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Diffusive gradient thin-films in seawater: time integrated technique for aqueous trace metal monitoring in impacted waterways

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Diffusive Gradient Thin-Films:
Time Integrated Passive Sampling for Metals in Receiving Waters of Puget Sound

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Introduction

As part of the ambient monitoring program being conducted for the Puget Sound Naval Shipyard & Intermediate Maintenance Facility (PSNS) at Naval Base Kitsap (NBK) in Sinclair and Dyes Inlets of the Puget Sound, receiving waters of the Inlets are routinely monitored for trace metals and toxicity to assess water quality status, track progress in achieving water quality goals, and demonstrate protection of aquatic life.

Recently, aqueous metal bioavailability using diffusive gradient thin-film (DGT) passive samplers has been incorporated into the monitoring program. When evaluating the success of best management practices implemented by generators, passive sampling allows for time-integrated capture as opposed to 1) grab sampling, which captures a single point in time, or 2) auto-sampler setup, which is cost prohibitive when monitoring across large areas. The utilization of DGTs allows for the measurement of trace metal concentrations via chelation of labile metals (free and weakly complexed species), which is a solution that more effectively represents the concentration of bioavailable metals and therefore more accurately represents the potential for biological effects, which is the ultimate goal of regulatory programs[1].

Method

A combination of laboratory performance tests and field deployed DGTs have been used to assess the reliability of the method to accurately measure labile concentrations of Cu, Pb, and Zn under baseline and episodic storm event conditions, at stations depicted in Figure 1.

During target windows, representative of both wet and dry periods, successively smaller deployment increments were overlapped by larger increments for determination of sensitivity limits and capture of pulse signatures. Increments ranged from 24 hours to 14 days.

Figure 1. DGT deployment locations for NBK monitoring program: PSNS (within Sinclair Inlet), Bangor, and reference locations in surrounding waters.

The basis for converting the mass of metal accumulated by the resin to the concentration in solution as measured by DGT (CDGT) is given in Zhang and Davidson 1995, and can be summarized as:

$$C_{DGT} = [\frac{C_e(V_g + V_e)}{f_e}]\Delta g / D_G A t$$

where C_e is the concentration metal eluted from the resin, V_g is the volume of the resin, V_e is the volume of HNO_3, f_e is the elution efficiency, Δg is the thickness of the diffusional path, D_G is the temperature dependent diffusion coefficient, A is the area of the polyethersulphone face exposed to seawater, and t is the deployment time.

DGTs were purchased from DGT® Research, Lancaster, Lancashire, where they are commercially available in the C-LSNM model for measurement of the cations monitored. C-LSNM contains a 0.40mm Chelex layer, a 0.78mm APA and 0.14mm polyethersulphone layer with an exposure area of 3.14cm^2 (Fig 2).

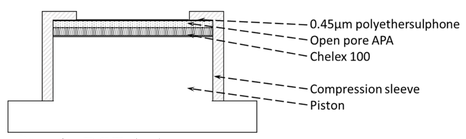

Figure 2. Components of a DGT device.

Results and Discussion

In situ DGT deployments have demonstrated that uptake response when narrowing the deployment focus from 14 days to 24 hours remains linear (Fig 3a). Variability in figure 3a is and expression of field replication and detection limits, given in Tables 1 and 2. Figure 3b illustrates the CDGT trends at each monitoring station over the course of 5 campaigns.

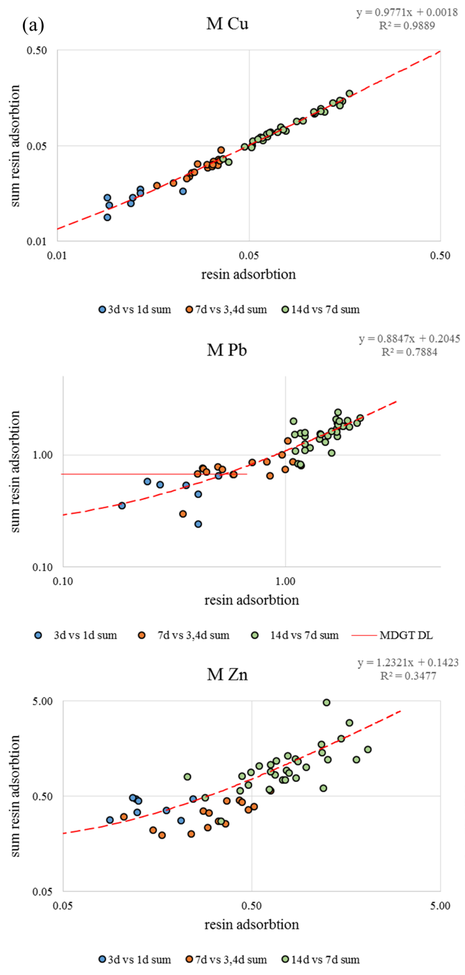

Figure 3. (a) Analyte sensitivity when moving from 14 days to 1 day deployment time, displayed as M (metal resin^{-1}) (*n* 1-day = 24; *n* 3, 4, and 14-day = 32; *n* 7-day = 64); (b) CDGT at monitoring stations during 5 campaigns (03/07/16-03/23/16; 08/24/16-09/08/16; 11/28/16-12/12/16; 03/16/17-03/29/17; 08/16/17-08/29/17), where 14 day CDGT is signified by bars grouped by station and chronological from left to right. Colored lines represent variation captured at sub 14 day times within the 14 day period.

Table 1. Field reproducibility* expressed as duplicate RPD between samplers.

Time (d)	Cu	Pb	Zn
1	15±17%	128±59%	70±48%
3,4	11±13%	36±33%	70±52%
7	7±7%	28±29%	53±48%
14	7±5%	12±11%	52±31%

*Reproducibility at ambient labile levels of: 0.0655-0.901µg L^{-1} Cu; 0.00260-0.0136µg L^{-1} Pb; 0.294-16.2µg L^{-1} Zn.

Table 2. CDGT detection limits*.

Time (d)	Cu	Pb	Zn
1	0.0492	0.00958	1.06
3,4	0.0164	0.00319	0.352
7	0.00702	0.00137	0.151
14	0.00351	0.000685	0.0755

*DGT detection limits were determined as 3 times the standard deviation of 8 blank replicates of the Chelex layer, weighted by exposure duration and temperature, after blank subtraction was applied.

Based on the results from DGTs deployed over different intervals spanning continuous deployments of 1-14 days and rainfall events of 0.4 – 3.2in/24hr, it was determined that reproducibility was affected mainly by, mass loading rate (time to equilibrium) which is proportional to free ion concentration, and presence of biofouling which can both increase the diffusive boundary thickness or act as a transport catalyst. Biofouling was only observed during the 03/07/16-03/23/16 campaign, and was due to non-inversion of samplers in respect to sunlight. Typical DGT surface cleanliness after 14 days of deployment is shown in Figure 4, where the lid has been removed from a polypropylene cage.

Figure 4. DGTs recovered post 14 day deployment.

Conclusions

- Cu as CDGT displayed excellent results at all deployment times between 1 and 14 days, showing high resolution of labile metal concentrations over varying spatial and temporal scales.
- Pb as CDGT displayed best results at deployment times >4 days at this test environments low ambient levels.
- Zn as CDGT displayed best results at deployment times ≥7 days. Zn diffusion is affected by a combination of Chelex selectivity, DOM kinetics, and possibly proximity to sources[3,4]. Field reproducibility will increase significantly as ambient levels approach regulatory ranges.
- The ability to conduct constant surveillance of bioavailable metals in marine environments under varying environmental conditions greatly improves the assessment of potential ecological effects from exposure to metals.
- DGT allows cost-effective monitoring of best management practices, and overcomes 1) the single point in time nature of grab samples, and 2) cost prohibitive auto-sampler setup.
- Future research should focus on rigorous comparison of lability (CDGT) to bioavailability (toxicity exposure levels) in order to apply for regulatory acceptance of CDGT values for protection of beneficial uses to watershed communities and industries.

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