





Linnæus University

LIFE SURE

Sediment Uptake and Remediation on an Ecological Basis

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Action B2 Installation and Minor scale tests

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nutrients

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1 Introduction and objectives

The LIFE-SURE project aims to demonstrate a disruptive, cost-effective and environmental sustainable dredging method for sediment extraction in shallow eutrophic waters. The project intends to test the technique in Malmfjärden bay located at Kalmar city. The water body currently presents problems of eutrophication. Additionally, the bay is transforming extremely shallow. The retrieved sediments will be employed in beneficial uses.

Linnaeus University (LNU) is one of the partners of LIFE-SURE, and its main roles are the monitoring of the system and lab testing of extraction methods. The action B2.3 or testing of extracting metals and/or phosphorous comprises the evaluation of methods for extracting metals and nutrients from contaminated sediments and slurry from the rejected water on a laboratory scale level.

The objective of this report is to present the characterisation of sediments and rejected water from the dewatering system and their potential for recovery. The tested extraction methods will also be described. Due to confidentially of unpublished data, the results of the experiments will be presented in the final report of the project.

2 Characterisation of sediments and rejected water

The potential to extract beneficial compounds depends on the characterisation of the sediments – water. The major potential is found in components with high concentrations since the amount retrieved by the extraction will be higher. Therefore, the first step to designing the extraction of nutrients and metals should always contemplate a complete characterisation of sediments or the matrix where the compounds will be extracted. The total concentration of metals is a poor indicator of potential extraction since the metals are bound with different chemical compounds, and depending on this linkage, the metals could be more easily or hardly released. Similarly, the characterisation of organic compounds contributes to determining potential risk pollution or interference in the extraction methods. The following section will present the speciation of metals for sediments, as well as a complete characterisation including total concentrations of nutrients and organic pollutants for sediments and rejected water.

2.1 Characterisation rejected water

The rejected water from the dewatering system was analysed three times during the pilot stage (summer 2020). The samples were taken at the outlet of the treatment system and were sent to an external laboratory for analysis. The characterisation is presented in Table 1. Organic pollutants present a low concentration. The concentrations of metals and nutrients are very low, and therefore, there is no potential of recovery. There will be no extraction of metals or nutrients from the reject water in the project.

Table 1. Characterisation of rejected water (mean $\pm S.D.$, n=3)

Parameter	Concentration
Arsenic (µg/l)	2.37 ± 0.47
Lead (µg/l)	<0.2
Cadmium (µg/l)	0.21 ± 0.31
Cobalt (µg/l)	0.49 ± 0.15
Copper (µg/l)	1.96 ± 1.72
Chrome (µg/l)	6.13 ± 2.67
Nickel (µg/l)	3.72 ± 0.94
Vanadium (μg/l)	3.70 ± 1.66
Zink (µg/l)	415 ± 223
Total phosphorous (mg/l)	0.04 ± 0.01
Total nitrogen (mg/l)	0.99 ± 0.32
COD (mg/l)	77.6 ± 19.0
pH	7.90 ± 0.74
Cond (µs/cm)	8.82 ± 0.11
PCB 7, sum (µg/l)	<10
PAH-L, sum (μg/l)	<0.10
PAH-M, sum (μg/l)	<0.20
PAH-H, sum (µg/l)	<0.3
BTEX, sum (μg/l)	<1
Aliphatic C5-16 (μg/l)	22 ± 13
Aliphatic C16-35 (μg/l)	<10
Aromatic C8-10 (µg/l)	<10
Aromatic C10-16 (µg/l)	<10
Aromatic C16-35 (μg/l)	<2
Oil index C10-40 (mg/l)	1 ± 0

2.2 Characterisation of sediments

The characterisation of sediments is presented in Table 2. Two samples were collected from the geotubes belonging to the dewatering system. The sampling was performed in summer of 2020. The samples were sent to an external laboratory for analysis. The sediment has a high concentration of nitrogen and a medium-high concentration of phosphorous. The metals have a low-medium concentration. The organic pollutants present a low concentration by the exemption of aliphatic compounds, which have a medium concentration explain by the addition of organic polymer during the dewatering system.

Table 2. Characterisation of sediments (mean \pm *S.D.,* n=2)

Parameter	Concentration
Solid content (%)	23.3 ± 0.1
Loss on ignition – organic content (%)	21.0 ± 2.1
Total organic carbon (TOC) (%)	8.05 ± 0.07
Strontium (Sb) (mg/kg)	<2.5
Arsenic (As) (mg/kg)	9.3 ± 0
Lead (Pb) (mg/kg)	61.5 ± 0.71

Parameter	Concentration
Cadmium (Cd) (mg/kg)	1.8 ± 0
Copper (Cu) (mg/kg)	63 ± 0
Chrome (Cr) (mg/kg)	33 ± 0
Nickel (Ni) (mg/kg)	31.5 ± 0.7
Zink (Zn) (mg/kg)	240 ± 0
Mercury (Hg) (mg/kg)	0.2 ± 0
Total Nitrogen (g/kg)	12 ± 0
Total Phosphorous (mg/kg)	1400 ± 0
Sulphur (S) (mg/kg)	$15,000 \pm 0$
PCB 7, sum (mg/kg)	0.0043 ± 0.0004
PAH-L, sum (mg/kg)	< 0.08
PAH-M, sum (mg/kg)	1.5 ± 0
PAH-H, sum (mg/kg)	1.1 ± 0
BTEX, sum (mg/kg)	<1
Aliphatic C5-16 (mg/kg)	280 ± 57
Aliphatic C16-35 (mg/kg)	73 ± 27
Aromatic C8-10 (mg/kg)	<0.8
Aromatic C10-16 (mg/kg)	<2
Aromatic C16-35 (mg/kg)	<1

During the action A1.1 "Verification of the chemical and biological status", sediments were extracted from the bay and were characterised. The results could be consulted on the <u>scientific</u> <u>publication</u> (Ferrans et al., 2019).

The speciation of metals from Malmfjärden sediments can be accessed on the <u>scientific</u> <u>publication</u> (Ferrans et al., 2021). The chosen method was the one developed by Tessier et al. (1979), where five chemical fractions are extracted. The first fraction (F1) is easily bioavailable since metals are linked with weak bonds. The second fraction (F2) contemplates trace elements that are bound to carbonates and are released with pH changes. The third fraction (F3) includes metals bind to iron and manganese oxides and can be released to the surroundings by reduction of available oxygen in the environment. Trace elements in the fourth fraction (F4) are bound to organic matter and sulphides and could be released by the increase in the available oxygen in the environment. Finally, the fifth fraction (F5) or residual fraction is related to metals that are part of the mineralogical structure of the sediment and are unlikely to be released to the environment.

Figure 1 shows the speciation of certain metals from sediments from Malmfjärden. Cu, Ni, Cr and Fe have their main connection with the residual fraction, following by the bond to F4. Therefore, an increase in the available oxygen could release about 20 to 40% of these metals. Zn and Pb have a wider distribution between the different fractions, presenting linkages with F5, F4, F3 and F2. The increase or decrease of available oxygen or changes in pH could release 40 to 60 % of Zn and Pb.

Based on the characterisation and speciation of metals from the sediments, it is possible to conclude that the sediments primarly present a potential to recover nitrogen and phosphorous. The concentration of metals is not as high as the one from nutrients, and the speciation suggests that only a certain amount of the metals could be extracted. The potential to extract metals is not as promising as for other elements. However, due to the dissemination nature of the LIFE-SURE, the extraction of metals will also be tested in order to assess extraction methods that could be implemented in a similar type of projects.

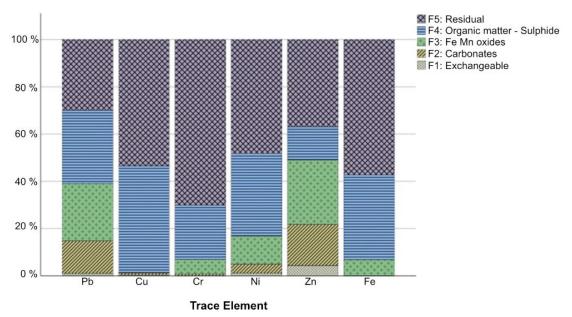


Figure 1. Speciation of metals from Malmfjärden sediments: Distribution of trace elements into the different chemical fractions. Source: (Ferrans, et al., 2021)

3 Testing of extraction of heavy metals and nutrients

3.1 Metal extraction

The extraction of metals from sediments will be tested on a laboratory scale using two different methods (chemical extraction and phytoremediation).

Chemical leaching is selected to extract trace elements since it is the most proven technique to release metals effectively. Other technologies, such as electro-kinetic methods, still use acids as a final step to mobilise the metals, and therefore, it is decided to start testing only with chemical leaching (Akcil et al., 2015). Phytoremediation is an effective method using plants to remove metals from sediments. The method will be tested due to its promising results and its economic efficiency (it could be up to 15 times cheaper than chemical or thermal treatments) (Jani et al., 2019). Bioleaching tests are discarded due to the low efficiency reported in cold regions such as Sweden (Akcil et al., 2015).

3.1.1 Chemical extraction

Chemical leaching is a proved technique, which can extract metals by dissolving or suspending them in an aqueous solution with a solvent. Several solutions are available in the market, and metal recovery commonly employs chemicals such as acids, surfactants and

chelation agents. Other important factors influencing the extraction of metals is the concentration of the agents, contact time, pH and solid to liquid ratios (Di Palma et al., 2011).

The chemical extraction tested by LNU focus on the removal of metals (see Figure 2). EDTA and EDDS were tested as chelating agents. EDTA is a well-known chelating that can form a soluble and stable complex with metals achieving effective removal rates. EDDS is another chelating agent reporting successful results and is environmental biodegradable (Akcil et al., 2015). The experiment focus on determining optimal conditions for pH and concentration of the chelating agents.

The results from the chemical leaching will be presented on the final report of the project since the data is part of a still unpublished scientific article.

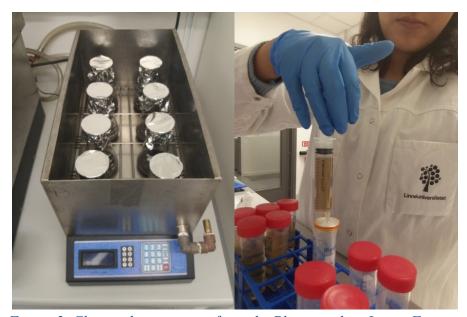


Figure 2. Chemical extraction of metals. Photo credits: Laura Ferrans

3.1.2 Phytoremediation

In the phytoremediation technique, hyper-accumulator plants are used to uptake metals from the sediments (Cristaldi et al., 2017). The up-taken trace elements could be recovered by incinerating the biomass and extracting the metals from the ashes with chemical leaching. More details about the use of phytoremediation to remove metals from sediments could be consulted in the scientific article (Jani et al., 2019) published with the help of the LIFE SURE project.

The phytoremediation experiment at LNU employed alfalfa (*Medicago sativa*) as a hyperaccumulator (see Figure 3). The experiment was run over control conditions in a greenhouse. The results still scientifically unpublished, and therefore, will be presented in the final report of the project.



Figure 3. Phytoremediation experiment at the greenhouse. Photo credits: Laura Ferrans

3.2 Nutrient recovery - extraction

The recovery of nutrients from sediments could be performed by directly using the sediments as a plant-growing substrate in the agriculture, plant-nursery or gardening sectors. This method was tested for the LIFE-SURE project since, in the future, it could be easy to implement in a pilot-scale. Additionally, an experiment to produce compost using sediments and biomass residues was also investigated. The produced compost could help to commercialise the sediments easily, and the mixture with other organic residues could improve the physical and chemical conditions of the plant-growing substrate. Finally, the direct extraction of phosphorous by chemical leaching will be tested since the method provides a final product with more pure phosphorous that can potentially be used a replacement of traditional fertilisers.

The results from the nutrient recovery experiments will be presented on the final report of the project since the data is part of a still unpublished scientific article.

3.2.1 Plants nutrient uptake

Using sediments as a plant-growing substrate represents a path to recycle nutrients since the plants directly absorb them from the sediments. The availability of the nutrients depends on the chemical forms of the elements (Kiani et al., 2021). The effectivity of local plants absorbing nitrogen, phosphorus and micronutrients from sediments of Malmfjärden was tested at LNU under control conditions at a greenhouse (see Figure 4). The experiment employed pure sediments and a mixture of sand and sediments to evaluate if the addition of other materials could improve the water holding capacity of the growing substrate.



Figure 4. Greenhouse experiment for nutrient uptake. Photo credits: Laura Ferrans

3.2.2 Composting

The use of sediments directly as a growing substrate could be challenging for legal and social reasons. Strict regulations might not allow the direct use of dredged sediments. Similarly, farmers might not be willing to use them due to the hesitation of impacts to their final agricultural products (Mattei et al., 2017). Therefore, it is important also to test methods to improve the physical and chemical conditions of dredged sediments. Co-composting was selected to be tested for the LIFE-SURE project since the technique has been widely used to produced organic fertilisers out of organic waste. The experiment was performed at LNU, and the sediments were mixed with beach wrack and green residues to improve the distribution of nutrients (see Figure 5).



Figure 5. Composting experiment at LNU. Photo credits: Laura Ferrans

3.2.3 Extraction of phosphorous

Phosphorous can be recovered under chemical precipitation. One of the most popular techniques is precipitation as struvite. The method precipitates phosphorus using different

agents such as magnesium oxide, sodium oxide and sodium citrate (Li et al., 2019). At LNU, the struvite process will be performed in 2021, and it will focus on finding the optimal value for variables such as pH, contact time and concentration of reagents.

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