

# Mesocosm Experiments Performed in 1975, 1993 and 2017 to Determine Changes in Release Rates of Zinc from Sediments Affected by an Old Mining Operation

Mattias Bäckström<sup>1</sup>, Lotta Sartz<sup>2</sup>

<sup>1</sup>*Man-Technology-Environment Research Centre, Örebro University, 701 82 Örebro, Sweden, mattias.backstrom@oru.se*

<sup>2</sup>*Bergskraft Bergslagen AB, Södra Kungsvägen 49, 692 30 Kumla, Sweden, lotta.sartz@bergskraft.se*

## Abstract

Processing of zinc/lead/silver ore started in Ämmeberg, Sweden, in 1860 and ceased in 1977. Water from the operation was discharged into a northern part of Lake Vättern called Kärrafjärden. Mesocosm experiments were performed on sediment cores sampled at the same five locations in 1976, 1993 and 2017 close to the mining operation. Experiments were performed in the same way as the original experiment in 1976 to determine the release rates of zinc as a function of time. In 2017 the release rates were in the range 0.18–1.5 for zinc, 0.00021–0.0015 for cadmium and 0.00098–0.016 mg/(d m<sup>2</sup>) for lead with the highest rates closest to the historical mining site.

Most of the reduction in release rates occurred between 1976 and 1993, while the difference between 1993 and 2017 was lower. This indicates that the release of zinc from the historical site is continuing, albeit at a substantially lower rate compared to 1976. It can also be concluded that this type of experiments can assist in understanding the mass transfer of trace elements from sediments to surface waters.

**Keywords:** Mining, Leaching, Sediments, Trace Elements, Release, Mass Transfer

## Introduction

Sediments impacted by historical mining operations can be an important secondary source for trace elements through different redistribution mechanisms (Ciszewski et al. 2012). It is important to understand what happens with trace elements in sediments when mining operations cease as this will increase the understanding about the possible future environmental impact.

Processing of zinc/lead/silver ore started in Ämmeberg, Sweden, in 1860 and operation ceased in 1977. During that period several different methods were used to process and enrich the ore; from mechanical treatment to more modern flotation. Water from the operation was discharged into a northern part of Lake Vättern called Kärrafjärden.

Sediments downstream Ämmeberg are contaminated with trace elements (primarily lead, zinc and cadmium) to a varying degree. Different external factors can affect the chemistry in the sediments and thus increase the mobility of the trace elements. Several

different leaching schemes for laboratory studies have been suggested to determine leachability of trace elements from sediments (Guo et al. 1997; Ciszewski et al. 2012; Cai et al. 2021). They are all, more or less, suffering from the drawback that the obtained results are difficult to translate into real world leachability. The purpose of the present investigation is to estimate the amount of trace elements (primarily zinc, lead and cadmium) that are being released from the sediments by determining the current release rates. Identical investigations were performed at the same sampling sites in 1976 (Borg et al. 1977) and 1993 (Göthberg et al. 1993), allowing the study of changes in the release rates since the operation closed in 1977.

## Methods

During the spring 2017 sediment cores were retrieved from 5 stations in the northern part of Lake Vättern (the second largest lake in Sweden) (fig. 1). Two replicates were retrieved from all stations and all 10

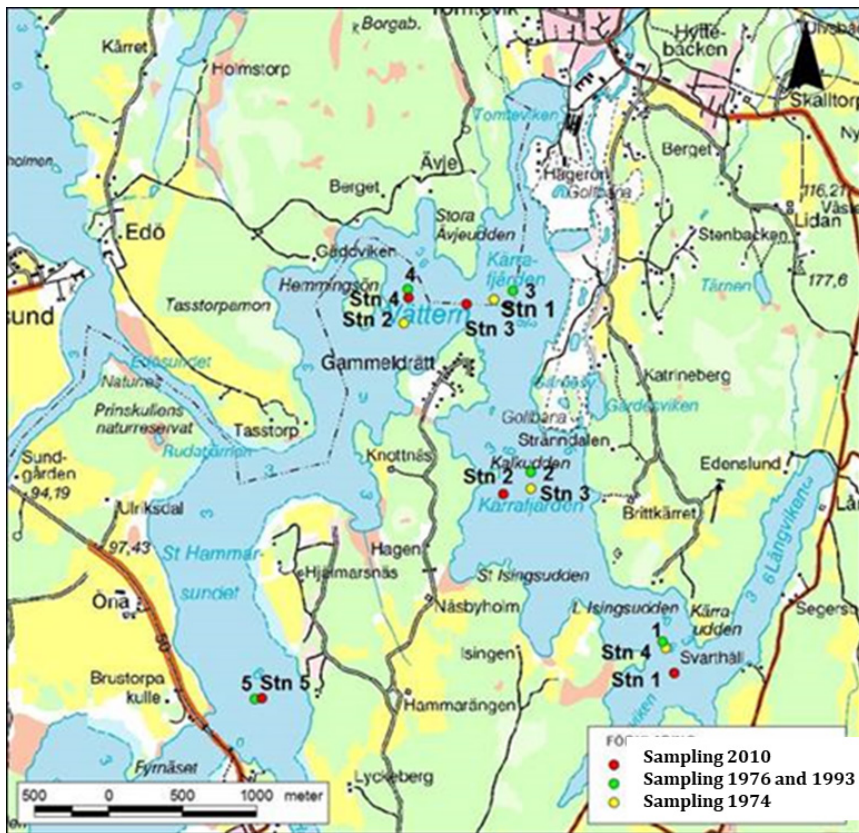


Figure 1 Illustration showing the sampling stations in 1976, 1993 and 2017 (green dots) in the northern part of Lake Vättern, Sweden. Discharge from the operation is just north of station 3 (green dot).

sediment cores were transported undisturbed to the laboratory and stored in a cold room. Dilution water for the mesocosm leaching experiments was collected in the northern part of the lake approximately 10 km from the sampling stations. This water has the same basic water chemistry as the water above the sediment cores, but with lower trace elements concentrations.

Mesocosm experiments were performed on sediment cores sampled in 2017 at the same five locations as in 1976 and 1993 close to the mining operation. Experiments were performed in the same way as the original experiment in 1976 to determine the release rates of cadmium, lead, sulfate and zinc as a function of time.

Mesocosm experiments were initiated by removing the original water from the sediment cores and gently adding 1 L dilution water instead. Mesocosm release rate

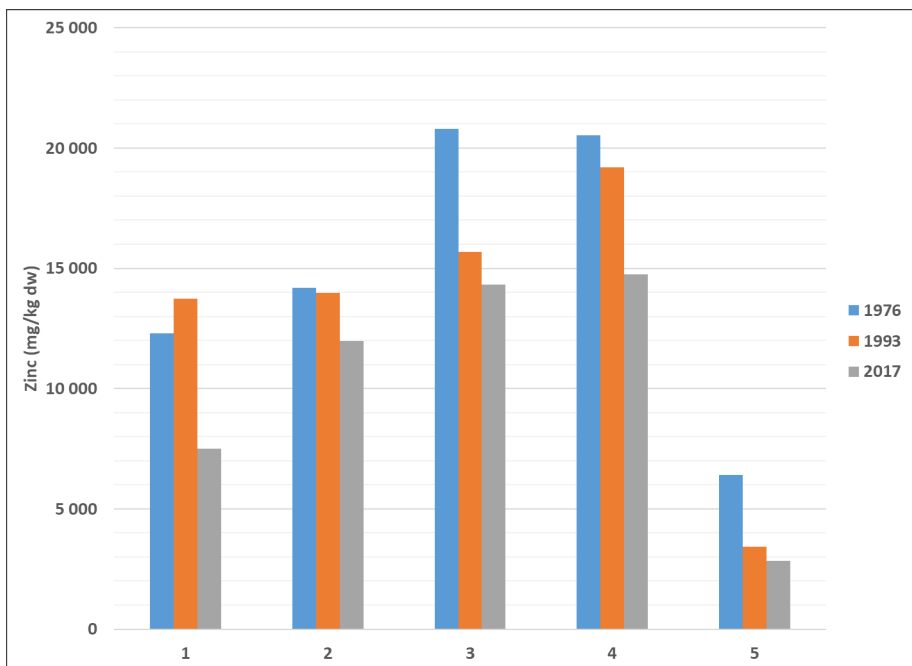
experiments were performed in duplicates at +8 °C. Lake water (dilution water) above the sediment surface was aerated slowly and samples were withdrawn after 1, 4, 11, 18, 33, 47, 62, 77 and 110 days and analysed for pH, sulfate and elements. At every sampling occasion 200 mL water was retrieved and replaced with fresh dilution water.

After the initial leaching period (110 days) the top organic sediment layer (approx. 0.5–1 cm) was removed from all sediment cores. The water was also replaced with fresh dilution water and the leaching experiments carried on for an additional 59 days. Samples were retrieved from the water (200 mL) after 4, 11, 18, 31 and 59 days in the same way as during the initial period. The purpose with the second leaching period is to study the release rates from the sediments without the presence of the surficial organic top layer. The removed top layer of the sediment cores was analysed



**Table 1** Total concentrations (mg/kg dw) for lead, cadmium, zinc, sulfur and carbon in 2017. a and b are replicates from the same sampling station. Station 3 is closest to the discharge point from the mining operation.

	Pb mg/kg dw	Cd mg/kg dw	Zn mg/kg dw	Sulfur %	Carbon %
1a	5 070	19.0	7 690	0.34	6.38
1b	4 930	18.7	7 300	0.28	6.00
2a	4 710	24.4	12 000	0.64	5.91
2b	4 710	25.0	12 000	0.57	5.88
3a	5 230	24.1	14 300	0.78	6.72
3b	5 420	24.0	14 300	0.93	6.58
4a	6 800	20.1	14 700	0.19	5.22
4b	6 970	20.7	14 800	0.26	5.32
5a	820	11.6	2 890	0.15	4.14
5b	810	11.6	2 800	0.15	3.89



**Figure 2** Total concentrations ( $n = 2$ ) of zinc (mg/kg dw) in the top layer (0–1 cm) of the sediments in 1976, 1993 and 2017.

for total trace element concentrations as well as for carbon and sulfur. In 1976 only a few elements were analysed and only zinc concentrations are thus reported here.

## Results and discussion

When it comes to the total concentrations in the top layer of the sediment cores (0–1 cm) it

is clear that the concentrations have decreased since 1976 and 1993 (tab. 1 and fig. 2).

It is also clear that the decrease in concentrations since 1993 is relatively modest at some stations considering the high initial concentrations. This indicates that either there is a source for trace elements to the sediments or that there are relevant redistribution

processes going on in the sediments. Total concentrations for cadmium, lead and sulfur can be found in tab. 1.

In fig. 3 the zinc concentrations ( $\mu\text{g/L}$ ) measured in the water above the sediment cores during the mesocosm experiments can be found. From the measurements the release rates in  $\text{mg}/(\text{d m}^2)$  have been calculated.

In 2017 the release rates were in the range 0.18–1.5 for zinc, 0.00021–0.0015 for cadmium and 0.00098–0.016  $\text{mg}/(\text{d m}^2)$  for lead with the highest rates closest to the historical mining site.

Calculated release rates ( $\text{mg}/(\text{d m}^2)$ ) for the initial 110 days are presented in tab. 2 below. The release rate is highest for zinc followed by lead. If you compare the release rates with the total concentrations all trace elements have roughly the same release rates, except for lead where the average release rate is approximately 75 times lower compared to zinc.

It is also clear that the highest release rates for zinc are still found closest to the old mining operation (2, 3 and 4). The highest release rates for sulfate are found at stations 1-3, with somewhat lower release rates at stations 3 and

4. Even though the total concentrations have not decreased dramatically since 1976 the release rates have decreased (fig. 4).

When the surficial organic sediments were removed after 110 days the release rates changes for some of the trace elements (tab. 3).

For the most interesting trace elements the release rates increase when the surficial sediments are removed (tab. 3). For lead, cadmium and zinc the average increase in release rates are +176%, +148% and +113%, respectively.

For sulfate the release decreases at station 1, while it increases at stations 2 and 3 and is roughly the same for stations 4 and 5. This indicate that there are oxidizable sulfides in the upper parts of the sediment cores.

The different sampling stations are assumed to represent different parts of the lake with different areas. By multiplying the area for each sampling station with the corresponding release rate a yearly amount released can be calculated. Considering the area of the different parts of the lake close to the historical mining site it was found that the release of zinc had decreased from 7.3 t/a in

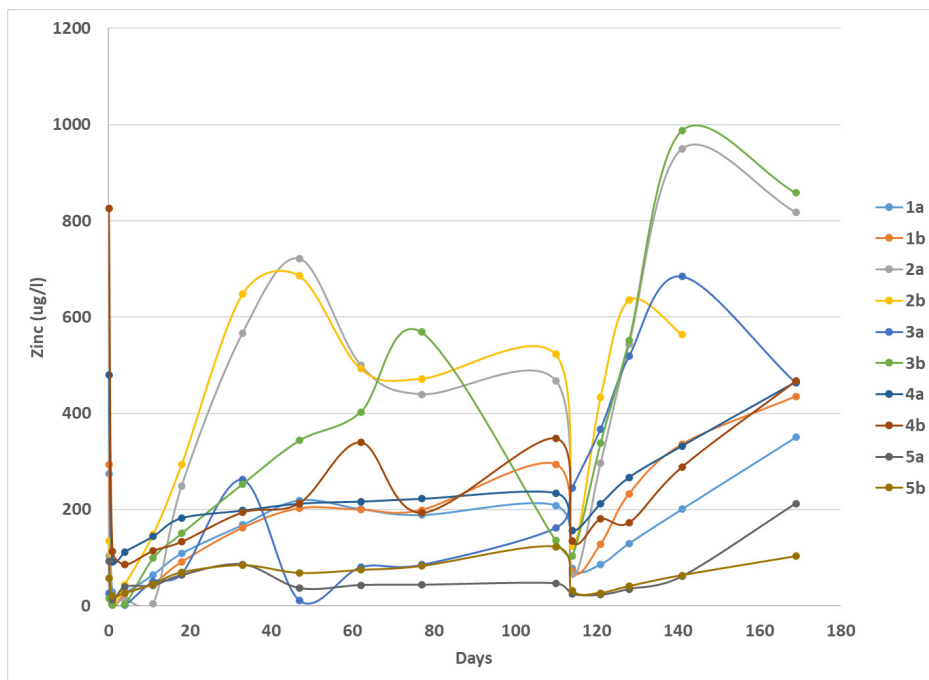


Figure 3 Concentrations of zinc ( $\mu\text{g/L}$ ) in all 10 systems. Day 0 is the original water. Note that at day 110 the surficial sediments were removed. Average zinc concentration in the dilution water was  $2.4 \mu\text{g/L}$  ( $n = 13$ ).



**Table 2** Release rates ( $\text{mg}/(\text{d m}^2)$ ) for lead, cadmium, zinc and sulfate during the first 110 days in 2017. a and b are replicates from the same sampling station.

	Pb $\text{mg}/(\text{d m}^2)$	Cd $\text{mg}/(\text{d m}^2)$	Zn $\text{mg}/(\text{d m}^2)$	Sulfate $\text{mg}/(\text{d m}^2)$
1a	0.0068	0.00086	0.73	597
1b	0.0082	0.0013	0.63	
2a	0.016	0.0011	1.36	350
2b	0.0074	0.0012	1.51	
3a	0.0031	0.00015	0.41	331
3b	0.0040	0.00038	1.19	
4a	0.0021	0.00093	0.69	256
4b	0.0077	0.0015	1.26	
5a	0.00098	0.00021	0.18	209
5b	0.0019	0.00022	0.30	

**Table 3** Release rates ( $\text{mg}/(\text{d m}^2)$ ) for lead, cadmium, zinc and sulfate after removal of the surficial sediments (day 110–169). a and b are replicates from the same sampling station.

	Pb $\text{mg}/(\text{d m}^2)$	Cd $\text{mg}/(\text{d m}^2)$	Zn $\text{mg}/(\text{d m}^2)$	Sulfate $\text{mg}/(\text{d m}^2)$
1a	0.016	0.0013	1.09	444
1b	0.022	0.0028	1.41	
2a	0.042	0.0026	2.84	400
2b	0.012	0.0012	3.65	
3a	0.024	0.0010	1.98	407
3b	0.015	0.0013	3.00	
4a	0.0097	0.0024	1.57	251
4b	0.0084	0.0019	1.49	
5a	0.0015	0.00091	0.58	201
5b	0.0031	0.00027	0.32	

1976 to 1.8 t/a in 2017 (75% reduction). In substantially larger areas further away from the site the release of zinc had decreased from 6.6 t/a in 1976 to 0.69 t/a in 2017 (90% reduction). Redistribution of zinc from the sediments thus partly explain missing pieces of the larger zinc mass balance budget for the entire area.

## Conclusions

From the mesocosm experiments it is clear that both the total concentrations and the release rates have decreased since the operations ceased, indicating that released trace elements get buried in the sediments with time. Most of the reduction in release

rates occurred between 1976 and 1993, while the difference between 1993 and 2017 is lower. In some cases, close to the site of the mining operation, the release rates had even increased somewhat. This indicates that the release of zinc from the historical site is continuing, albeit at a substantially lower rate compared to 1976. It can also be concluded that this type of experiments can assist in understanding the mass transfer of trace elements from sediments to surface waters.

## Acknowledgements

Zinkgruvan Mining AB and SWECO AB are acknowledged for providing funding for this study.

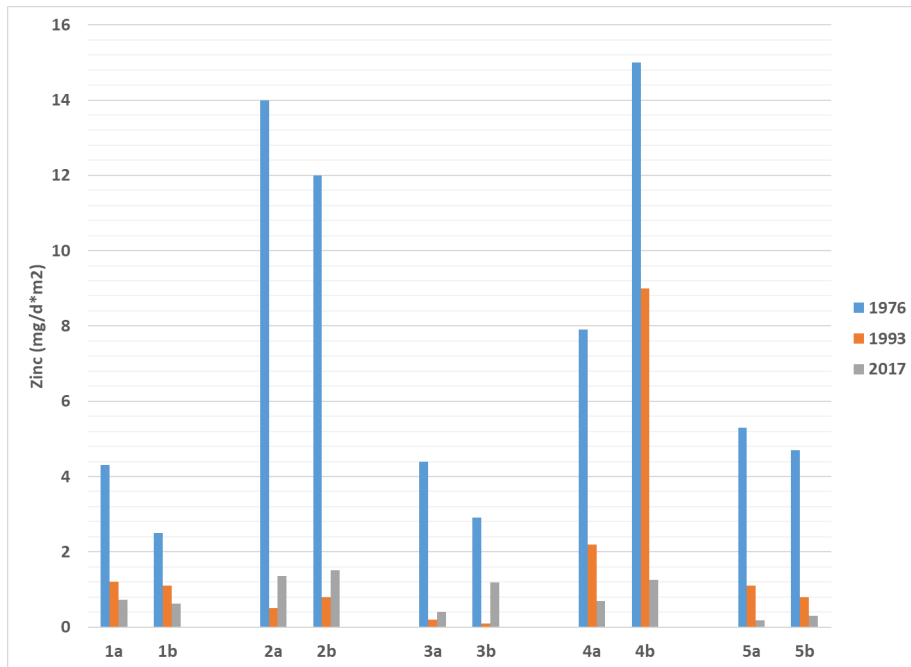


Figure 4 Release rates ( $\text{mg}/(\text{d} \cdot \text{m}^2)$ ) for zinc during the years 1976, 1993 and 2017.

## References

- Borg H, Lithner G, Unger M (1977) Metallavgång från förorenat Vätternsediment – Resultat av laboratorieförsök. SNV PM 821, Statens Naturvårdsverk (in Swedish)
- Cai Y, Xu N, Meng F, Li F, Xie Y, Zhang H (2021) Speciation and release kinetics simulation of Zn and Cd from river sediments contaminated by gold mining. *Water Air Soil Pollut* 232: 21
- Ciszewski D, Kubsik U, Aleksander-Kwaterczak U (2012) Long-term dispersal of heavy metals in a catchment affected by historic lead and zinc mining. *J Soils Sediments* 12: 1445-1462
- Guo T, DeLaune RD, Patrick Jr WH (1997) The influence of sediment redox chemistry on chemically active forms of arsenic, cadmium and zinc in estuarine sediment. *Environ Int* 23(3): 305-316
- Göthberg A, Lithner G, Fröberg E, Johansson A-M, Korhonen M (1993) Minskad utlösningspotential för zink och kadmium i Kärrafjärdens sediment och möjliga orsaker. ITM rapport 30, Stockholms universitet (in Swedish)