

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



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Introduction

As part an ambient monitoring program being conducted for the Puget Sound Naval Shipyard & Intermediate Maintenance Facility (PSNS&IMF) at Naval Base Kitsap (NBK) Bremerton in Sinclair and Dyes Inlets of the Puget Sound (Fig. 1), 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. The DGT samplers are selective for free and weakly complexed metal species, allowing uptake to mimic diffusion limited bioavailability¹. This provides a monitoring solution by which episodic events are captured that provides a better representation of the potential for biological effects.



Figure 1. DGT deployment locations within Sinclair Inlet, NBK Bangor, and reference locations in surrounding waters.

The relationship between metal accumulated by the resin to the concentration in solution (C_{DGT}) is calculated as²:

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

Where:

- C_e is the concentration metal eluted from 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 diffusion coefficient,
- A is the area exposed to seawater, and
- t is the deployment time.

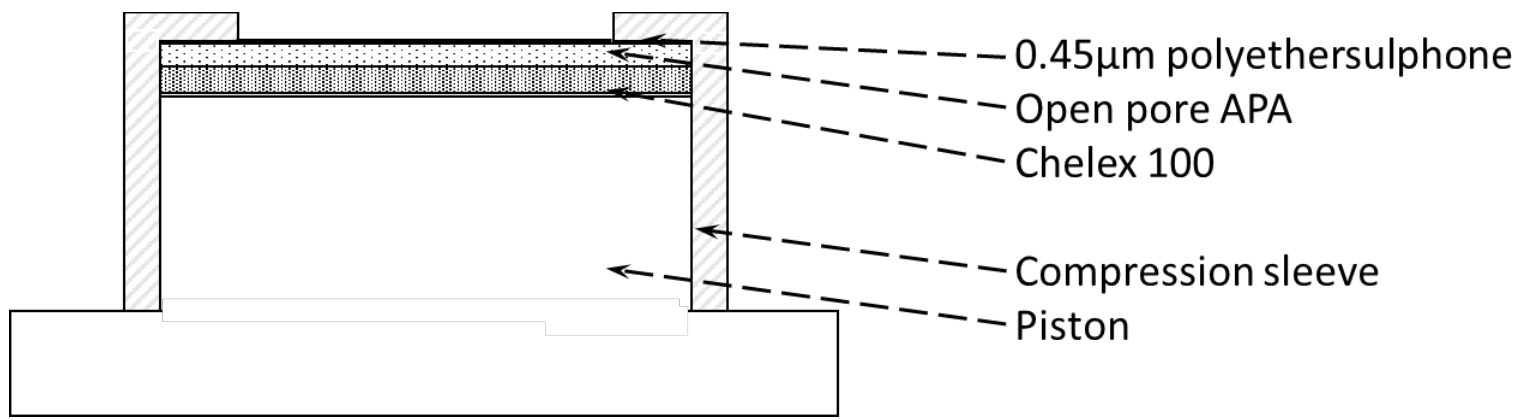


Figure 2. Components of a DGT device.

DGTs were purchased from DGT® Research, Lancaster, UK. The device consists of a plastic housing that holds the 0.40 mm Chelex layer, a 0.78 mm agarose cross-linked polyacrylamide (APA) hydrogel, and a 0.14 mm polyethersulphone membrane with an exposure area of 3.14 cm² (Fig. 2).



Results and Discussion

DGT deployments from 14 days to 1 day showed linear uptake (Fig 3a), while the Relative Percent Difference (RPD) of field duplicates (Table 1) and detection limits (Table 2) varied by deployment period. The trends of metal uptake at each monitoring station over the course of 5 sampling campaigns is shown for Cu, Pb, and Zn (Fig 3b).



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) C_{DGT} 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 C_{DGT} is signified by bars grouped by station and chronological from left to right. Colored lines represent variation captured 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: 0.0655-0.901 µg L⁻¹ Cu; 0.00260-0.0136 µg L⁻¹ Pb; 0.294-16.2 µg L⁻¹ Zn.

Table 2. C_{DGT} 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.

Based on the results from DGTs deployed over different intervals spanning continuous deployments of 3-14 days and rainfall events of 0.4 – 3.2 inches within a 24 hr period, it was determined that reproducibility was affected by mass loading rate (time to equilibrium), which was 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 March 2016 campaign, and was likely due to sunlight and increased algal growth on the sampler. Typical DGT surface cleanliness was improved (Fig. 4) when the DGTs were oriented downward.

Conclusions

- Cu:** C_{DGT} 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:** Due to very low ambient concentrations, C_{DGT} required deployment times >4 days.
- Zn:** C_{DGT} results were best at deployment times ≥7 days. Zn diffusion is affected by a combination of Chelex selectivity, kinetics of dissolved organic matter (DOM), gel purity, and proximity to sources^{3,4}. Reproducibility will improve if ambient levels approach regulatory thresholds.
- The ability to conduct constant surveillance of bioavailable metals in marine and fresh water environments under varying environmental conditions greatly improves the assessment of potential ecological effects from exposure to metals.
- DGT deployments allows for cost-effective monitoring of best management practice (BMP) performance
- Future research should focus on rigorous comparison of labile species (C_{DGT}) to bioavailability (toxicity exposure levels) to gain regulatory acceptance of C_{DGT} values for protection of beneficial uses.



Figure 4. DGTs recovered after 14 days.

References

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