WATER QUALITY AND METAL TRANSPORT IN WATER-COVERED MINE TAILINGS DEPOSITS AT SULPHIDE ORE MINES – *IN SITU* MEASUREMENTS AND MODELLING BY DGT SAMPLERS

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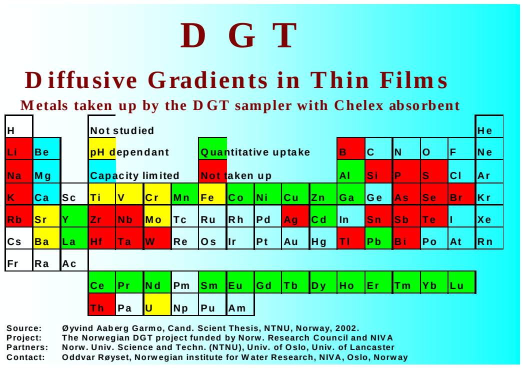
ABSTRACT

This poster to Mine Water 2009, presents results from studies of metals in the surface layers of a mine tailing sediment from a water covered pyrite mine tailing dam in Norway. We used the Diffusive Gradients in Thin films (DGT) probe in parallell with Diffusive Equilbrium in Thin Films (DET) probe and a modified peeper to collect metals in porewater. Metals were determined with Inductively Coupled Plasma Mass Spectrometry (ICPMS). The aim was to get high resolution (5-10mm) profile of pore water metal concentrations of the top sediment, to assess potential for leakage of metals over the sediment surface, and to describe processes in the top sediments regulating the release of metals. Results from this study are presented, and show that DGT/DET technology is a new and useful tool in such studies.

1. INTRODUCTION

NIVA (Norwegian Institute for Water Research) works with sampling and fractionation systems of metal ions in water. A major aim is to separate 1) The labile (free ion) metal ion fraction from those bound in 2) Particles/colloids and 3) Anionic (humic bound) compounds. The labile fraction is generally considered to be the most toxic.. With the SCF fractionation it is possible to determine the 3 fractions above separately, while the DGT sampler collects the labile fraction directly. The first applications of DGTs at NIVA, were in effect studies of metals on fish in acid surface waters and in Norwegian aquaculture, where the sampler was established as a good prediction tool for especially toxic effects of Aluminium (Al) and Iron (Fe) for fish (trout) in acid waters. The SCF sampler gives additional information of fractionation, and helps evaluate potential for effects. The samplers are shown o Figure 1 below.

Figure 1 NIVAs metal fractionation tools from left: 1) Two DGT samplers, 2) SCF sampler with filter, 3) SCF sampler mounted on sampling syringe, 4) Pore water centrifugation separation tool, 5) DGT/DETsediment probe (similar in shape)	Figure 2 Metals collected by the normal DGT sampler with chelex adsorbent (imino diacetic acid ion exhange resin). The elements collected have green colour.
	 Source: Øyvind Aaberg Garmo, Cand. Scient Thesis, NTNU, Norway, 2002. Project: The Norwegian DGT project funded by Norw. Research Council and NIVA Partners: Norw. Univ. Science and Techn. (NTNU), Univ. of Oslo, Univ. of Lancaster Contact: Oddvar Røyset, Norwegian institute for Water Research, NIVA, Oslo, Norway

2. THE USE OF DGT SAMPLERS IN MINE TAILING SEDIMENTS STUDIES

In addition to conventional DGT samplers (Figure 1), we have also studied the DGT-probe sampler for depth profiles of metals in pore water of sediments. This work presents results from studies of metals in the surface layers of a mine tailing sediment from a water covered pyrite mine tailing pond. We used the DGT probe in parallell with Diffusive Equilbrium in Thin Films (DET) probes and a modified peeper to collect metals in porewater. The aim was to get high resolution (5-10mm) profile of pore water metal concentrations of the top sediment, to assess potential for leakage of metals over the sediment surface, and to describe processes in the top sediments regulating the release of metals

3. INTRODUCTION TO THE DGT PASSIVE SAMPLER

The first passive sampler for inorganic ions was described in 1994 (Davison and Zhang 1994). The first studies were focussed on the classical divalent heavy metals (Pb, Cd, Cu, Zn, Co, Ni). The DGT samplers have from 1995 found numerous applications in freshwater, seawater, soils and sediments as reviewed by Davison et al. (2000, 2001). Benefits of the DGT technique are: (1) The sampler integrates/collects the labile free ions, (2) is little affected by environmental factors such as pH, pressure, salinity, temperature,, (3) high sampling capacity (up to months without overloading) and (4) high sensitivity with LOD from 0.001 – 0.1 µg/L per 24 h. The diffusive properties of passive samplers have been reviewed and explained by Zhang and Davison (2000) and by Garmo, Røyset et al. (2003). The uptake rate estimated from diffusion theory is around 10 – 20 ml/24 h for a standard DGT sampler. Details of diffusive theory needed to calculate uptake rates related to the DGT sampler are explained in the publications above, and are not .

NIVA started to test and further develop the DGT technology in 2000. The sampler collected most high priority heavy metals (Pb, Cd, Cu, Zn, Co, Ni), the three-acid reactive metals Al, Fe, Mn, the whole lanthanide group, and a few more metals. The DGT periodic table developed by NIVA (Figure 3), shows that 24 metals are quantitatively taken up while additional 8 other elements are promising (Garmo, Røyset et al. 2003). In later studies the DGT sampler predicted gill uptake and physiological stress response imposed by aluminium for trout (Garmo, Røyset, Rosseland et al 2005), and showed also promise in assessments of effect of iron (Fe) towards fish (Aatland, Kroglund, Røyset, Garmo, 2003). Both the DGT sampler and the DGT probe have been examined in mesocosm studies of marine environments and sediments.

4. METHODS

All DGT and DET equipment is delivered by DGT Research Ltd, UK (www. dgtresearch.com). NIVA have established a new set of diffusion coefficients and more efficient and accurate elution procedures in order to improve the accuracy of the sampler. At NIVAs laboratory metals from DGTs are determined by plasmachemistry by Inductively Coupled Plasma Mass Atomic Emission or Mass Spectrometry (ICPAES, ICPMS, ICP-HRMS). The methods are accredited according to ISO/EN 17025. Normally the analysis program by ICPMS comprises 55 metals, so that all possible situations may be covered.

In this study 3 sampling systems were studied:

1. The normal DGT probe, which collects the metal ions by diffusion. After exposure the sampler adsorbent is cut into 5 or 10 mm units. This gives then a space resolution of 5 or 10 mm.
2. The DET probe which is a micropeeper. This collects the equilibrium concentration of the elements in the porewater. The DET sampler was of the high resolution type with discrete cells of 2 mm each. After exposure 2 to 5 cells were added together giving a space resolution of 5 or 10 mm.
3. A conventional porewater peeper. This was modified so that it was possible to pump porewater out of the sediment during exposure. This peeper was 200 mm long and divided in 10 mm cells and a space resolution of 15 mm. Thin Teflon tubes were connected to each 10 mm cells, and the porewater was withdrawn from each cell by connecting the tubes to to a peristaltic pump. The fractions were collected in PE bottles by a peristaltic pump from a boat during sampling
4. The active window length of both the DGT and DET probes are 150 mm. The probes were placed in into the sediment with 20 mm of the active window above the sediment surface. This was done by divers at about 5 m depth of the sediment pond.
5. The samplers were exposed for 6 to 24 hours. The segments of the samplers were eluted with nitric acid and analysis of metals in samples were performed by ICPMS.

The DGTs probes were inserted vertically into the sediment to measure vertical profiles of metal ions by diffusion into the chelex a adsorbent. The DGT profiles are determined both by initial undisturbed pore water concentration, diffusive transport rates in pore water and release rates in the vicinity of the DGT surface. The calculations of concentration were performed by the DGT diffusive models developed by Zhang and Davison.

5. RESULTS AND DISCUSSION

Mine Tailing Sediment Studies At Loekken Mine

Norway has a mine industry of various kinds including metals and minerals. Many of the mines are based on pyrite ores, and the environmental effects have been examined by NIVA in studies since 1970 (Iversen et al 1997, 1999, 2003, 2005, and Arnesen 1999). One of the most common disposal techniques for the tailings have been by water covered tailing dams. The tailings have been disposed in small lakes or ponds, with a water cover of a few meters on top. One of the most studies pyrite tailing dams has been the one at the Bjørndalen tailings pond at Loekken mine in mid Norway. The tailings contains about 36 % S. Deposition ceased in 1987. The discharge from the tailing dam have been a serious risk to the salmon fisheries of the important salmon river Orkla.

NIVA has previously developed a simple model for simulating flux of sulphate and metal ions from water-covered sulphide-containing flotation tailings from sulphide ore mines. The model calculates how the flux develops over time based on oxygen supply as limiting factor for the reactions in the tailings. Experiences with the model have been gained from a number of deposits in Norway and Sweden, (Iversen, Arnesen et al.1997).

The First DGT Probe Study

In 2003 -2004 only the DGT probes were studied for release of metals to the pore-water in the upper sediment layers (Iversen et al 2003).

The concentration profiles for Zn, Fe and Cu are shown in the figure 3 and 4 below. The two probes give similar DGT profiles, with differences only in the details which may be caused by different sediment environments around. The water /sediment surface is between 10-20 mm below the top of the sampler so that the 2 - 4 upper sampling points reflect the water concentration above the sediment surface.

The Fe profiles have maximum C_{DGT} of about 20 mg/l in both probes at sediment depths 4 to 8 cm in in both probes. Towards the sediment surface there is an almost linear reduction towards C_{DGT} values of about 0.5 mg/l close to the sediment surface, close to the value found in the water above the sediment. The peak in Fe concentrations found at 4 – 8 cm is similar to what we normally find in marine sediments, and is probably due to release of Fe(II) by oxidation of sulphides. We expect this peak to be the weathering front by oxygen transport from the surface of the sediment.

Zn has a marked peak in concentrations at 4-6 cm depth, partly overlapping with the Fe peak, but the peak maximum a bit shifted upwards. Maximum C_{DGT} concentrations are 3 – 4 mg/L. The concentrations decrease towards the surface in both profiles, reaching a minimum of about 0.5 mg/L,

The pattern for Cu is not so clear, as a more flat concentration profile is observed towards the sediment surface, but a small decrease in concentration can be observed towards the top. However the concentration above the sediment surface (the upper 2 4 points) is in the same range as found in the water.

Figure 3
Dept Profiles obtained by the DGT probe 1

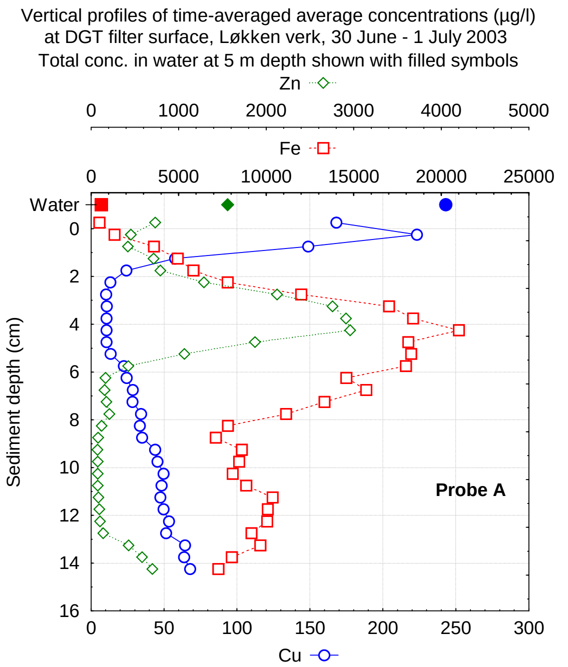
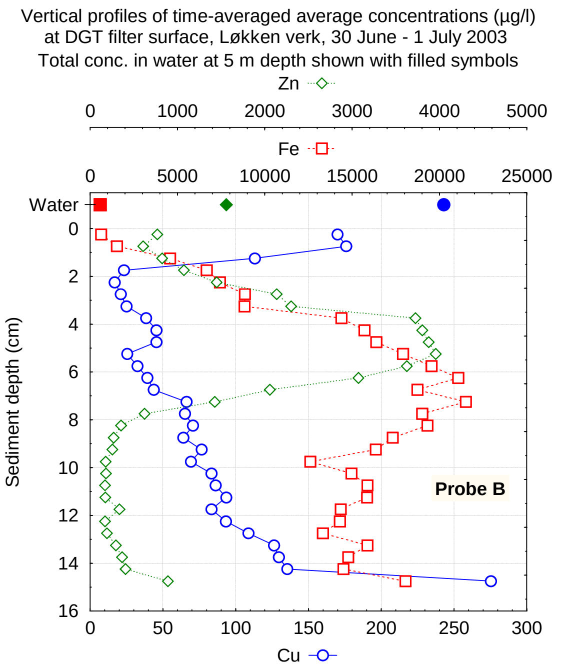


Figure 4
Dept Profiles obtained by the DGT probe 2



Comparison of DGT, DET and a Micropeepger

This project was followed up in 2008. This time we compared the 3 different samplers DGT; DET and the micro-peeper, to study the performance of the 3 different samplers over a depth of about150 mm from the top of the profile. The data are shown in the figures 5, 6, and 7 below.

The general pattern for the DGT probe is similar to what obtained in the 2003 study. Some more scatter is observed in the dept profile which probably is caused by problems during sampling. An increase of the Fe and Zn concentration is observed with a peak at 30 to 60 mm depth. A similar peak pattern is observed for the DET probe for Fe but not so clear for Zn. The differences between the DGT and DET probes are probably due to the different uptake process, which is diffusion by the DGT and equilibrium concentration by the DET. This must be further explored to understand the details.

For the peeper there is also a peak shaped pattern with dept, but the space resolution of this sampler is much lower (about 20 mm). The profiles are not so detailed as for the DGT and DET probes due to lager cells in the peeper compared to DGT/DET.

An interesting feature which now could be determined by ICPMS, was the possibility to determine sulphur. The sulphur concentrations of the DGT and the peeper, are in the same concentration range of 10 to 100 mg S/L. All samplers show an increase in sulphur concentrations by depth. An advantage of the peeper is the possibility to take larger sample volumes for additional parameters to be determined, such as pH and possible further speciation of elements in the pore water.

Generally a reduction is observed in concentration towards the top of the sediment profile for Fe, Zn and S, which indicates a diffusive transport out of the sediment profiles over the sediment water surface.

6. MODEL CALCULATIONS

At present we are reassessing the data for the 2 different investigations to examine the use of these data in the release models for metals from the pyrite sediments (Bjerkeng and Iversen 2009). An example is given for Fe. The vertical gradient of C_{DGT} for Fe ions in the upper 1-2 cm of the sediment is about 4 mg/l per cm. With a diffusion coefficient of about 4x10-6 cm^2/s (taking some tortuosity into account), this corresponds to an estimated upwards Fe flux from 15 to 50 kg/day per km^2 sediment area, if the ratio C_0/C_{DGT} range between 1:1 and 4:1. The observed concentration of Fe in the dam was 0.5 mg/L, which is within the lower range of previous measurements after the mine was closed in 1987. The yearly runoff estimates are between 6 and 15 litres/second, combined with concentrations ranging from 0.5 to 1 mg/L, it corresponds to a flux of Fe from the dam in the range from 0.3 to 1.3 kg/day, or about 10 % of the estimated flux from the sediment. Even though both estimates are given as wide ranges, it seems clear that the major part of Fe released from the sulphides is precipitated at the sediment surface as $Fe(OH)_3$. This is also confirmed by visual inspection of the upper part of the sediment.

7. CONCLUSIONS

This is one of the first studies of DGT/DET probes and peepers studied together in pyrite mine tailing sediments. The results show that the samplers describe distinct dept profile patterns of the metals in the porewater of the top 150 mm of the sediments.

The combination of the DGT/DET/peeper with ICPMS gives powerful data, as most elements of interest can be determined. Also the major elements such as sulphur can be determined, which can describe oxidation of the reduced sulphur/sulphide compounds as this may control the release of the sulphide bound metals in the top sediment. In this study we have only examined the patterns for the four elements Cu, Zn, Fe and S. As all the about 25 elements shown in the DGT periodic table (Figure 2) can be determined, the sampler have potential as a general metal assessment tool for most metals associated with mine tailings and acid mine drainage.

The concentrations of sulphur determined by the DET micropeeper and the normal peeper are in the same range, showing that both samplers can be used for the description of the sulphur profile. An increase of sulphur concentration with dept is generally observed.

A peak shaped pattern from about 40 – 80 mm for iron (Fe) is observed, probably due to oxidation of reduced Fe sulphides. This is supported by that similar profiles are also observed for Mn (not shown here, but most sediment profile studies show similar patterns for Fe and Mn). This may indicate how deep down in the sediment the oxygen is transported and indicate the dept of the ongoing oxidation process and weathering of the top sediment. This is important as it can indicate the oxidation mitigated release processes of metal in the top sediment.

For Fe and Zn a decrease in concentration is observed at the upper 50 mm of the sediment indication release of metal from the top of the sediment profile into the water phase.

The DGT and DET technology applied for such sediment studies are still in an early phase, and the understanding is still limited. This work shows that the technology have potential to get a very detailed description of the processed going on in the top of mine tailing sediments. More research is needed to explore the potential of the technology for such studies to take advantage of the generated data. But the samplers have potential towards better understanding of the processes and how to use the new tools to improve the models for estimation of release of metals from mine tailing sediments.

Figure 5
Dept Profiles obtained by the DGT probes

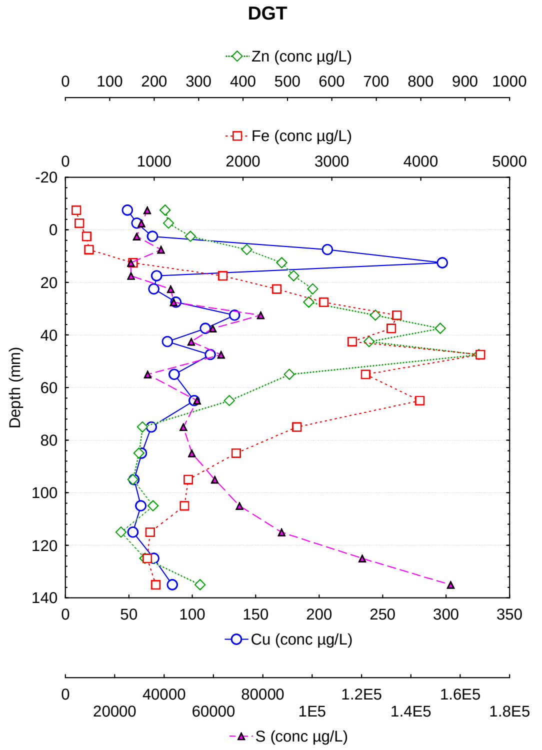


Figure 6
Dept Profiles obtained by the DET probe

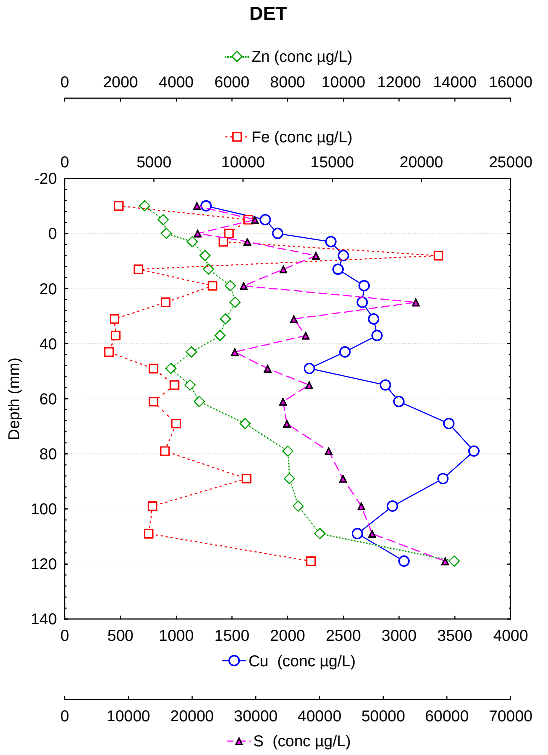
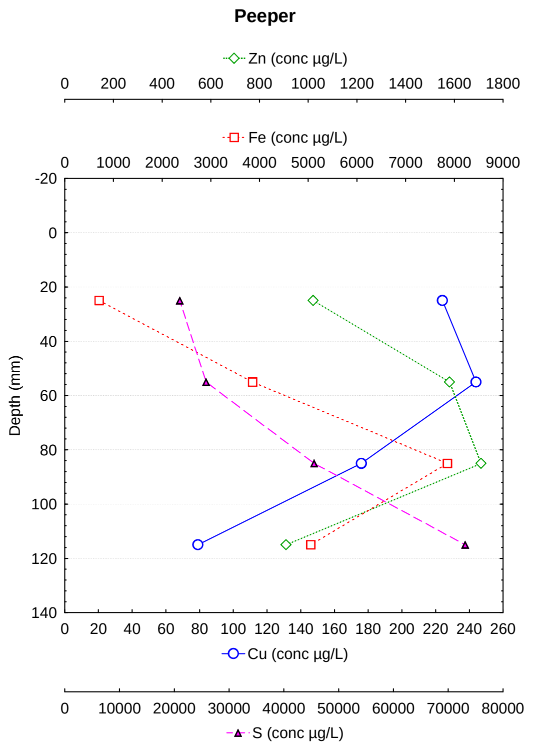


Figure 7 Dept Profiles obtained by the porewater peeper sampler



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