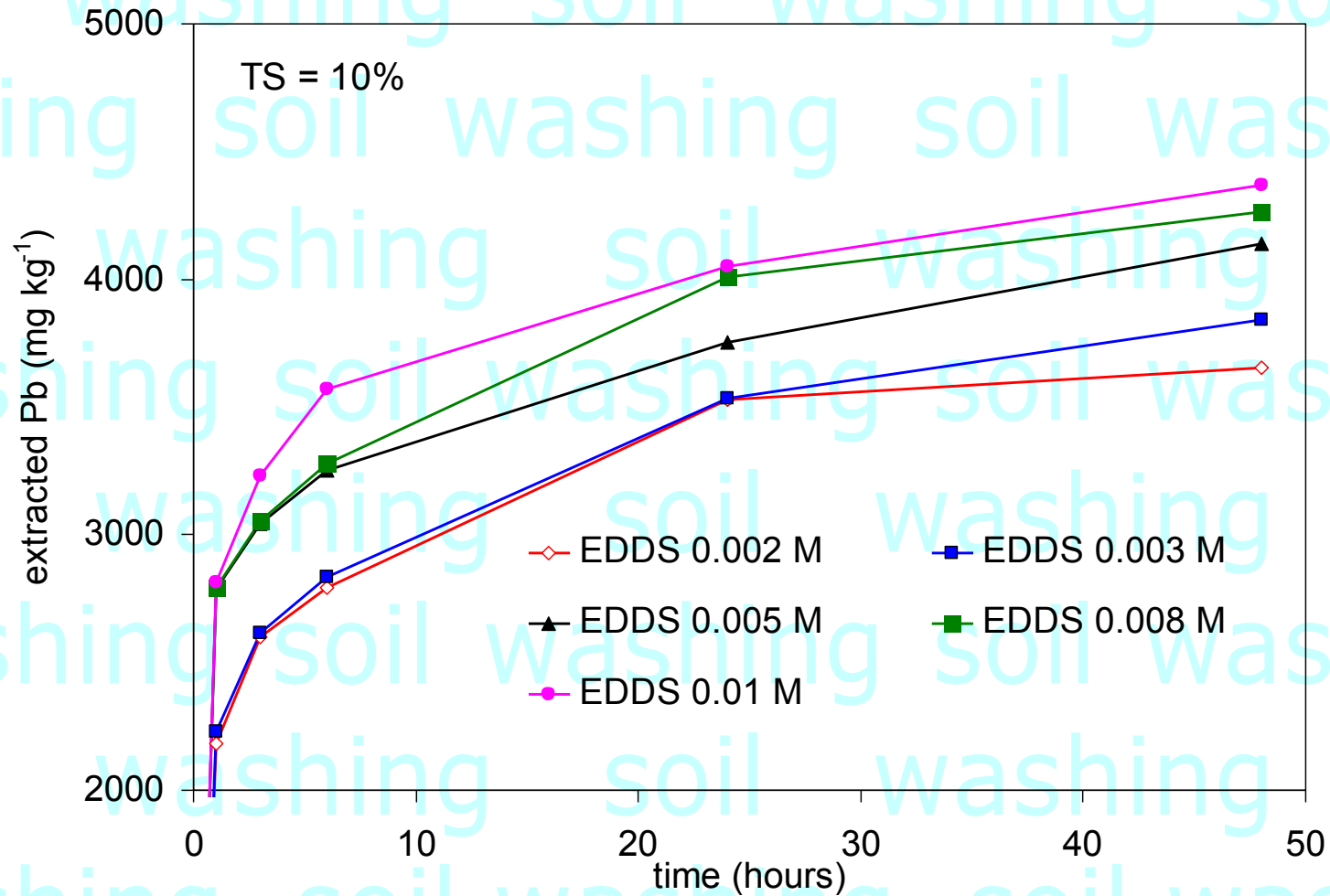
$$t = 0 \quad [Me - L] = 0$$

$$[Me - L] = \frac{k_1}{k_1 + k_2} [Me - S]_{t=0} [1 - \exp(-(k_1 + k_2)t)]$$

# Kinetics - chelants

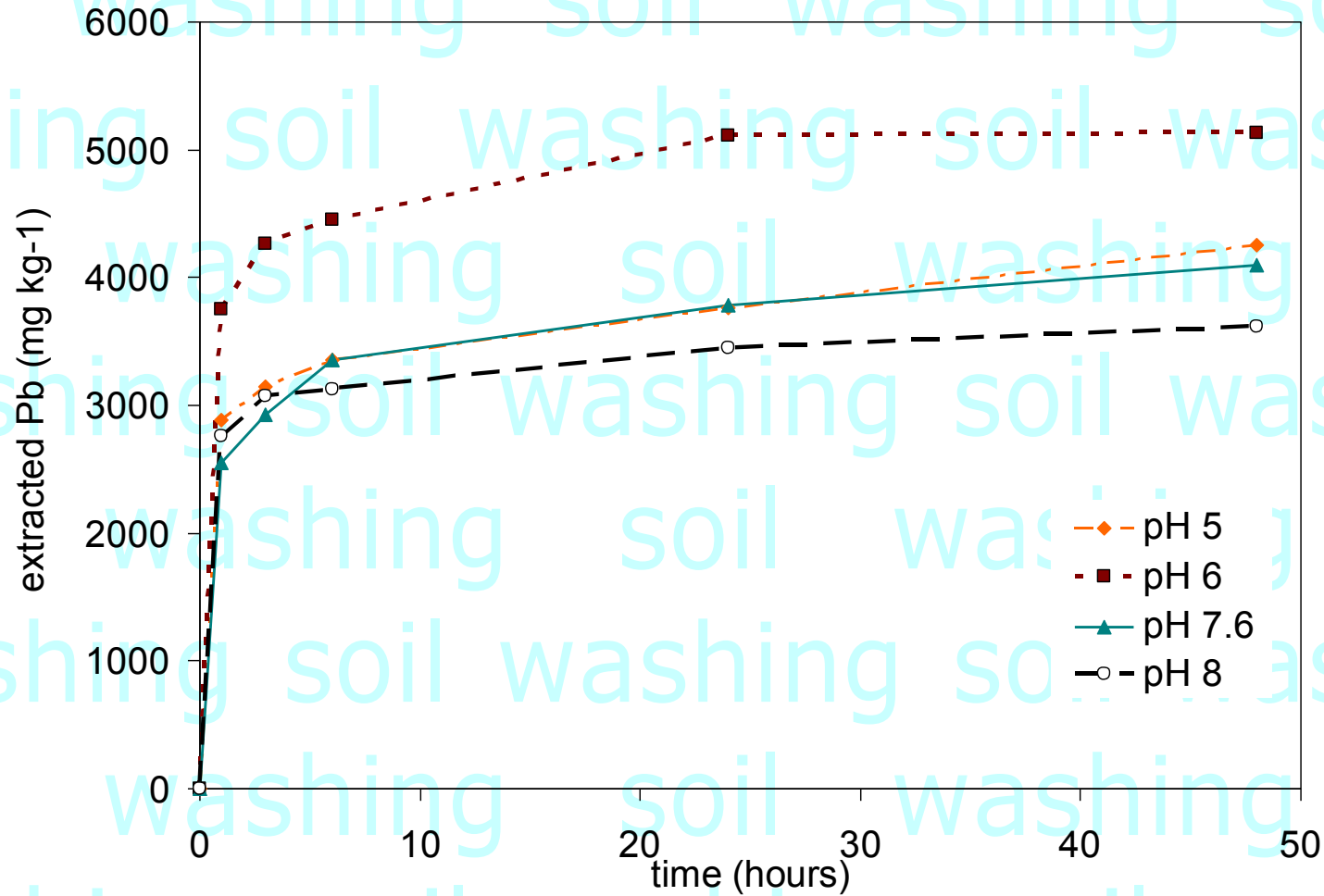


# Kinetics - chelants

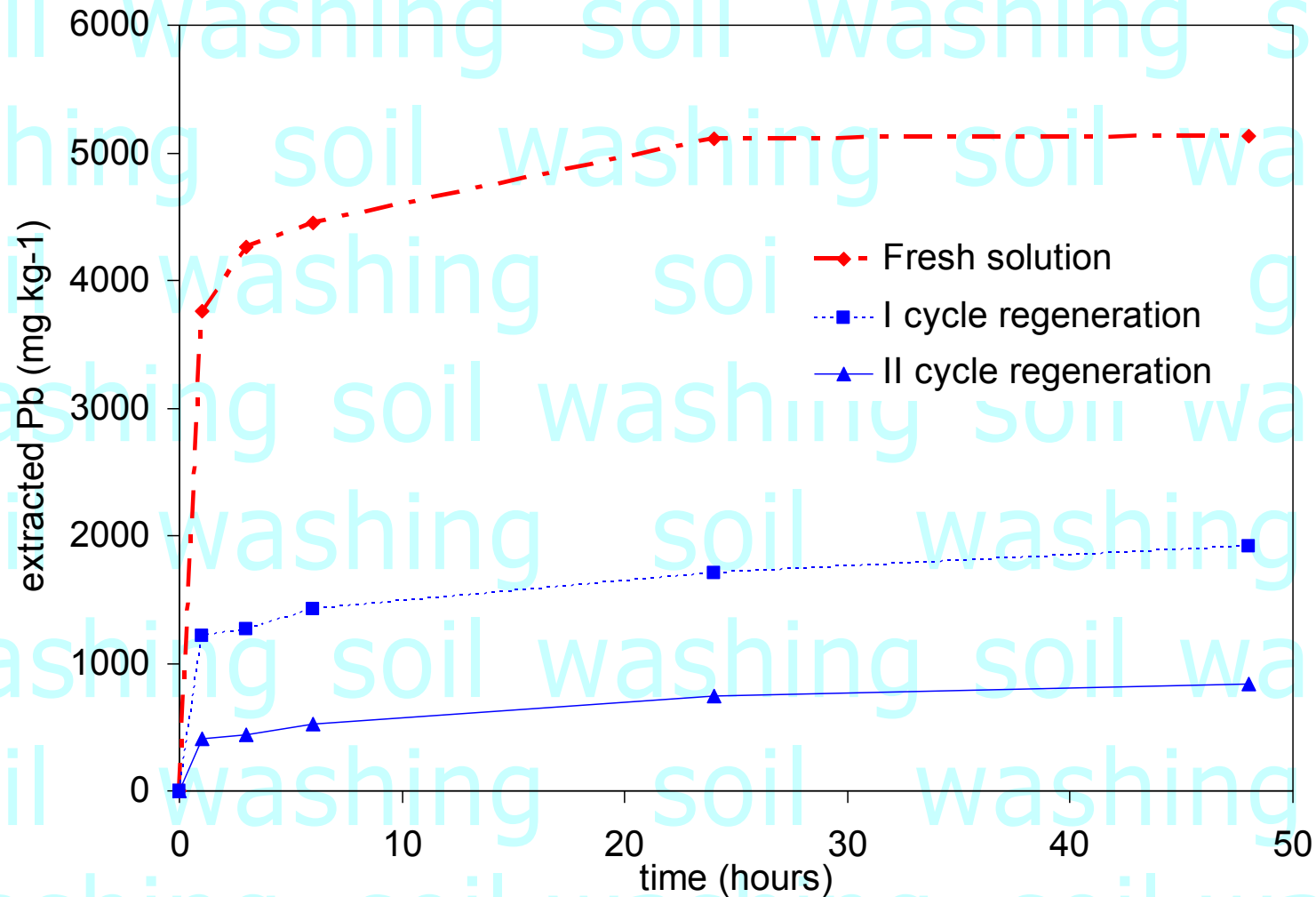




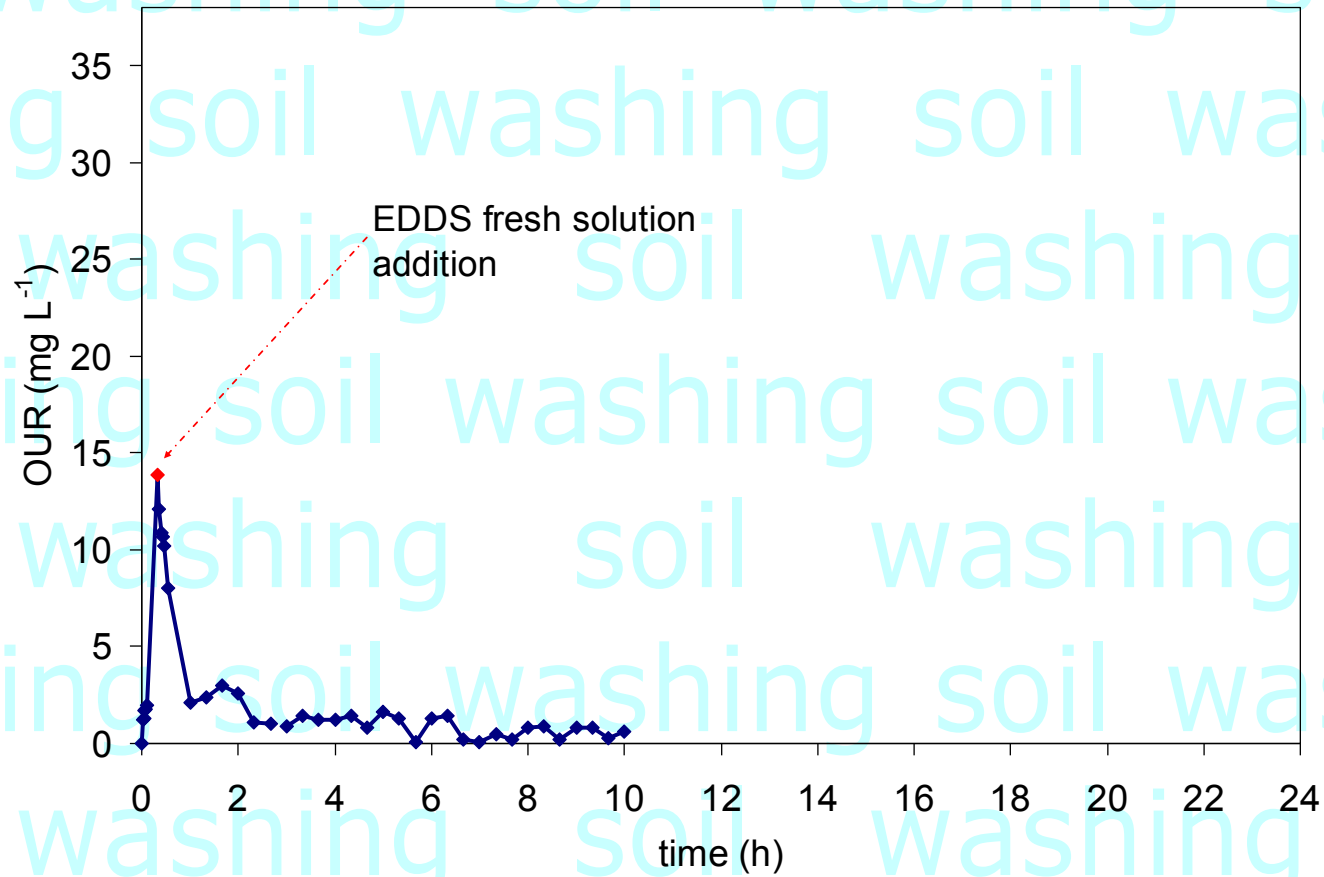
# Kinetics - chelants



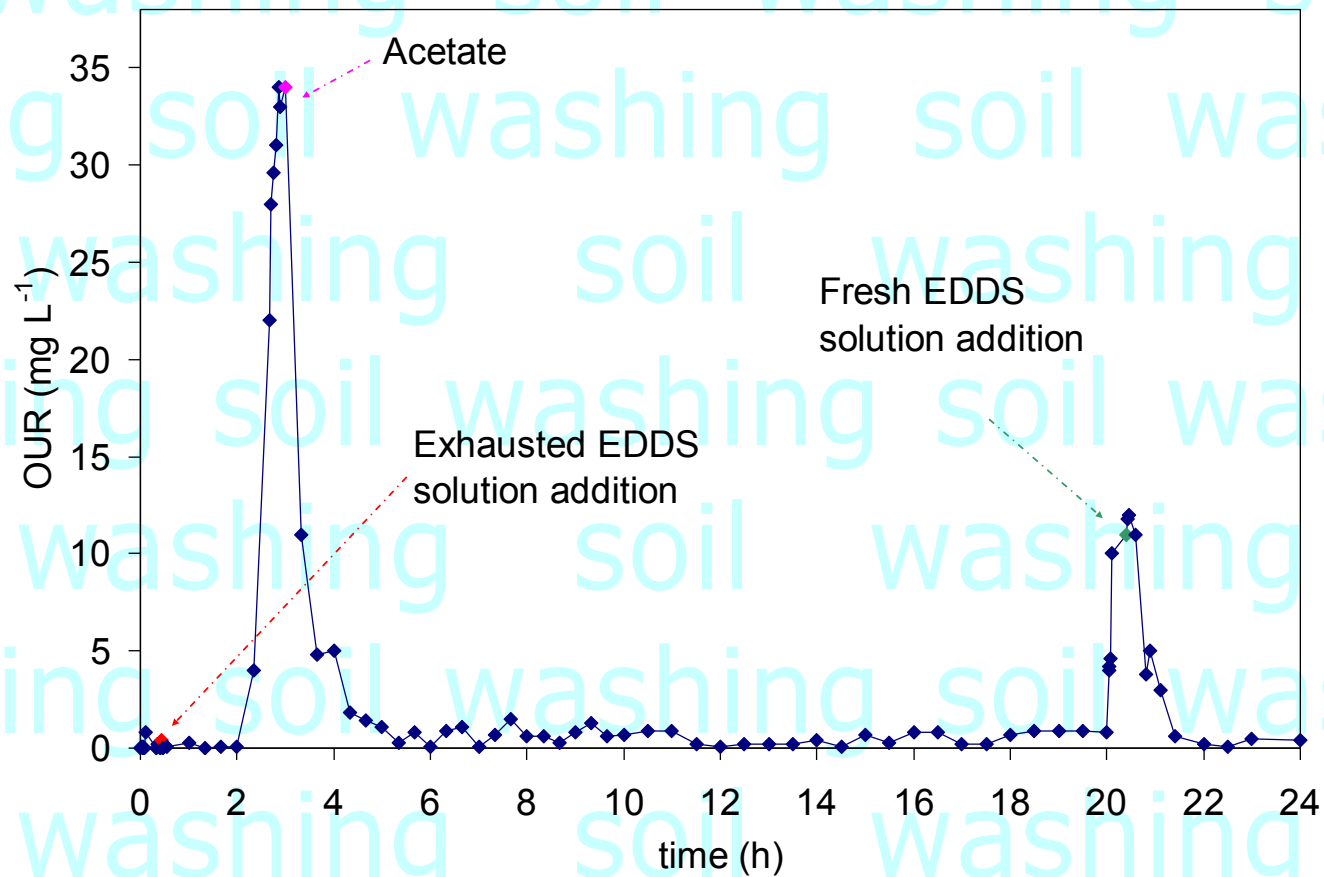
# Exhausted solutions



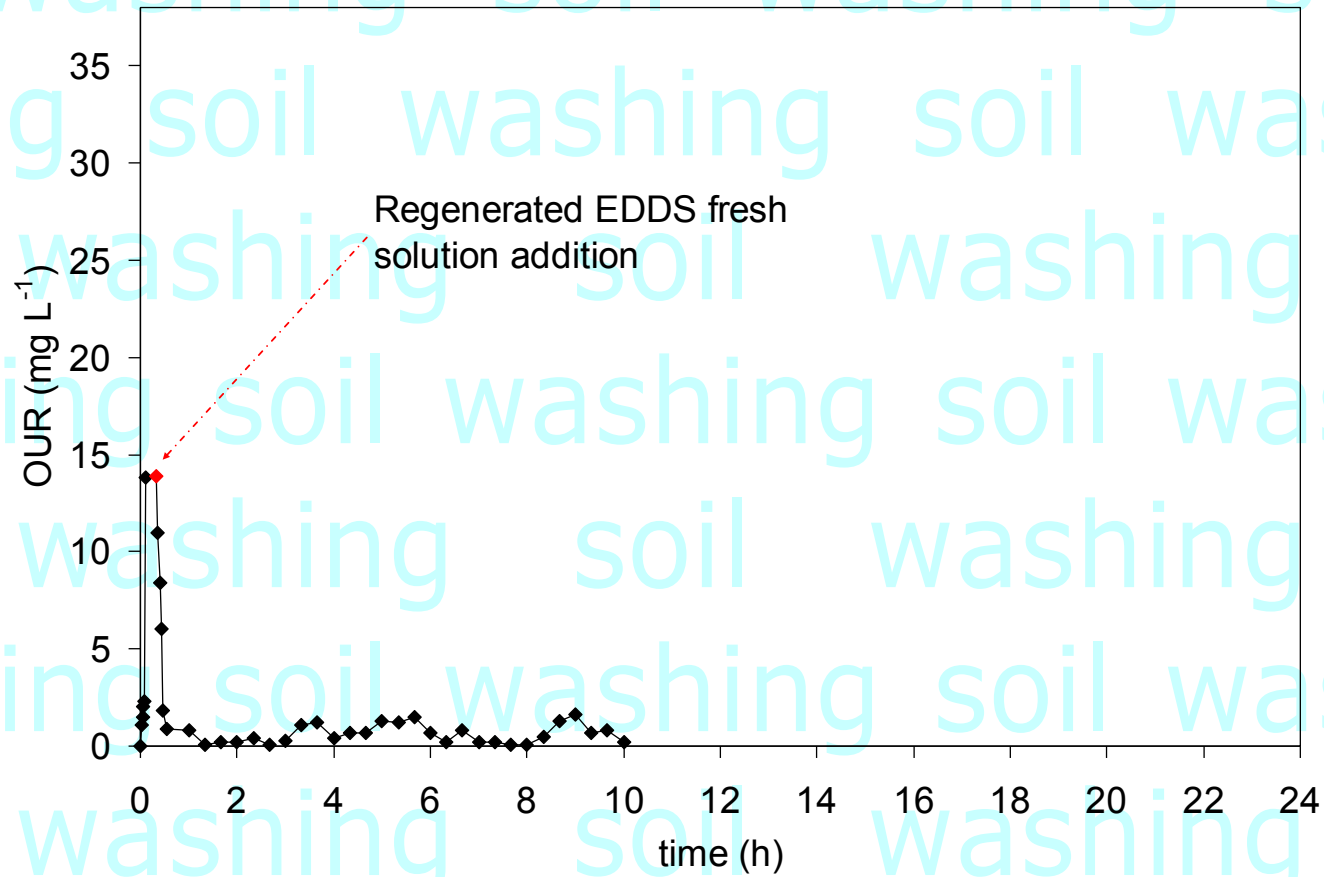
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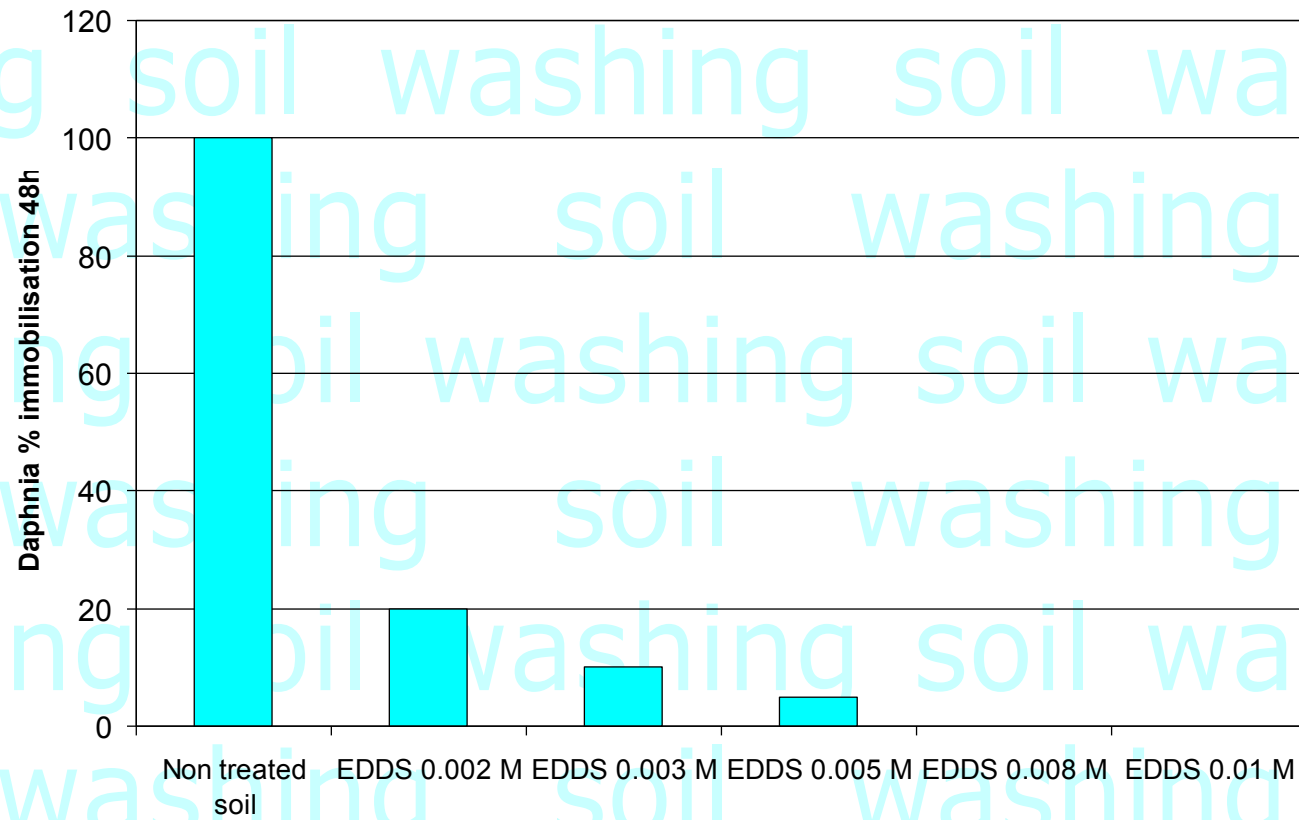
# Exhausted solutions



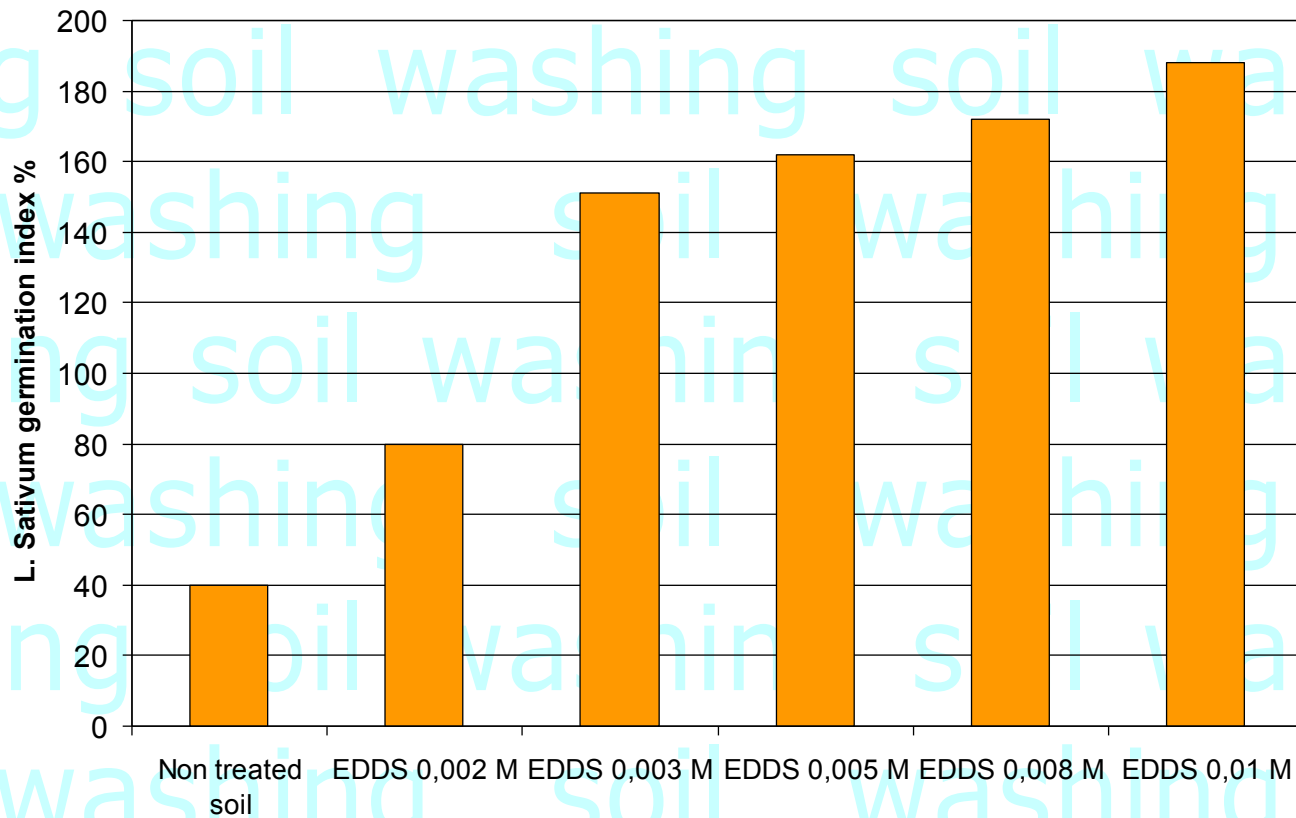
# Exhausted solutions



# Soil reuse



# Soil reuse











What you are not going to tell me,  
..... although you really would!

- Do you really think I was listening to your boring presentation?
- Don't you think you have a terrible Italian accent?
- Where did you find such a tremendous necktie?