

The First Deployment of DGT/DET for Assessment of Metals in Sediment Pore Water at Songkhla Lake, Thailand

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Abstract. The techniques of diffusive equilibrium in thin films (DET) and diffusive gradients in thin films (DGT) were used for the first time in the Outer Section of Songkhla Lake in order to obtain high resolution profiles of total dissolved and labile trace metals in the sediment porewater. These tools provide useful information on sediment biogeochemistry and benthic fluxes. DGT measures labile metal species in situ by immobilizing them on a resin gel after diffusion through a diffusive gel whereas for DET equilibrium is established between the DET gel and the porewater. The expedition was carried in July, 2011 under the collaborative research program between the Laboratory of Analytical and Environmental Chemistry, Vrije Universiteit Brussel and the Marine and Coastal Resources Institute, Prince of Songkla University. Six DET probes and six DGT probes were deployed at the mouths of the Phawong, Samrong and U-Taphao canals. Methodology and method performance is described.

Keywords: DET, DGT, Songkhla Lake, metal, sediment porewater

1. Introduction

Songkhla Lake is the largest shallow lagoon in Thailand with 3 water regimes (brackish water, fresh-water and seawater). It is located in 3 southern provinces (Phattalung, Songkhla and Nakhon Si Thammarat) and provides diversified natural resources for 1.8 million people residing around the lake. The lake is a major fishing ground for mollusks, crustaceans and fish and is intensively used for the aquaculture of sea bass. The catchments area of about 8,729 km² consists mostly of lowland rice fields, rubber plantations and forest-covered hills, but contains rapidly growing cities such as Hat Yai and Songkhla. This has led to increased discharges into the lake from human activities including urbanization, industrialization and agriculture. Recently the Lake has faced serious problems which have been summarized in an ONEP [1] report as follows: a) a steady decline of the upstream forest and mangrove, b) soil erosion and sedimentation in the waterways and in the lake, c) overuse of ground water, d) severe flooding, e) over-fishing, f) unsanitary drainage from urban areas, g) industrial waste discharges (mainly related to rubber and food products), h) pollution from boats and fish waste from Songkhla harbour, i) lack of effective management etc.

Trace element concentrations in sediments of Songkhla Lake, especially the outer section of the lake (i.e. at the mouths of the Phawong, Samrong and U-Taphao canals) were significantly enriched in trace elements due to release of municipal, agricultural and industrial discharges entering the lake through the canals. Large amounts of organic matter are also transported by the canals, resulting in anoxic conditions in the sediments, which may in turn affect the mobility and bioavailability of the pollutants [2]. Sediment porewater, the dissolved phase of sediment, is in equilibrium with the solid phase. Knowledge of porewater concentration is useful in assessing sediment contamination and in evaluating the contribution of sediments to the pollution of the overlying water column [3]. Depth profiles of metals in the sediment porewater are important to understand diagenetic reactions involving release or uptake the metals within sediments. The profiles of trace metals in sediment have been determined by different methods. There are conventional methods such as a sectioning sediment cores, followed by centrifugation or squeezing [4-5] and in situ equilibration of dialysis

cells [6-7] but they have a common limitation in as insufficient spatial resolution. Dialysis peepers can provide a good estimation of content of solutes in pore water[8-9], however, these require relatively long equilibration times (days/weeks).

The technique of diffusive equilibrium in thin films known as DET [10] is similar to dialysis, but the sampling medium is a hydrogel instead of a solution retained by a dialysis membrane. As for dialysis, solutes equilibrate within the solution held in the sampler (the hydrogel is typically 95% water). The collected species depend on the pore size of the outer membrane and the hydrogel itself. Equilibrium concentrations of solutes are measurement for sufficiently long deployment times. In the DET technique using constrained probes, metals diffuse from the pore water into small strips (1mm intervals) of agarose gel (pore size 20nm) until equilibrium with the pore water is reached. With this technique no preconcentration is obtained, nor a selection of compounds as long as the pore size allows diffusion. This technique thus provides information on the total dissolved species concentration.

In the technique of diffusive gradients in thin films (DGT) developed by Zhang and Davison [11], an acrylamide diffusive gel (pore size 10nm) is backed by a resin gel (Chelex) which binds (trace) metals. Within a few minutes of deployment, a linear concentration gradient is established between the resin gel and the solution. The DGT technique has been applied successfully to measure the concentration profiles of labile metals in water, soil water, fresh water and marine sediment [11-15]. The DET technique has been used to measure the concentrations of total dissolved metal species, major ions and cations and nutrients in freshwater and marine environments [10, 13, 16-21] in sediment pore water at high spatial resolution. As the species are not preconcentrated during deployment, but are diluted during elution, detection limits are higher than those using DGT.

At present, the DET/DGT method has been introduced for the first time in the Outer Section of Songkhla Lake (Figure 1) in order to evaluate the trace element concentrations in sediment porewater. This work has been carried out under the collaborative research project between Laboratory of Analytical and Environmental Chemistry (ANCH), Vrije Universiteit Brussel (VUB), Belgium and Marine and Coastal Resources Institute (MACORIN), Prince of Songkla University (PSU), Thailand.

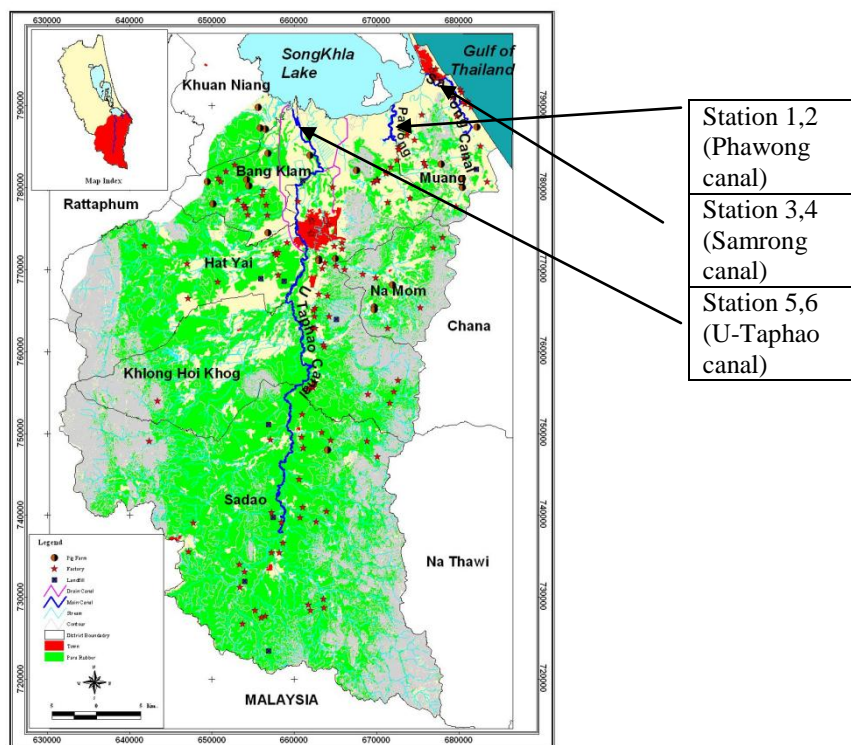


Fig. 1: Location of sampling stations in the Outer Section of Songkhla Lake in July, 2011.

1.1. Methodology

Preparation of DGT probe

The DGT probe consists of three layers: the cellulose acetate 0.45 μm membrane filter, the diffusive layer and the resin layer. The diffusive gel solution (15% acrylamide, 0.3% cross-linker) was prepared by mixing 15 ml DGT gel cross-linker (DGT-research), 47.5 ml deionized water and 37.5 ml acrylamide solution (40%). The diffusive gel (0.8 mm thickness) was prepared by adding 70 μl ammonium persulphate solution and 25 μl TEMED solution to 10 ml of the gel solution. To cast the gels, the solution is carefully pipette between two glass plates with a 0.5mm spacer between the two plates. The assembly is placed in an oven at 44 $^{\circ}\text{C}$ for at least an hour until the gel is completely set. The gel is then removed from the glass plates and placed in deionized water for 24 hours to hydrate. Then the gel is stored in a 0.01M NaCl solution.

To prepare the resin gel (0.4mm thickness) the Chelex resin (200-400 Mesh) was first soaked with MQ water for at least one hour. 10 ml of gel solution was put into a container and 3.5g Chelex resin, 50 μl ammonium persulphate and 15 μl TEMED solution was added. The solution was mixed vigorously and pipette between two glass plates with a 0.25 mm spacer between the plates. This assembly is also placed in an oven at 44 $^{\circ}\text{C}$ for an hour and after setting the gel is removed and hydrated in deionized water and stored in deionized water at 4 $^{\circ}\text{C}$.

The DGT probe: The diffusive gel and resin gel were cut into a fixed size (width 2.8 cm and height 16 cm) using a gel cutter and the filter membrane were cut in to the same size. The chelex gel was laid on the base plate with the resin side facing upwards. A strip of the diffusive gel was placed on the top of the chelex gel and followed a filter membrane. Finally, the window plate was put on the top of the assembly and pressed together.

Preparation of DET probe

The DET probe consists of two layers: the filter membrane and the diffusive gel. The constrained DET probes were 180mm*40mm, with a window of 150mm*18mm open to the sediment and consist of 75 1-mm slits with a 1mm interval between the slits. The slits were filled with agarose gel (1.5%). To prepare the probes deionized water is heated to 80 $^{\circ}\text{C}$ in a water bath and the agarose powder is added. When the mixture clears the gel has been formed. To cast the gel, the hot agarose gel is pipette into the slits, ensuring that all cells are filled and that no gel remains in the ridges between the gels. The gel is then covered by a filter membrane and the plate window is placed on top of the assembly and pressed firmly.

Deployment and retrieval of DGT and DET

After preparation, and just before sampling, the DET and DGT probes were deoxygenated in a bottle with 0.01 M NaCl solution by purging with nitrogen gas for 24 hours. After deoxygenation, the bottles were closed tightly and brought to the field. The probes were inserted gently and straight into the sediment by a diver. At each site one DGT and one DET probe was placed back to back. The probes were left there for 24 hours. After 24 hours the DGT and DET probes were retrieved and brought back to the laboratory for further treatment.

DGT sample treatment and analysis

After 24 hour deployment in the field, the probes were pulled out from the sediment. The surface was rinsed and the window was opened carefully. The gels together with the filter membranes were carefully lifted and on a clean flat surface. Then the top filter membrane and the diffusive gels were removed and the resin gel was left. The resin gel was cut into 0.5cm-pieces and put into the polyethylene (PE) tubes (Figure 8) and 2 ml HNO_3 1 M was added for elution. For analysis, the samples were further diluted to 10 ml with deionized water.

DET sample treatment and analysis

After 24 hours of deployment in the field, the probe was brought back to lab. The surface was rinsed carefully with Milli-Q water and the window was opened gently. The 75 strips of agarose gel (approximately 20 μl) were excavated from the probe and put into pre-weighed clean PE tubes. The tubes containing gels were weighed to calculate the exact weight of gel in each strip. Metals were extracted from the gels with 1 ml 1M HNO_3 . Then samples were diluted to 5ml analyzed by HR-ICP-MS.

Analysis of metals

High Resolution Sector Field Inductively Coupled Plasma Mass Spectrometry (HR-ICPMS) model Thermo Finnigan Element II was used to measure the concentrations of metals in the sediment porewater sample.

1.2. Results and Discussion

Method performance: detection limits

Blank DET and DGT probes underwent all steps apart from deployment, including casting, probe construction, deoxygenating. They were treated in the same way as the sample probes. The DGT probe was sliced in 32 5mm intervals, 10 slices were randomly chosen for analysis. For the DET probe 10 slices were randomly chosen from the 75 blank slices for analysis.

DGT blanks are expressed in $\mu\text{g/L}$ (Table 1). The latter were calculated using the same deployment time as the probes in the sediments (24h). Detection limits were calculated as 3 times the standard deviation of the blanks. DET blanks were calculated taking the dilution factor into account (Table 1). As the result of the high blanks of the agarose gel for certain elements and important dilution factor (around 50) only the concentrations of Fe, Mn, As and Co were at least ten times higher than the detection limit.

Table 1. Blanks and detection limits for the DGT and DET gels

Element	DGT		DET	
	DGT blank	Detection limit	DET blank	Detection limit
	($\mu\text{g/L}$)	($\mu\text{g/L}$)	($\mu\text{g/L}$)	($\mu\text{g/L}$)
Cd	0.004 ± 0.001	0.003	0.22 ± 0.04	0.13
Pb	0.070 ± 0.034	0.010	5.60 ± 0.97	2.90
Mn	0.076 ± 0.054	0.160	9.66 ± 2.60	7.81
Fe	1.019 ± 0.771	2.300	197 ± 51	155.00
Co	0.004 ± 0.002	0.006	0.28 ± 0.13	0.39
Ni	0.69 ± 0.08	0.240	77 ± 6	20.00
Cu	0.15 ± 0.03	0.090	6.6 ± 2	6.00
Zn	3.3 ± 0.9	2.500	173 ± 61	184.00
As	0.001 ± 0.0003	0.001	0.14 ± 0.05	0.16

Trace elements concentrations

The DGT profiles of Cu, Zn, Cd and Pb show surface maximum, probably linked to organic matter degradation. We observed extremely high concentrations of As at Phawong and U-Taphao Canals with the maximum value of 1,000 and 2,800 $\mu\text{g/L}$, respectively [22] .

1.3. Conclusions

It is beneficial to apply these techniques to be used in Songkhla Lake, in order to evaluate trace metals fluxes of pollutants to and from the sediment. It becomes more important to develop tools for the assessment of high resolution profiles in sediments and its implication on sediment quality management of Songkhla Lake. Measuring trace metals by using DET and DGT equipments should be continued and seasonal experiments should be investigated.

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2. References

- [1] Office of Natural Resources and Environmental Policy and Planning (ONEP). Master Plan for Songkhla Lake Basin Development, 2005.

- [2] S. Pradit, G. Wattayakorn, S. Angsupanich, M. Leermakers and W. Baeyens. Distribution of Trace Elements in Sediments and Biota of Songkhla Lake, Southern Thailand. *Water, Air, Soil Pollut.*, 2010, 206, 155-174.
- [3] J. Aggett and G.A. O'Brien. Detailed model for the mobility of arsenic in lacustrine sediments based on measurements in Lake Ohakuri. *Environ. Sci. Technol.*, 1985, 19, 231-238.
- [4] Y. Gao. Development of novel tools for the assessment of high resolution profiles in sediment. *Master thesis*, 2003, Vrije Universiteit Brussel, Belgium.
- [5] K.B. Takoeta. Trace metal behavior in freshwater sediments. *Master thesis*, 2004, Vrije Universiteit Brussel, Belgium.
- [6] P.T. Teasdale, G.E. Batley, S.C. Apte and I.T. Webster. Pore water sampling with sediment peepers. *Trends Anal. Chem.*, 1995, 14, 250-256.
- [7] B. Garban, D. Ollivon, M. Poulin, V. Gaultier and A. Chesterikoff. Exchanges at the sediment-water interface in the river Seine, downstream from Paris. *Water Res.*, 1995, 29, 473-481.
- [8] J. Smith and M.D. Melville. Iron monosulfide formation and oxidation in drain bottom sediments of an acid sulfate soil environment. *Appl. Geochem.*, 2004, 19, 1837-1853.
- [9] P.H. Jacobs. A new rechargeable dialysis pore water sampler for monitoring sub aqueous in situ sediment caps. *Water Res.*, 2002, 36, 3121-3129.
- [10] W. Davison, G.W. Grime, J.A.W. Morgan and K. Clarke. Distribution of dissolved iron in sediment pore waters at submillimetre resolution. *Nature*, 1991, 352, 323-324.
- [11] H. Zhang, W. Davison, R.J.G. Mortimer, M.D. Krom, P.J. Hayes and I.M. Davies. Localized remobilization of metals in marine sediment. *Sci. Total Environ.*, 2002, 296:175-187.
- [12] G.R.Fones, W. Davison and J. Hamiton-Taylor. The fine-scale remobilization of metals in the surface sediment of the North-East Atlantic. *Cont. Shelf. Res.*, 2004, 24, 1485-1504.
- [13] M. Leermakers, Y. Gao, C. Gabelle, S. Lojen, M. Wartel and W. Baeyen, Determination of high resolution pore water profiles of trace metals in sediments of the Rupel River (Belgium) using DET (diffusive equilibrium in thin films) and DGT (diffusive gradients in thin films) techniques. *Water, Air, Soil Pollut.*, 2005, 166, 265-286.
- [14] Y. Gao, M. Leermakers, C. Gabelle, P. Divis, G. Billon, B. Ouddane, J-C Fischer, S. Wartel and W. Baeyens. High-resolution profiles of trace metals in the porewaters of riverine sediment assessed by DET and DGT. *Sci. Total Environ.*, 2006, 362, 266-277.
- [15] Y. Gao, M. Leermakers, M. Elskens, G. Billon, B. Ouddane, J-C Fischer and W. Baeyens. High resolution profiles of thallium, manganese and iron assessed by DET and DGT techniques in riverine sediment pore waters. *Sci. Total Environ.*, 2007, 373, 526-533.
- [16] W. Davison, H. Zhang and G. Grime. Performant characteristics of gel probes used for measuring pore waters, *Environ. Sci. Technol.*, 1994, 28, 1623-1632.
- [17] W. Davison, G. Fones and G.W. Grime. Dissolved metals in surface sediments and microbial mat at 100 μm resolution. *Nature*, 1997, 387, 885-888.
- [18] Y. Gao, L. Lesven, D. Gillan, K. Sabbe, G. Billon, S. De Galan, M. Elskens, W. Baeyens and M. Leermakers, Geochemical behavior of trace elements in subtidal marine sediments of the Belgian coast. *Mar. Chem.*, 2009, 117, 88-96.
- [19] Y. Gao, W. Baeyens, S. De Galan, A. Proffijn and M. Leermakers. Radium mobility in sediments: application of sequential extraction and DGT techniques. *Environ. Pollut.*, 2010, 158, 2439-2445.
- [20] Y. Gao, M. Leermakers, A. Pede, A. Magnier, K. Sabbe, B. L. Cabana, G. Billon, W. Baeyens and D.C. Gillan. Response of DET and DGT trace metal profiles in sediments to phytodetritus mineralization., *J. Environ. Chem.*, 2011. (in press)
- [21] M. Leermakers, Y. Gao, J. Navez, A. Poffijn, K. Croes and W. Baeyens. Radium analysis by sector field ICP-MS in combination with the Diffusive Gradients in Thin Films (DGT) technique. *Journal of Analytical Atomic Spectrometry*, *Journal of Analytical Atomic Spectrometry*, 2009, DOI: 10.1039/b821472g.
- [22] S. Pradit, Y. Gao, A. Faiboon, S. De Galan, W. Baeyens, and M. Leemaker. 2013. Application of DET (Diffusive Equilibrium in Thin Films) and DGT (Diffusive Gradients in Thin Films) techniques in the study of the mobility of sediment bound metals in the Outer Section of Songkhla Lake, Southern Thailand. *Environ. Monit. Assess.* 2013, 185: 4207-4220.