# Recovery of Toxic Elements from Sediments of Eutrophic Fresh-Waters

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**Introduction**

The historical lack of adequate wastewater treatment has resulted in deposition of significant pools of phosphate and nitrogen in urban freshwater sediments. Although wastewater treatment has improved during the past decades, eutrophication continues to shatter the water quality due to the continued release and re-absorption of nutrient from the sediments. Dredging would permanently remove the sediment as a nutrient source, and could potentially lead to recirculation of the nutrients and organics as soil amendment materials. Commonly, however, urban freshwater sediments also contain elevated levels of toxic elements, such as Cd, Cr, Cu, Ni, Pb, and Zn arising from centuries of human activity along the available fresh water sources. Regulations require deposition of such sediments in hazardous waste landfills, an economical and infrastructural challenge due to which restoration has largely been restricted to temporary solutions such as bio-manipulation, sediment coverage or stabilization with aluminum.

The feasibility of electrodialytic remediation (EDR) of sludge contaminated by heavy metals when suspended in an aqueous solution was documented by removal of Cu, Pb and Zn from harbor sediments (Pedersen *et al.* 2017*)* and extraction of P, Cd, Cu, Cr, Pb, Zn, Ni from wastewater sludge (Ebbers et al. 2015). The goal of this work was to investigate whether EDR is a feasible method to remediate fresh water sediments contaminated by Cd, Cr, Cu, Ni, Pb, and Zn, and whether the resulting product is suitable to amend poor agricultural soils.

**Materials and methods**

Two sediments were collected from the heavily contaminated system of lakes and millponds, Mølleåsystemet north of Copenhagen, Denmark; Bagsværd lake and Raadvad millpond. A third sample was taken from a less contaminated lake in Jutland, Denmark: Bygholm lake. Prior to treatment, coarse grains were removed by sieving through a 2 mm sieve (cell experiments) or a 1 mm sieve (stack experiment). All sediment samples were subjected to experimental EDR in laboratory scale in cylindrical Plexiglas-cells with three compartments (fig. 1a) also used by Ebbers *et al.* 2015. Four experiments of variable duration (72 to 336 hours) were made at a liquid to solid ratio (L/S) of 4, and the voltage drop was kept constant at 15V. The most contaminated sediment was in addition subjected to experimental treatment in an electrodialysis stack resembling conventional electrodialysis though with specially designed spacers for the grains to pass (fig. 1b) similar to the one used by Jensen *et al.* 2015. One experiment was made treating 500g sediment at 0,9 mA/cm$^2$ with a retention-time of 17 hours.

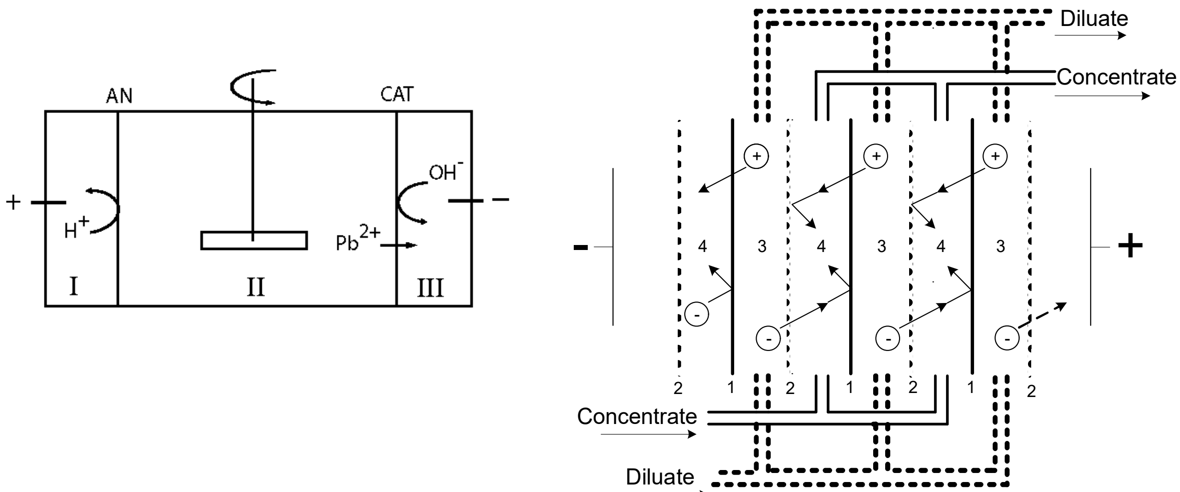


**Figure 1. a)** Schematic view of a cell used for experimental EDR remediation of soil-fines in suspension. AN = anion-exchange membrane, CAT = cation-exchange membrane. b) Schematic view of electrodialysis stack.

**Results and discussion**

The results of the treatments in the three-compartment electrodialytic cell (table 1) showed that all target elements can be reduced in freshwater sediment by EDR, but that efficiency varies among sediments. The removal order of the elements was Zn=Cd>Ni>As>Pb=Cu>Cr. The pH was a main governing parameter: Element removal was observed from the least carbonate rich sediment (Raadvad) at pH<2 while not at pH>4.8. The two carbonate rich sediments (Bygholm and Bagsværd) never reached pH<6. Nevertheless 40% Cd was removed from the Bygholm sediment and 16% Pb was removed from the Bagsværd sediment. Indicating that elements in the carbonate rich sediments are weaker bound, which is in accordance with the findings of Ottosen *et al.* 2001. The cell-experiments showed increased removal with time, and only for Cd and Zn from Raadvad which were extracted > 90%, the removal rate decreased during the treatment.

**Table 1.** Acid digestible content of toxic elements in the three sediments (mg/kg). *Limiting value for soil to be considered clean. *Limiting values for use of sludge as soil amendment according to Danish legislation.

| Sediment | Element | Initial cell ppm | Final cell ppm | Removal cell (%) | Initial stack ppm | Final stack ppm | Removal stack (%) | Limit value* ppm | Limit value** ppm |
|---|---|---|---|---|---|---|---|---|---|
| **Raadvad** | As | 16 | 7 | 56 | 33 | 15 | 55 | - | 20 |
| | Cd | 18 | 1.5 | 92 | 17 | 3.3 | 81 | 0.8 | 0.5 |
| | Cr | 293 | 238 | 19 | 346 | - | - | 100 | 500 |
| | Cu | 808 | 218 | 73 | 1200 | 793 | 34 | 1000 | 500 |
| | Ni | 37 | 10 | 73 | 84 | - | - | 30 | 30 |
| | Pb | 666 | 157 | 76 | 694 | 496 | 29 | 120 | 40 |
| | Zn | 1274 | 68 | 95 | 1496 | 174 | 88 | 4000 | 500 |
| **Bygholm** | As | 90 | 79 | 12 | - | - | - | - | 20 |
| | Cd | 1.1 | 0.7 | 36 | - | - | - | 0.8 | 0.5 |
| **Bagsværd** | Cd | 1.4 | 1.4 | 0 | 2.1 | 1.7 | 19 | 0.8 | 0.5 |
| | Pb | 69 | 58 | 16 | 110 | 50 | 55 | 120 | 40 |

During treatment sediment characteristics changed (table 2). Most particular was the pH drop accompanied by a significant reduction in $CaCO_3$ content. Prior to use for soil amendment after EDR, $CaCO_3$ would thus have to be re-introduced. No significant change in the organic content, Fe or N were detected, while the macronutrients P, Al and K significantly reduced, suggesting the final product would end up nutrient deficient. While also suggesting that recovery of P, a priority-listed resource, might be a feasible option, as suggested by Ebbers *et al.* (2015) for P from sewage sludge.

**Table 2.** Characteristics of the Raadvad sediments prior to and after electrodialytic treatment.

| | Initial | After EDR in cell | After EDR in stack |
|---|---|---|---|
| **pH** | 6.5 | 2.0 | 2.9 |
| **Conductivity [mS/cm]** | 2.2 | 2.3 | 0.8 |
| **N [g/kg]** | 20 | 22 | 18 |
| **P[g/kg]** | 3.2 | 2.2 | 1.0 |
| **$CaCO_3$ [g/kg]** | 38 | 8 | 0.3 |
| **TOC [g/kg]** | 492 | 549 | 326 |
| **Fe [g/kg]** | 22.4 | 15.4 | 20.9 |
| **Al [g/kg]** | 9.7 | 3.9 | 4.9 |
| **K [mg/kg]** | 1203 | 960 | 674 |

**Conclusion**

Electrodialysis is a feasible method for removal and recovery of heavy metals and phosphorous from sediments of eutrophic fresh-water recipients, and the stack setup is feasible for upscaling and reduced treatment time. The resulting sediment may be valuable for soil amendment though depleted in major nutrients (except from N) and with requirement for lime addition.

**References**


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