Heap leaching of Pb and Zn contaminated soil using ozone/UV treatment of EDTA extractants

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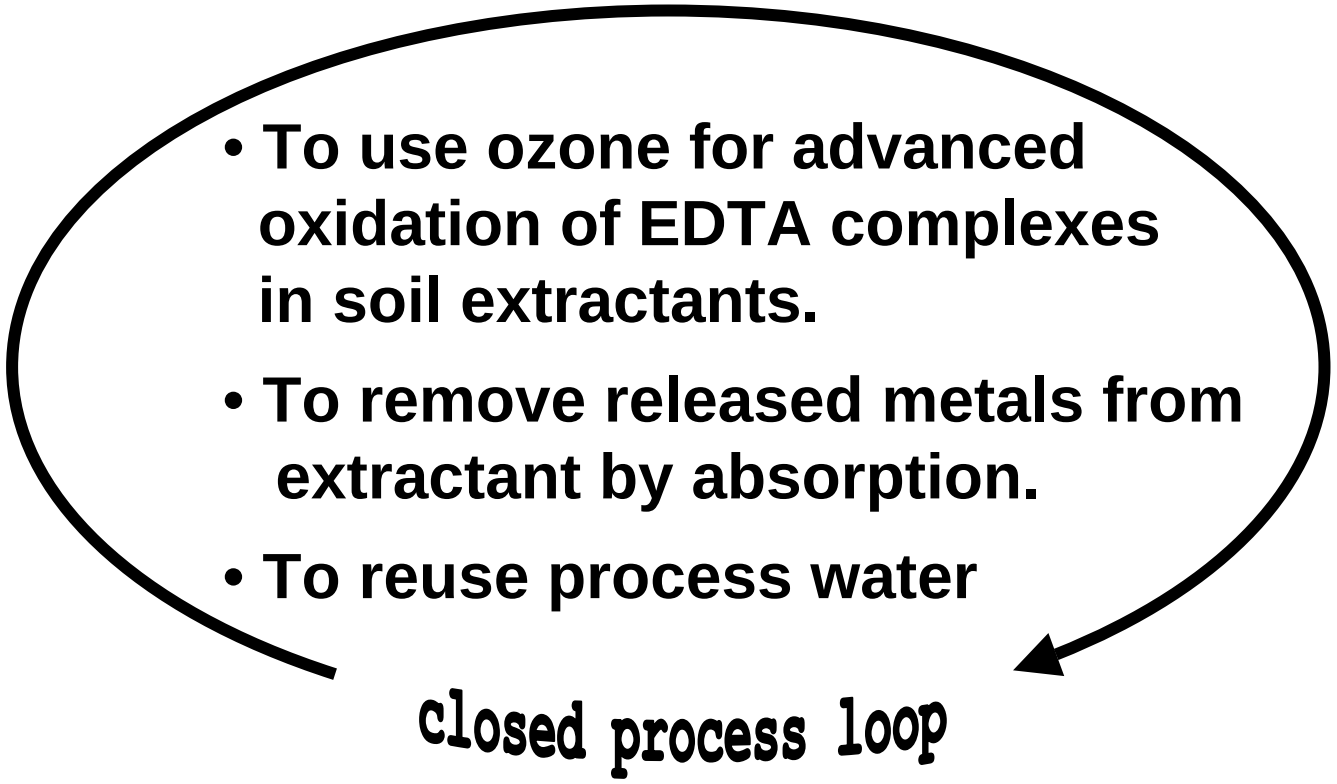
- **Acid and chelator soil washing are the two most prevalent heavy metal removal methods.**
- **For soils contaminated primarily with Pb, EDTA is in most cases the most effective.**
- **Soil washing involve extraction of soil slurry or soil leaching.**

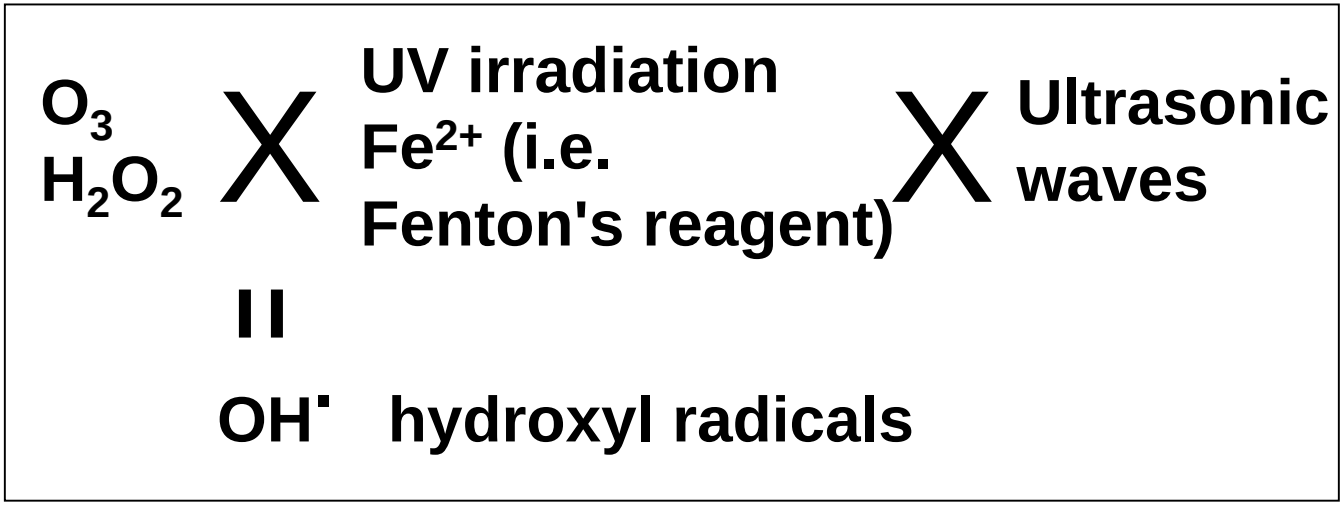
Problems:

- **separation of chelator-heavy metals complexes from the waste extractant.**
- **chelator and water recycling.**

OBJECTIVES:


• To use ozone for advanced oxidation of EDTA complexes in soil extractants.
• To remove released metals from extractant by absorption.
• To reuse process water
closed process loop

Advanced Oxidation Processes (AOP):



Use of AOP:

- **Wastewater treatment.**
- **Remediation of soils contaminated with organic xenobiotics.**
- **Treatment of EDTA containing decontamination waters from the nuclear industry .**

Physical and chemical characteristics and fractionation of Pb and Zn in the used soil (Mežica Vally, Slovenia)

Soil properties		
pH ($CaCl_2$)	7.1	
organic matter (%)	9.3	
P (mg kg^{-1})	61.8	
CO_3^- (mg kg^{-1})	15.4	
CEC (mmol C^+ 100 g^{-1})	23.3	
sand (%)	56.3	
silt (%)	32.6	
clay (%)	11.1	
texture	Sandy loam – sandy	
total Pb (mg kg^{-1})	1243±68	
total Zn (mg kg^{-1})	1190±116	
Fractionation[a]	Pb (%)	Zn (%)
in soil solution	0.07±0.04	0.05±0.01
exchangeable	0.27±0.02	0.20±0.20
bound to carbonate	24.1±0.3	7.60±0.25
bound to Fe and Mn oxides	0.28±0.04	2.17±0.02
bound to organic matter	56.2±1.4	15.0±0.7
residual fraction	8.04±0.4	61.0±2.57
Recovery	89.0	86.1

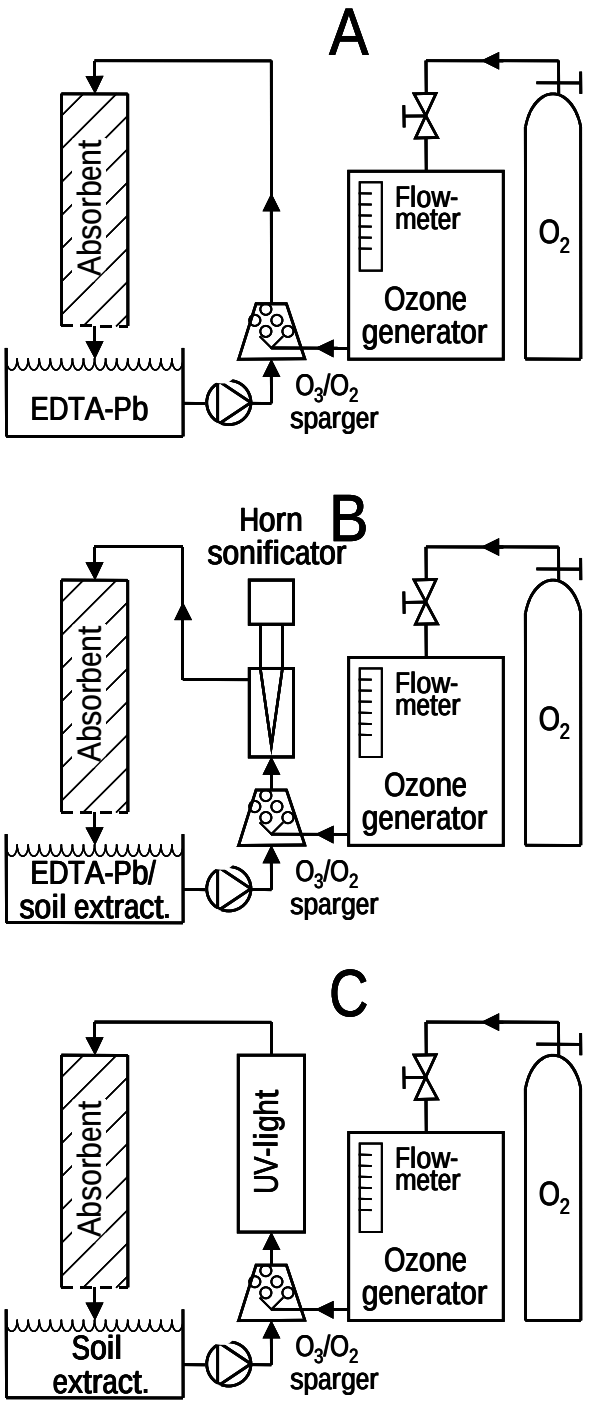
[a] Means and standard deviations (n = 3) are presented.

Different OP were tested for treatment of:

a.) Pb-EDTA water solution
b.) wastewaters after soil leaching/extraction with EDTA

in an:

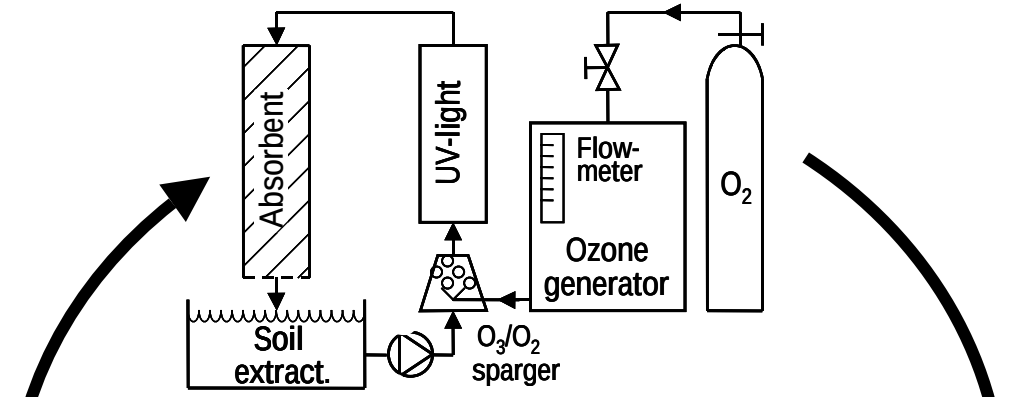
(A) ozone treatment unit
(B) ozone/ultrasonic treatment unit
(C) ozone/UV treatment unit

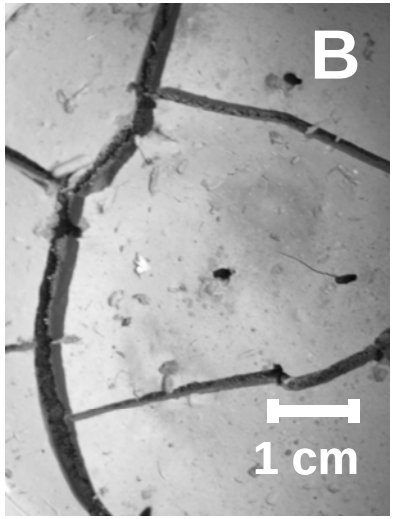


Concentration of Pb in Pb-EDTA water solution and in wastewater obtained after soil extraction with EDTA, after treatment with different OP and absorption of released Pb.

AOP	Treated liquid phase	Pb (mg L^{-1}) treatment cycle		
		0	1	5
ozone	Pb-EDTA solution (9.7 M)	1930	993	2
ozone/ultra waves	Pb-EDTA solution (9.7 M)	1955	752	4
ozone/ultra waves	soil leachate (80 mmol kg^{-1} EDTA)	792	770	742
ozone/UV irradiation	soil leachate (40 mmol kg^{-1} EDTA)	403	276	1
ozone/UV irradiation	soil leachate (80 mmol kg^{-1} EDTA)	792	695	20

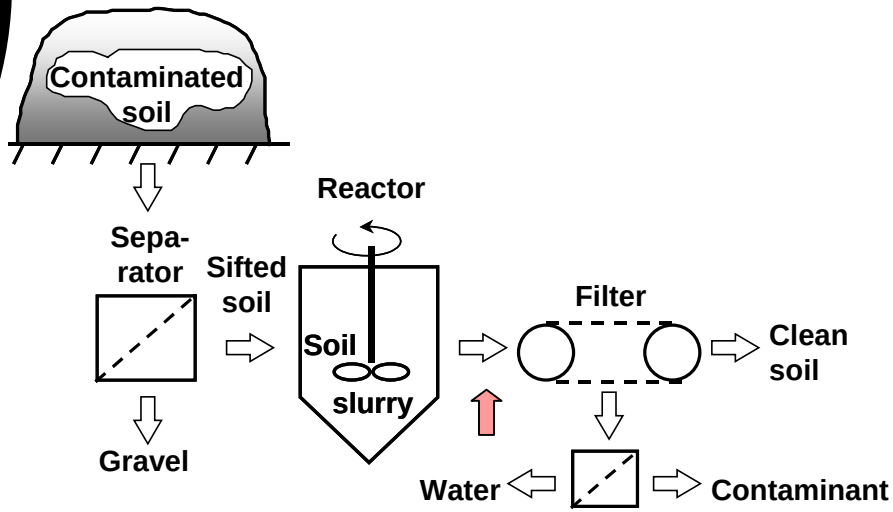
Extraction of soil slurry with 5, 10, 20 40 mmol kg^{-1} EDTA in reactor, reuse of treated extractant for soil rinsing



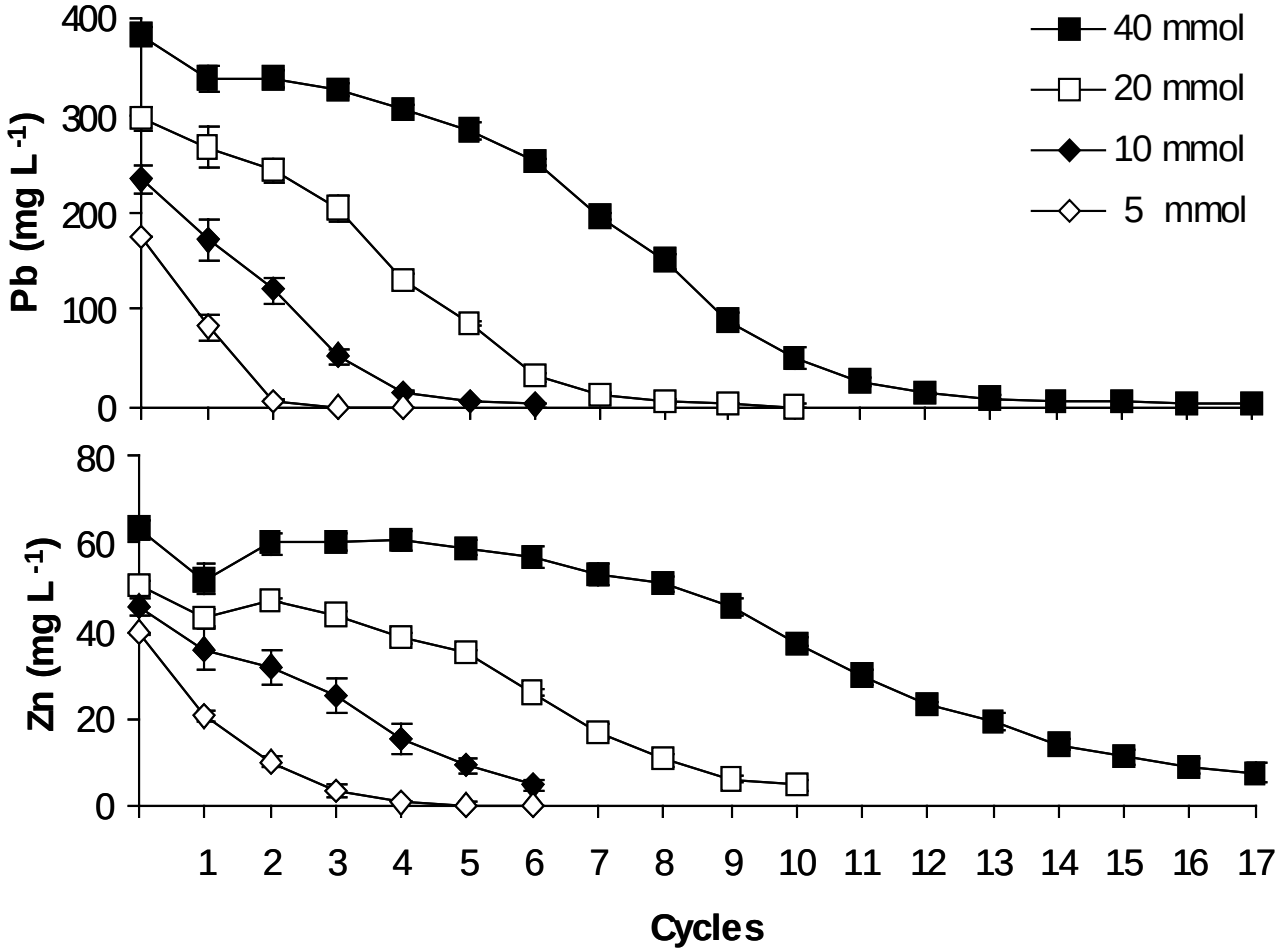


Pb removal: 54.5 ± 2,5%

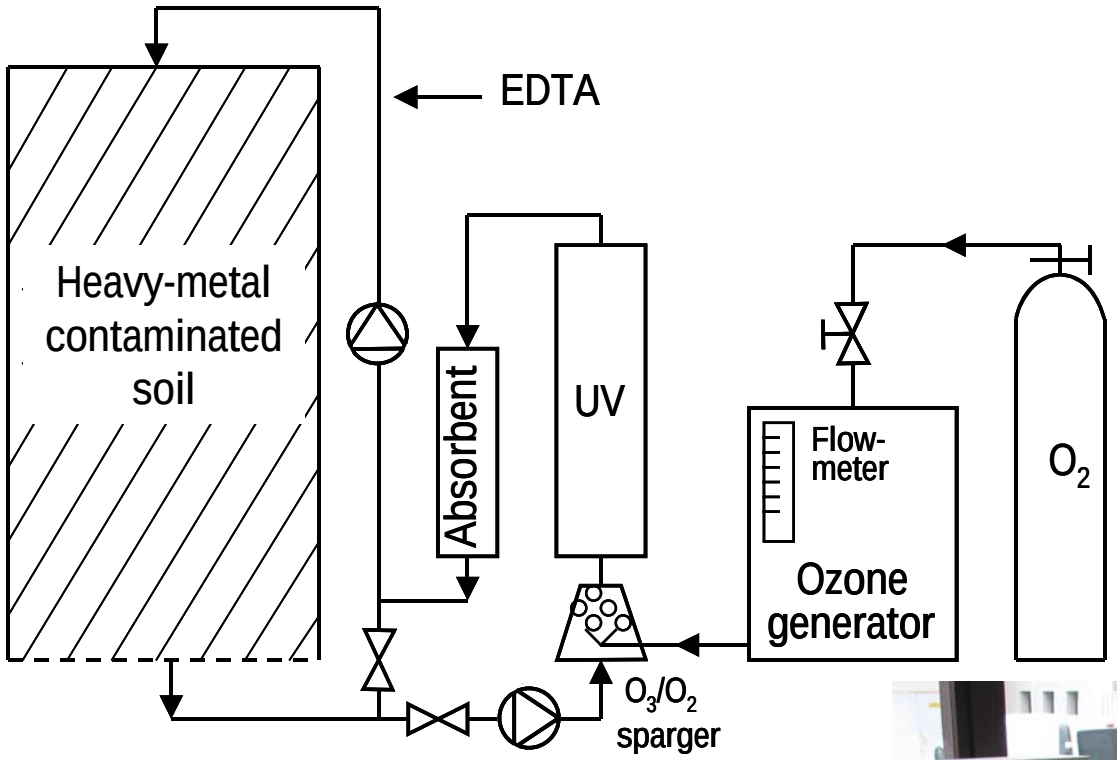
with 40 mmol kg^{-1} EDTA (9.9 ± 0.7% Zn removal)



Concentration of Pb and Zn in wastewaters obtained after soil extraction with 5 - 40 mmol kg^{-1} EDTA, during treatment in the ozone/UV unit in several cycles (n = 3, ± SD).



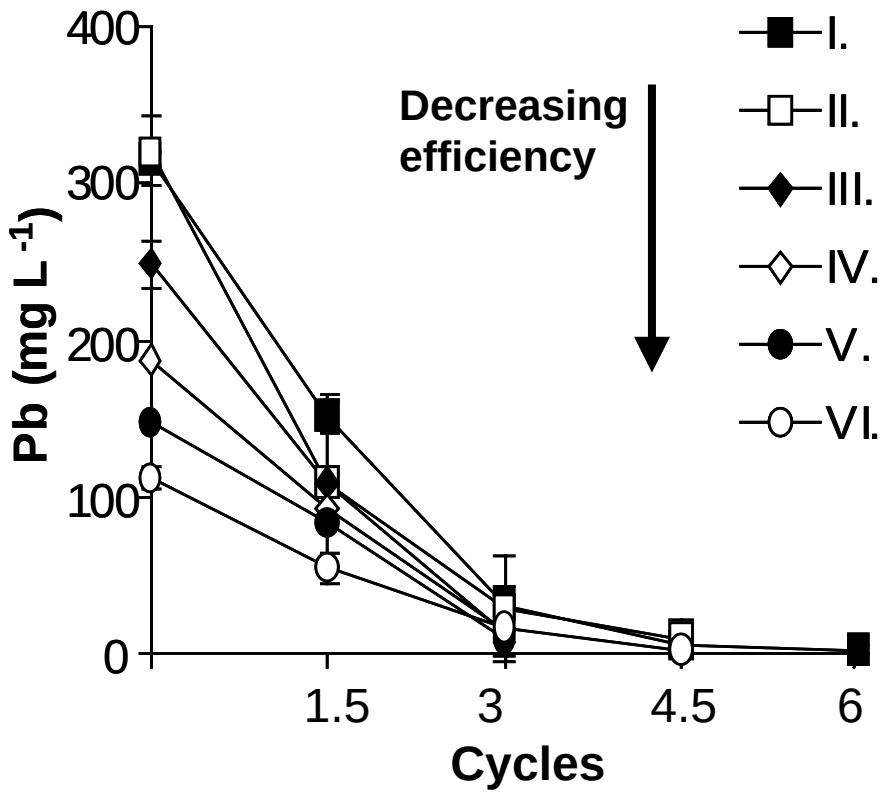
Heap leaching using EDTA and O_3/UV



SIMULATION:

- **4.5 kg of soil was placed in a column 24 cm high.**
- **Treatment with 6 consecutive (2.5 mmol kg^{-1}) EDTA additions in 3.1 L water.**
- **Extractant was circulated through O_3/UV unit (absorbent: Slovakite).**

Heap leaching using EDTA and O_3/UV



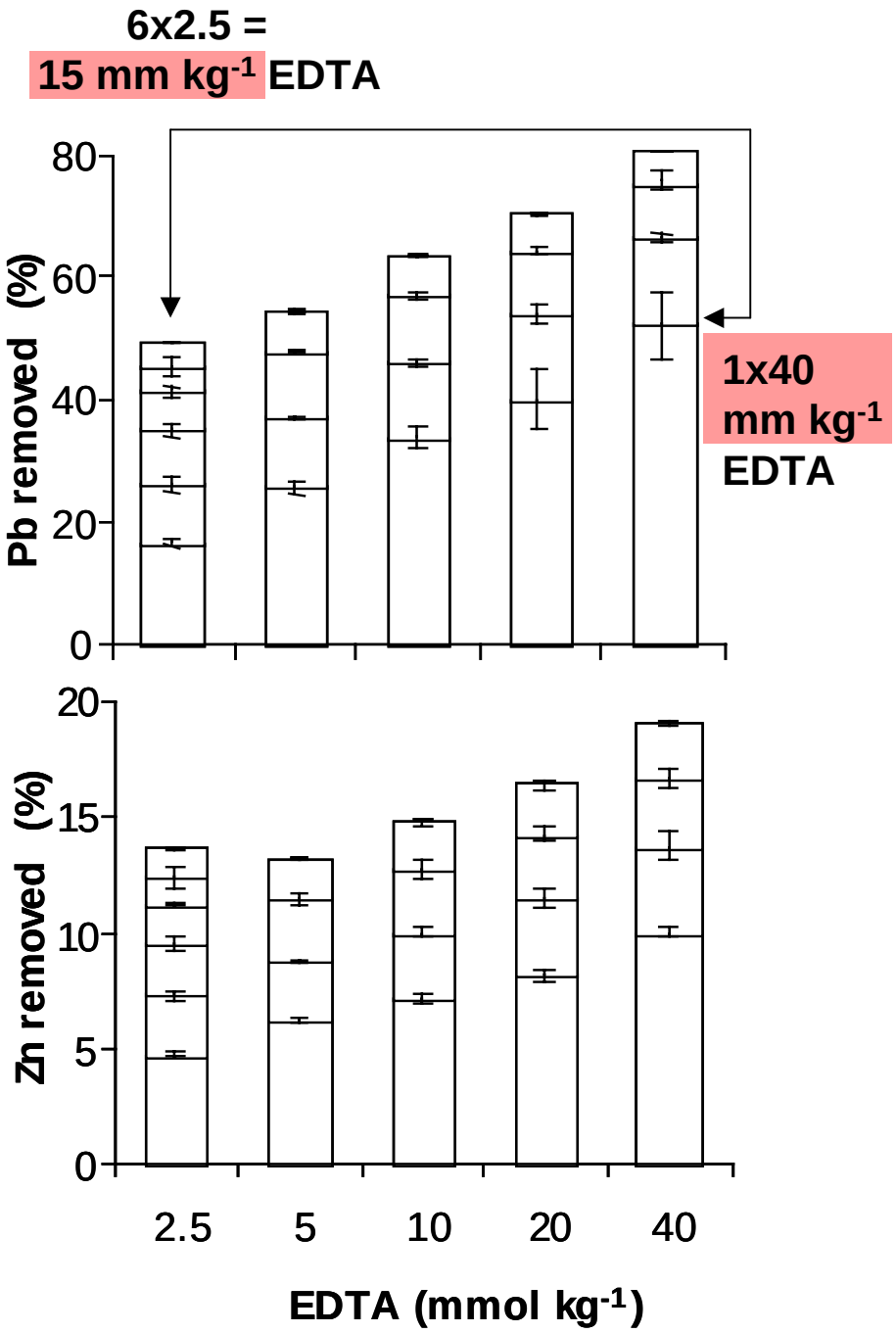
Pb in extractants during heap leaching with I- VI consecutive additions of 2.5 mmol kg-1 EDTA. Extractants were treated with O_3/UV in 3.5-6 treatment cycles.

Pb removal: 49.6 ± 0.6 %

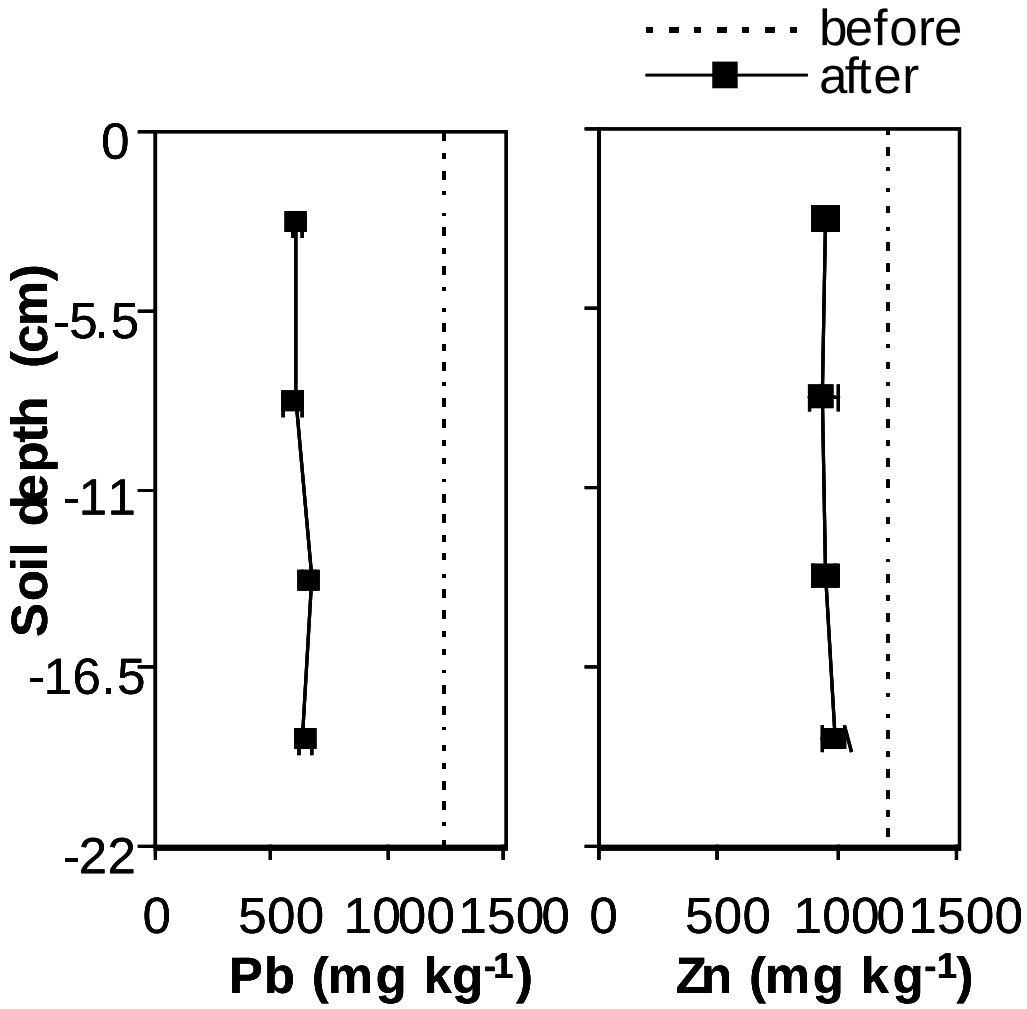
with 15 mmol kg^{-1} EDTA
(19.9 ± 1.7% Zn)

NO wastewaters
NO emissions
LOW water consumption
SOIL GENTLE method

Consecutive EDTA treatment is more effective



The removal of soil Pb and Zn after repetitive heap leaching using various EDTA concentrations (n = 3, ± SD).



Pb and Zn concentration through the soil profile in soil column before and after heap leaching with 6- consecutive additions of 2.5 mmol kg^{-1} EDTA (n = 3, ± SD).

Final wastewater:

pH = 7.45±0.04
1.98±2.17 mg L^{-1} Pb
4.55±2.36 mg L^{-1} Zn
0.05±0.04 mM EDTA
0.66±0.55 mg L^{-1} Fe
167.6±28.5 mg L^{-1} Ca
(Ca in the tap water 85.3 mg L^{-1})

CONCLUSIONS

For soils contaminated primarily with Pb, treating the EDTA extractants with ozone/ UV and reuse of extractants enables efficient soil heap leaching with very little or no wastewater generation, easy control over emissions, and lowers the requirements for process water.

Methods that recycle not only the process water but also the chelator:

- **trans-complexation,**
- **reverse osmosis**
- **anion exchange resins**

may become economically more feasible.

Advantage of AOP in a closed loop process:

- ***treatment of final wastewater***
- ***technically simple***
- ***robustness***
- ***direct soil ozonation***
- ***removal of organic xenobiotics***

Robustness:

- different metals
- different chelators

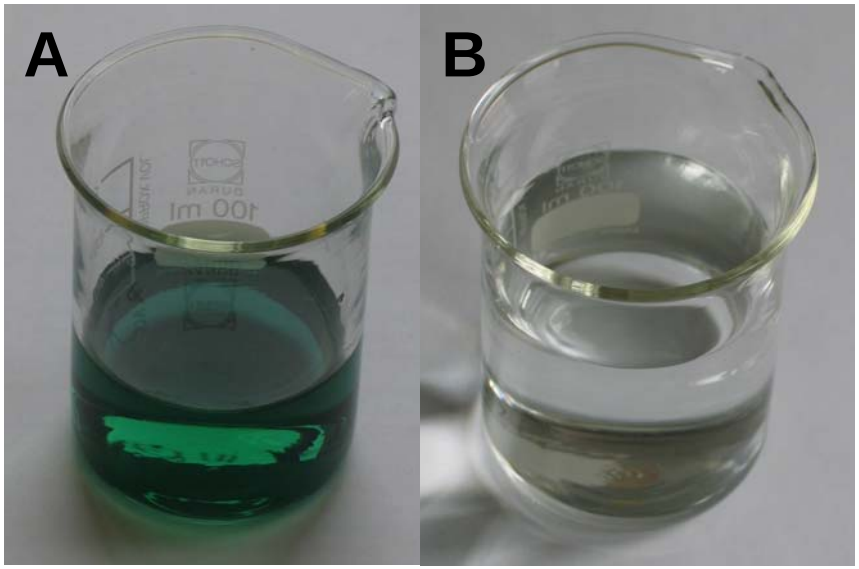
Heap leaching (AOP, closed loop, laboratory scale) of contaminated vineyard soil (Medana, Slovenia) with 412±11 mg kg^{-1} Cu using ethylenediamine disuccinate.

Cu removal:

47.5 ± 7.4 %

with 1 X 5 mmol kg^{-1} [S,S]-EDDS

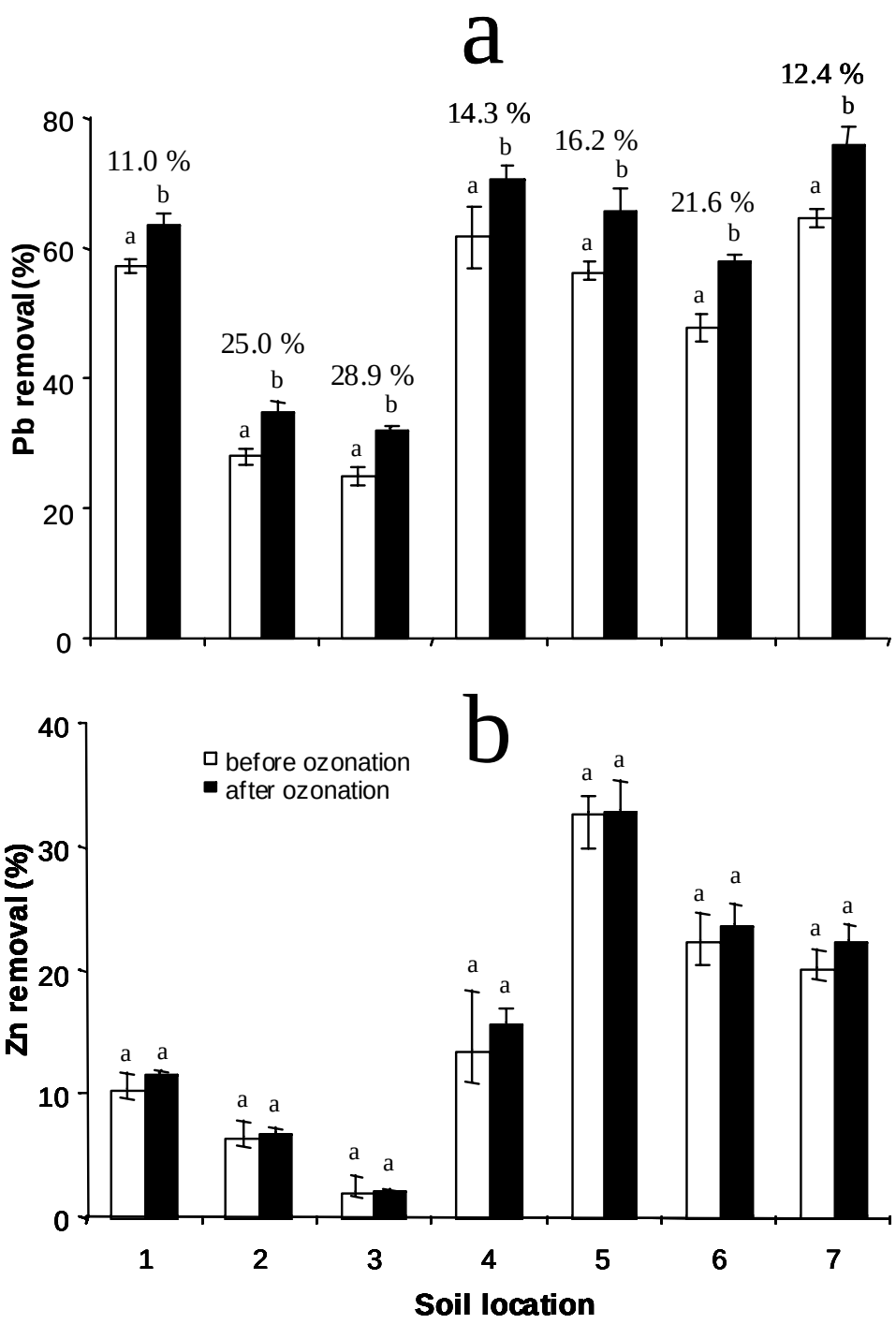
Cu in the wastewater: 2.6±0.7 mg L^{-1}



Initial (A) and final (B) extractant (wastewater)

Direct soil ozonation

- **removal of organic xenobiotics**
- **enhanced extractability**



EDTA extraction of Pb (a) and Zn (b) before and after ozonation of soils from 7 different locations in the Mežica Vally (Slovenia). Data within the Figure 2a denote the percentage increase of Pb extractability after ozonation.

a, b denote statistically different treatments according to the Duncan test ($p < 0.05$). ($n = 3 \pm SD$).

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