Evaluation of the in situ, time-integrated DGT technique by monitoring changes in heavy metal concentrations in estuarine waters

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Abstract

Various natural and anthropogenic processes influence heavy metal concentrations within estuaries. In situ, time-integrated DGT measurements made over concurrent tidal phases found significantly higher concentrations of Cu (*probability-p* = 0.017), Zn (p = 0.003) and Ni (p = 0.003) during the flood phase, because the incoming tide passes several point sources. DGT-reactive Cu concentrations significantly decreased with increased tidal-flushing and vice versa within a marina (*correlation-r* = -0.788, p = 0.02). DGT measurements also recorded significant increases in Cu (4 out of 4 sites, $p < 0.001$) and Zn (3 out of 4 sites, $p \leq 0.015$) after a 24 mm rainfall event. Finally, DGT-reactive Cu increased significantly ($p < 0.001$) during peak boating times, due to increased numbers of Cu-antifouled boats. This study demonstrates that, with judicious selection of deployment times, DGT measurements enable changes in heavy metal concentrations to be related to various cycles and events within estuaries.

Demonstration of the usefulness of DGT as a monitoring tool for heavy metals in dynamic estuaries

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Keywords: DGT; heavy metals; tides; stormwater run-off; antifouled boats

1. Introduction

The development of robust in situ measurement techniques for monitoring contaminants, such as heavy metals, in aquatic systems remains a priority. Apart from the potential advantages of minimising sampling artefacts and allowing selective measurement of contaminant species, in situ measurements often provide better quality information on important aquatic processes compared with other monitoring approaches (Buffle and Horvai, 2000). There are three different approaches to in situ monitoring (Davison et al., 2000): (1) continuous in situ measurement, such as with galvanic dissolved oxygen electrodes and pH electrodes; (2) time-series (discrete) in situ measurement - this approach may actually be an automated in situ sampling followed by rapid on-site measurement, such as with a continuous flow or flow injection analyser (Buffle and Horvai, 2000; Laës et al., 2005; Sarradin et al., 2005), but most continuous measurement sensors can also be used to make time-series measurements; and (3) continual in situ sampling (time-integrated) followed by analysis in a laboratory, such as the diffusive gradients in a thin film (DGT) technique (Davison and Zhang, 1994; Zhang and Davison, 1995; Davison et al., et al. 2000; Zhang and Davison, 2000; Twiss and Moffet, 2002; Dunn et al., 2003) or other 'passive samplers' (Kot et al., 2000; Luellen and Shea, 2003; Verweij et al., 2004).

These three approaches to in situ measurement give very different results, as compared in Figure 1 using hypothetical results for an analyte in an extremely dynamic system. Continual measurement of the changing analyte concentration provides the most accurate measurement. However, as few analytes can be measured continuously, discrete or time-integrated in situ measurements may have to be used instead. As DGT and other time-integrated techniques require sufficient deployment time to accumulate

or equilibrate the analytes to enable measurement, discrete in situ measurements can usually be made more frequently (e.g. nine discrete measurements are made over the deployment period of the hypothetical data compared with four deployments for the time-integrated approach). The discrete techniques, like conventional grab samples, provide a measurement of the analyte concentration only at the time of measurement. In Figure 1 these points are joined, as they are typically shown, although no information is known about the analyte concentration between the measurements.

The time-integrated measurement provides very different information, as the monitoring devices are deployed continually in the water, with the analyte species accumulated by diffusion and chelation, ion exchange or partitioning. In the case of the DGT technique, analyte species diffuse across a layer of defined thickness (the diffusive layer, which is usually made of polyacrylamide hydrogel covered with a protective membrane) followed by strong binding to a binding layer (usually Chelex-100 resin cast within polyacrylamide hydrogel) (Davison et al., 2000). When measuring heavy metals, DGT selectively accumulates free metal cations, simple inorganic complexes and labile metal-NOM (natural organic matter) complexes in a highly operational but reproducible manner (Zhang and Davison, 2000; Twiss and Moffett, 2002; Dunn et al., 2003; Scally et al., 2003; Li et al., 2005). The measured species have therefore been described as DGT-reactive or DGT-labile.

The binding layer is removed in the laboratory and measured, with the amount of analyte quantified by a relationship derived from Fick's First Law of Diffusion (DiGiano et al., 1988), widely known now as the DGT equation (Davison et al., 2000). One value, as indicated in Figure 1 by a flat line across each of the four DGT deployment periods, shows the average analyte concentration for each deployment. With this approach, all changes in concentration that are longer than the time scale of

response for DGT will influence the final time-averaged measurement (Scally et al., 2003; Sigg et al., 2006), although no information is given about when the changes occurred or the extent of the change.

The advantages of continual in situ measurement are therefore readily apparent. The sample of discrete data given here indicates that only general changes in analyte concentrations are observed, whereas the time-integrated data seems to indicate only the broadest of trends. Of course, both approaches (2) and (3) allow for measurements to be made at increased frequency, which will provide better quality information. This choice of measurement frequency is crucial when developing a monitoring program. Figure 1 demonstrates the relative amount of information obtained by each of the three approaches. The challenge for researchers of time-averaged measurements, like the DGT technique, is to demonstrate how it can be best used to investigate aquatic processes, in particular within dynamic systems.

Estuaries are the most dynamic aquatic system, with many natural or anthropogenic influences causing changes in heavy metal concentrations. The purpose of this study was to determine whether time-integrated, in situ DGT measurements could be used to monitor changes in various heavy metal (Ni, Cu, Zn, Pb) concentrations in response to four processes/conditions: tidal cycles, tidal flushing, urban stormwater run-off, and number of vessels with Cu-antifouled hulls.

2. Materials and methods

2.1. Description of study location

This study was undertaken within the Broadwater situated in the southern-most reaches of Moreton Bay in south-east Queensland, Australia (Figure 2). The Broadwater is a subtropical lagoon characterised by exposed sandbanks, mangrove islands and seagrass beds, with extensive residential canal and commercial developments on the western shores. The Broadwater is generally shallow, with a mean tidal range of 1.5 m (micro-tidal) (Moss and Cox, 1999). Oceanic exchange occurs through the Seaway (near Wavebreak Island) and Jumpinpin Bar. Tidal flows through the Seaway into the Broadwater average approximately 106 ML on each tide (Moss and Cox, 1999), resulting in a very strong flushing effect within the Broadwater. Freshwater enters the Broadwater mostly through the Nerang River, Coomera River (north and south arms), and Pimpama River, as well as through numerous smaller creeks. DGT measurements were made at each of the 12 sites shown in Figure 2.

2.2. Field sampling design

Investigation of the effect of tidal cycles on Cu, Zn, Ni and Pb concentrations measured by DGT occurred over 3-6/12/2001 at Ephraim Island. DGT probes (n = 3) were deployed, using sampling systems described by Dunn et al. (2003), during four near-consecutive high tide, low tide, ebb tide and flood tide phases, respectively, for 6 h each time. The three DGT probes were then re-used for three subsequent, same tidal phases, making an overall accumulation period of 24 h for each DGT.

Investigation of the effect of tidal flushing on Cu, Zn, Ni and Pb concentrations measured by DGT occurred during August to September 2003 at four sites (Runaway Bay Marina, Jumpinpin, Marine Stadium and Wavebreak Island). DGT probes (n = 3) were deployed consecutively for 3-4 days over a four-week period.

Investigation of the effect of stormwater run-off on Cu, Zn, Ni and Pb concentrations measured by DGT occurred over December 2001 to January 2002 at four sites (Lands End Canal, Runaway Bay Canal, Hollywell and Paradise Point Anchorage). DGT probes (n = 3) were deployed for 24 h twice at each site, initially during a period of no rainfall (22-23/12/2001) and then during a period of rainfall (16-17/1/2002, 24 mm, lasting approximately 6 h into the 24 h deployment period).

Investigation of the effect of Cu-antifouled boat numbers on Cu, Zn, Ni and Pb concentrations measured by DGT occurred during December 2001 to January 2002 at six sites (Marine Stadium, Ephraim Island, Tipplers Passage, Wavebreak Island, Curtis Anchorage and Dux Anchorage). DGT probes (n = 3) were deployed for 24 h twice at each site, initially during a period of generally low recreational boat usage (3-22/12/2001) and subsequently during a period of typically high recreational boat usage (4-7/1/2002) within the Gold Coast Broadwater (Warnken and Leon, 2006). Recreational boats estimated to be using Cu-antifouling paint were counted for every 4 h during the 24 h deployment at each site using an approach described in Warnken et al. (2004). The results are shown in Table 1, which supported past observations.

During each sampling period, water temperature, pH, dissolved oxygen and specific conductance were measured *in situ* and recorded with a multi-probe analyser (TPS 90-FLMV model, TPS Pty. Ltd.) at a depth of approximately 1 m. Turbidity was recorded on-site using a nephelometric turbidity meter (2100 Turbidimeter, HACH). Rainfall conditions and tidal level were also recorded during each sampling event.

2.3. General experimental

Trace analysis cleaning and handling techniques were used throughout this study. All water used in this study was deionised (Milli-Q Element). All plastic-ware and glassware (gel casting plates only) were acid-washed in 1:10 nitric acid (Analytical Grade) followed by thorough rinsing with water. Suprapur nitric acid (Merck) was used for preserving samples and standards and for eluting metals from the DGT binding layer. All cleaning, solution preparation and sample handling were undertaken wearing disposable powder-free gloves (Flexi).

2.4. Preparation and measurement of DGT devices

Sheets of polyacrylamide hydrogel, used for the diffusive layers, were prepared as described previously (Dunn et al., 2003), with 0.05 cm thick spacers. These sheets were hydrated and washed in water and stored in 0.01 M $NaNO_3$. Sheets of polyacrylamide hydrogel containing Chelex-100 resin (Bio-Rad) (the binding layer), also prepared as described previously (Dunn et al., 2003), were hydrated, washed and stored in water. Discs of 2.5 cm diameter diffusive and binding layers were cut from the respective sheets and incorporated into DGT probes as described in Dunn et al., (2003), along with 0.45 µm cellulose nitrate membrane as a protective cover.

DGT probes were deployed using an apparatus described in Dunn et al., 2003. The exact deployment time was recorded, along with the average water temperature for each deployment period. Upon return to the laboratory, the probes, including ones used as blanks (approximately 10% of the total number), were disassembled and the binding layer placed in a microcentrifuge tube.

The binding layers were eluted in 1 mL of 1 M HNO_3 for 24 h. The binding layer was then removed from the eluent solution, followed by a three- or four-fold dilution of

the eluent (with water). The eluent solutions were analysed by inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer SCIEX ELAN® 6100) at ALS Environmental (Brisbane). Recoveries of multi-element spiked samples were >90%. All analyses with relative standard deviations >10% of the three replicates measurements were repeated. The mass of accumulated metals was measured and thus the DGT-reactive metal concentrations in the waters were calculated using the DGT equation: (DiGiano et al., 1988; Davison and Zhang, 1994; Davison et al., 2000).

$$C = m.\Delta g/D.A.t \qquad \text{(eq. 1)}$$

Where, C (ng cm^{-3} = μg L^{-1}) is the average DGT-reactive metal concentration over the deployment time (t, s); m (ng) is the mass of metal accumulated; A (cm^2) is the area of the DGT probe exposed to the water; Δg (cm) is the thickness of the diffusive gel and the membrane; and, D (cm^2 s^{-1}) is the diffusion coefficient of the free metal ion in the diffusion gel (DGT Research, 2003), which is derived from the free ion diffusion coefficients in sea water (Li and Gregory, 1974), at the average temperature over the deployment period.

For sampling conducted between December 2001 - January 2002, the mean mass and the standard deviation (*S*) of the blanks (n = 12) for each element in the binding layers were found to be 0.57±0.26 ng cm^{-2} for Cu, 0.08±0.02 ng cm^{-2} for Pb, 71.84±7.2 ng cm^{-2} for Zn and 2.48±0.40 ng cm^{-2} for Ni. For approximately 1-day (86400 s) deployments, and with Δg = 0.08 cm and A = 3.14 cm^2, this gave method detection limits (3×*S*) of 0.041 μg L^{-1} for Cu (D = 5.74×10^{-6} cm^2 s^{-1}), 0.002 μg L^{-1} for Pb (D = 7.40×10^{-6} cm^2 s^{-1}), 1.13 μg L^{-1} for Zn (D = 5.60×10^{-6} cm^2 s^{-1}) and 0.066 μg L^{-1} for Ni (D = 5.32×10^{-6} cm^2 s^{-1}).

For sampling conducted between August - September 2003, the mean mass and the standard deviation (*S*) of the blanks (n = 26) for each element in the binding layers were

found to be 0.90±1.73 ng cm^{-2} for Cu, 0.28±0.37 ng cm^{-2} for Pb, 196.61±224.48 ng cm^{-2} for Zn and 1.48±2.04 ng cm^{-2} for Ni. For approximately 3-day (259200 s) deployments, this gave method detection limits (3×*S*) of 0.083 μg L^{-1} for Cu (D = 5.27×10^{-6} cm^2 s^{-1}), 0.014 μg L^{-1} for Pb (D = 6.79×10^{-6} cm^2 s^{-1}), 11 μg L^{-1} for Zn (D = 5.14×10^{-6} cm^2 s^{-1}) and 0.106 μg L^{-1} for Ni (D = 4.88×10^{-6} cm^2 s^{-1}). Blank values were subtracted from the (m/A, ng cm^{-2}) measurement of the respective element for each DGT measurement before conversion to the concentration value.

3. Results and discussion

3.1. Effect of tidal cycles on DGT measurements

DGT-reactive Cu, Zn, Ni and Pb concentrations measured during four near-consecutive high, low, flood and ebb tidal phases at Ephraim Island are given in Figure 3. The four deployments of 6 h each allowed the metals to accumulate to a level that was readily measurable, equivalent to a 24 h deployment. With this sampling program there was an overlap of approximately 3 h between adjacent tidal phases (i.e. the first 3 h of the high-tide measurement overlapped with the last 3 h of the flood-tide measurement and the last 3 h of the high-tide measurement overlapped with the first 3 h of the ebb-tide measurement, and so on). Even with these factors, it is apparent from Figure 3 that the DGT-reactive Cu, Zn and Ni concentrations during the flood tidal phases were higher than each of these metal concentrations measured for all of the other tidal phases. 1-way ANOVA tests ($\alpha = 0.05$, $df1 = 3$, $df2 = 8$) showed that for Cu ($p = 0.017$), Zn ($p = 0.003$) and Ni ($p = 0.003$) there were significant differences between the DGT-reactive concentrations measured. LSD post-hoc tests indicated that for Zn ($p \leq$

0.002) and Ni ($p \leq 0.002$) the flood phase was significantly different from the other tidal phases. For Cu the flood phase was significantly different ($p \leq 0.023$) from the ebb- and high-tide phases, but not the low tide ($p = 0.06$), which was marginal. The ANOVA test indicated that there were no significant differences between the DGT-reactive Pb concentrations measured.

This result is somewhat different to expectations within estuarine systems, where generally the flushing of an area with cleaner marine waters results in a decrease of observed metal concentrations during the high tide. One likely explanation for these observations is that there are two large marinas located between the Seaway (the nearest mouth to the ocean) and Ephraim Island. The flood tide passes north along the foreshore where the marinas, as well as several canal estates and numerous stormwater drains, are situated before passing the Ephraim Island site. Due to the influence of these various potential sources, the incoming water is likely to have elevated levels of heavy metals. The outgoing tide brings water from the nearby Coomera River past the site, which also has a lot of development, including canal estates and stormwater drains, but may also flow from north of Ephraim Island where there are fewer potential metal sources nearby.

3.2. Effect of tidal flushing on DGT measurements

The DGT-reactive Cu concentrations at Runaway Bay Marina (B), Marine Stadium (C) and Jumpinpin (D) from the 4-week time-series deployment in August - September 2003 are shown in Figure 4, along with the 24 h cumulative tidal difference (A) (i.e. [high tide 1 + high tide 2] – [low tide 1 + low tide 2]). Tidal heights are as measured at The Seaway, which will be very close to the tide at each of the sites measured. A higher

value for tidal difference means there was a greater tidal movement of water or greater tidal flushing than occurs with a lower value. Another factor influencing these Cu concentrations was a 72 mm rainfall event during the first week of the time series, which is also shown in Figure 4.

DGT-reactive Cu at Runaway Bay Marina changes inversely with the degree of tidal flushing. A very high DGT-reactive Cu concentration (3.74 μg L^{-1}) was measured throughout the rainfall event. This measurement corresponded with a period of low tidal flushing. As the tidal exchange increased, the DGT-reactive Cu concentrations decreased to 1.54 μg L^{-1} when the tidal flushing was greatest. Then the Cu concentrations increased again as tidal exchange decreased, followed by another decrease in Cu with an increase in tidal exchange. This interaction suggests that there is a fairly continual but varying input of Cu into the waters within Runaway Bay Marina, which can come from sources such as antifouled boats, hard-stand activities, and stormwater run-off. By averaging the cumulative tidal height for each DGT deployment time, a correlation with the DGT-reactive Cu concentrations can be sought ($\alpha = 0.05$, $df = 7$, $r = -0.788$, $p = 0.02$). This strong and significant correlation suggests that the changes in Cu concentrations are strongly influenced by the tidal exchange. It is likely, as supported by Figure 4, that rainfall run-off also greatly increases the Cu concentrations within the marina. Other sources such as antifouled boats would likely be a more consistent source of Cu.

DGT-reactive Cu concentrations at Jumpinpin also increased dramatically following the rainfall event that coincided with a tidal-exchange minima. The observed Cu concentration then decreased as the tidal exchange increased. The interaction between these two factors for the second tidal flushing minima and maxima were not so strong. Jumpinpin is the northern connection with the ocean, and an extensive estuarine

delta has formed adjacent to the coastal lagoon. Here it appears that the rainfall event influenced the changes in Cu concentrations more so than tidal flushing.

A similar interaction to that observed in Runaway Bay Marina was observed at Marine Stadium and Ephraim Island (not shown, but very similar to Marine Stadium results), except the concentrations were not as high. Also the rainfall event seemed to increase the DGT-reactive Cu concentrations to a small degree only, but appeared instead to broaden the peak. The periods of greatest tidal exchange did correspond with the lowest Cu concentrations and the periods of lowest tidal flushing corresponded with the highest Cu concentrations. The changes in Cu concentrations were proportionally less at Marine Stadium and Ephraim Island compared with those at Jumpinpin and Runaway Bay Marina, in particular. This may be due to the relative depth of each site.

3.3. Effect of stormwater run-off on DGT measurements

DGT-reactive Cu, Zn, Pb and Ni concentrations (Table 2) were measured during 'dry' conditions (no recorded rainfall) (22-23/1/2002) and were compared to measurements conducted during a 24 mm rainfall event (15-16/1/2002, rainfall lasted approximately 6 h into the 24 h sample period) at four sites (Lands End Canal, Runaway Bay Canal, Hollywell, Paradise Point anchorage). DGT probes were deployed just as the rainfall occurred and, therefore, would have measured during any "first-flush" event (Bertrand-Krajewski, et al., 1998; Delectic, 1998).

In general, increased DGT-reactive metal concentrations were observed during the rainfall deployment for Cu (4 out of 4 sites), Zn (3 out of 4) and Ni (4 out of 4). 2-way ANOVA tests ($\alpha = 0.05$, $df1 = 3$, $df2 = 16$) indicated that for Cu ($p < 0.001$) and Zn ($p \leq$

0.015), each of the observed increases in concentration was significant. Only the increase at Paradise Point Anchorage ($p < 0.001$) was significant for Ni. Only one of the Cu increases was greater than 40% whereas, for Zn, all three increases were greater than 40%.

The tidal flushing was estimated at each of these sites, as above, in case these trends in Cu and Ni DGT measurements could be explained by tidal exchange. However, the cumulative tidal difference for 48 h around the rainfall deployment was 4.53, a high value indicating that there was a high rate of tidal exchange, which would have decreased the concentrations, not made them higher. Also the tidal exchange was much lower during the no-rainfall deployment (2.59 m). These results suggest that the main influence on the two deployments was rainfall run-off.

Run-off and associated pollutant loads from urban watersheds originate from both pervious and impervious surfaces. The amount of pollutant transported to receiving bodies by rainfall depends on the characteristics of the various surfaces present, the amount of pollutant accumulated during the preceding dry period and the energy of the runoff (Harrison et al., 1985; Hamilton et al., 1987; Stotz, 1987; Dannecker et al., 1990; Hvitved-Jacobsen and Yousef 1991; Hewitt and Rashed 1992; Vaze and Chiew 2002). Each of the four sites monitored had stormwater drains and extensive impervious surfaces in their run-off 'catchments'. The observed increases in metal concentrations during the rainfall are assumed to be a direct result of urban and highway run-off, where vehicles deposit metal residues in addition to metal leaching from sealed surfaces (Gnecco et al., 2005; Kim et al., 2005). Other terrestrial non-point sources may also have been contributing factors in the observed increase in metal concentrations.

3.4. Effect of antifouled boat numbers on DGT measurements

Cu, Zn, Ni and Pb concentrations were measured over 24 h periods, in months with typically different boat numbers within the Gold Coast Broadwater. Table 1 shows that the mean number of antifouled vessels recorded during the peak boating seasons at six anchorages were, in every case, higher than the numbers recorded at each anchorage outside of the peak boating season. Comparisons made between the DGT-reactive metal concentrations measured at each sample location are shown in Table 3. It is apparent that only Cu concentrations increase at all sites. 2-way ANOVA tests ($\alpha = 0.05$, $df1 = 5$, $df2 = 24$) confirmed that there was a significant difference between the peak and non-peak Cu concentrations ($p < 0.001$). LSD post-hoc tests determined that the Cu increases at Ephraim Island, Marine Stadium, Tipplers Passage and Dux Anchorage were each significant ($p \leq 0.004$). The two sites that did not have significant increases in Cu concentrations (Wavebreak Island and Curtis Anchorage) had both the smallest number of antifouled boats and the smallest increase in antifouled boat numbers. During these deployment periods, the effects of tidal flushing and rainfall were able to be excluded as having an influence on these results. These observations support the conclusion that the measured Cu was leaching from the antifouling paint on the boat hulls. These data has previously been analysed in a different way by Warnken et al. (2004), but the same conclusion was supported.

The effect of possible changes in metal speciation, in response to the various aquatic events, on the operational DGT-reactive measurements needs to be considered. A change in the DGT-reactive metal concentration could be due to a change in the total metal concentration, with the various metal species remaining in proportion, or it could

be due to a change in the speciation, without any change in total metal concentration. Both types of changes are likely to occur together. For this study, it did not matter why the DGT-reactive metal concentrations changed, it only mattered that they changed in a statistically significant manner, in response to an event, and that the changes were able to be generally explained with regard to known effects of each event. If significant changes in the DGT-reactive concentration did not occur, then it was likely that no substantial changes in metal speciation or concentration occurred either.

4. Conclusions

These results demonstrate that, with judicious selection of the deployment period of the probes, changes in heavy metal concentrations due to estuarine events (stormwater run-off, recreational boating season) and cycles (tidal currents and flushing) were observed using the DGT technique. While some of the processes monitored still require further study to determine their overall importance to estuarine heavy metal concentrations, DGT is confirmed as a useful monitoring device. Events that occur over the most convenient time-scale for DGT measurements of 6-72 h can be investigated as demonstrated in this study. Furthermore, the time-integrated approach of techniques like DGT becomes most useful when monitoring several locations influenced by a single event.

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Figure captions

Fig. 1. Measurement of hypothetical changes in analyte concentration by: *in* situ continual measurement (——); in situ discrete measurement (···●···); in situ time-averaged measurement (- -○- -); grab sample collection and laboratory analysis (●).

Fig. 2. Map of the Broadwater (Gold Coast, Australia) showing sampling sites used for this study.

Fig. 3. Mean DGT-reactive heavy metal concentrations (n = 3) measured over four near-consecutive flood, high, ebb and low tidal phases; total deployment time = 24 h.

Fig. 4. Changes in DGT-reactive Cu concentrations with 24 h cumulative tidal difference (A, tidal flushing) at (B) Runaway Bay Marina, (C) Marine Stadium and (D) Jumpinpin.

Table 1
Mean number of antifouled vessels observed over 24 h sample periods based on observations at 4 h intervals (rounded to nearest integer)

	Antifouled boat numbers for peak and off-peak seasons	
Sample location	***Off-peak season***	***Peak season***
Marine Stadium	32	58
Wavebreak Island	7	17
Ephraim Island	7	16
Tipplers Passage	34	105
Dux Anchorage	6	51
Curtis Anchorage	5	11

Table 2
Changes in mean DGT-reactive heavy metal concentrations (n = 3) at 4 sites in the Gold Coast Broadwater after a prolonged rain event (24 mm); all heavy metal concentrations are in µg L^{-1}

Location		**No rain**	**s.d.**	**Rain**	**s.d.**	**Difference**	**Percent change**
Lands End Canal	Ni	0.07	0.01	0.09	0.01	0.02	29
	Pb	0.05	<0.01	0.04	<0.01	-0.01	-20
	Cu	0.14	0.01	0.29	0.03	0.15	107
	Zn	0.83	0.29	1.23	0.16	0.40	48
Runaway Bay Canal	Ni	0.07	0.01	0.08	0.01	0.01	14
	Pb	0.05	<0.01	0.04	<0.01	-0.01	-20
	Cu	0.28	0.01	0.33	0.01	0.05	18
	Zn	0.43	0.18	1.28	0.18	0.85	198
Hollywell Canal	Ni	0.07	0.01	0.09	0.01	0.02	29
	Pb	0.04	<0.01	0.04	<0.01	0.00	0
	Cu	0.27	0.01	0.33	0.02	0.06	22
	Zn	0.65	0.09	1.22	0.15	0.57	88
Paradise Point Anchorage	Ni	0.08	0.01	0.12	0.01	0.04	50
	Pb	0.05	<0.01	0.06	0.01	0.01	20
	Cu	0.28	0.02	0.38	0.02	0.10	36
	Zn	0.77	0.08	0.62	0.08	-0.15	-19

Table 3
Changes in mean DGT-reactive heavy metal concentrations (n = 3) at 6 sites in the Gold Coast Broadwater for 24 h sampling events during off season and peak season boating activities; all heavy metal concentrations are in µg L^{-1}

Location		**Off-peak**	**s.d.**	**Peak**	**s.d.**	**Difference**	**Percent change**
Ephraim Island	Ni	0.06	0.01	0.05	<0.01	-0.01	-17
	Pb	0.05	0.01	0.06	<0.01	0.01	20
	Cu	**0.13**	**0.01**	**0.20**	**0.02**	**0.07**	**54**
	Zn	3.62	0.40	3.91	0.41	0.29	8
Marine Stadium	Ni	0.09	0.01	0.40	0.03	0.31	344
	Pb	0.39	0.04	0.24	0.02	-0.15	-38
	Cu	**0.31**	**0.02**	**0.50**	**0.02**	**0.19**	**61**
	Zn	3.88	0.06	4.71	0.44	0.83	21
Wavebreak Island	Ni	0.06	0.01	0.06	0.01	0.00	0
	Pb	0.16	0.02	0.05	<0.01	-0.11	-69
	Cu	**0.24**	**0.02**	**0.25**	**0.01**	**0.01**	**4**
	Zn	3.26	0.61	1.93	0.21	-1.33	-41
Tipplers Passage	Ni	0.19	0.05	0.25	0.02	0.06	32
	Pb	0.09	0.01	0.04	0.01	-0.05	-55
	Cu	**0.26**	**0.03**	**0.41**	**0.02**	**0.15**	**58**
	Zn	2.50	0.31	1.96	0.26	-0.54	-22
Dux Anchorage	Ni	0.12	0.04	0.18	0.03	0.06	50
	Pb	0.08	0.02	0.18	0.02	0.10	125
	Cu	**0.29**	**0.03**	**0.40**	**0.02**	**0.11**	**38**
	Zn	2.60	0.33	2.19	0.31	-0.41	-16
Curtis Anchorage	Ni	0.05	0.01	0.03	0.01	-0.02	-40
	Pb	0.10	0.02	0.15	0.01	0.05	50
	Cu	**0.20**	**0.02**	**0.24**	**0.02**	**0.04**	**20**
	Zn	2.18	1.02	1.68	0.19	-0.50	-23

Figure 1

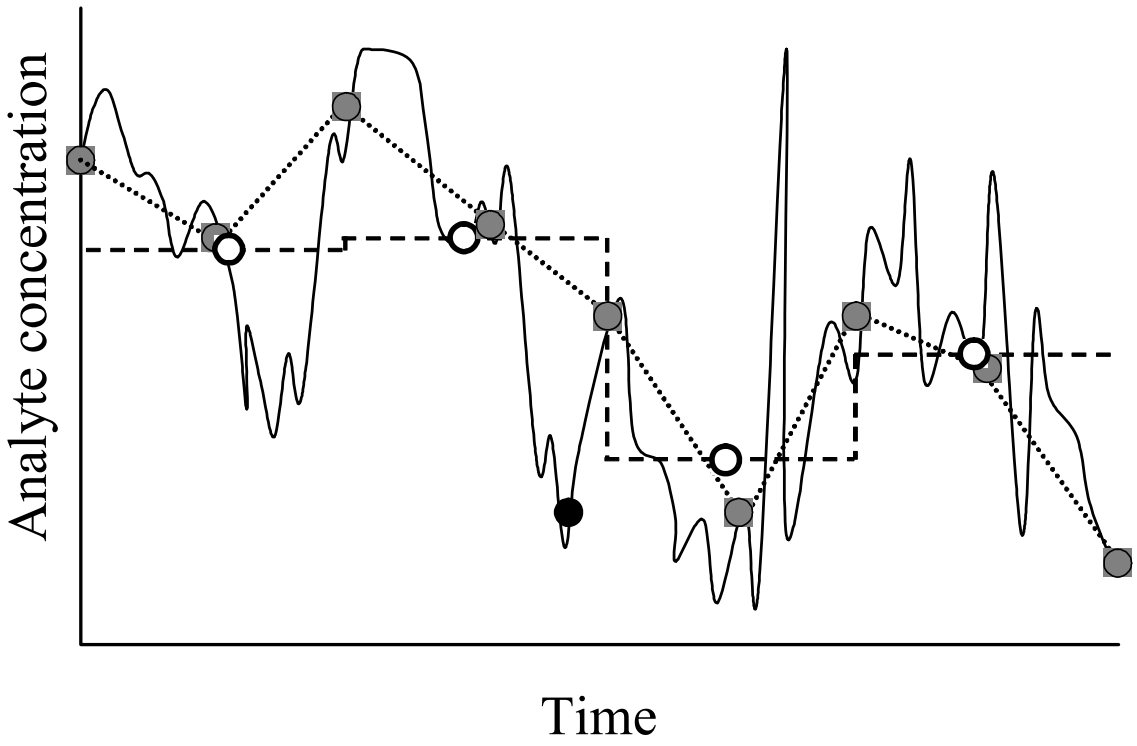


Figure 2

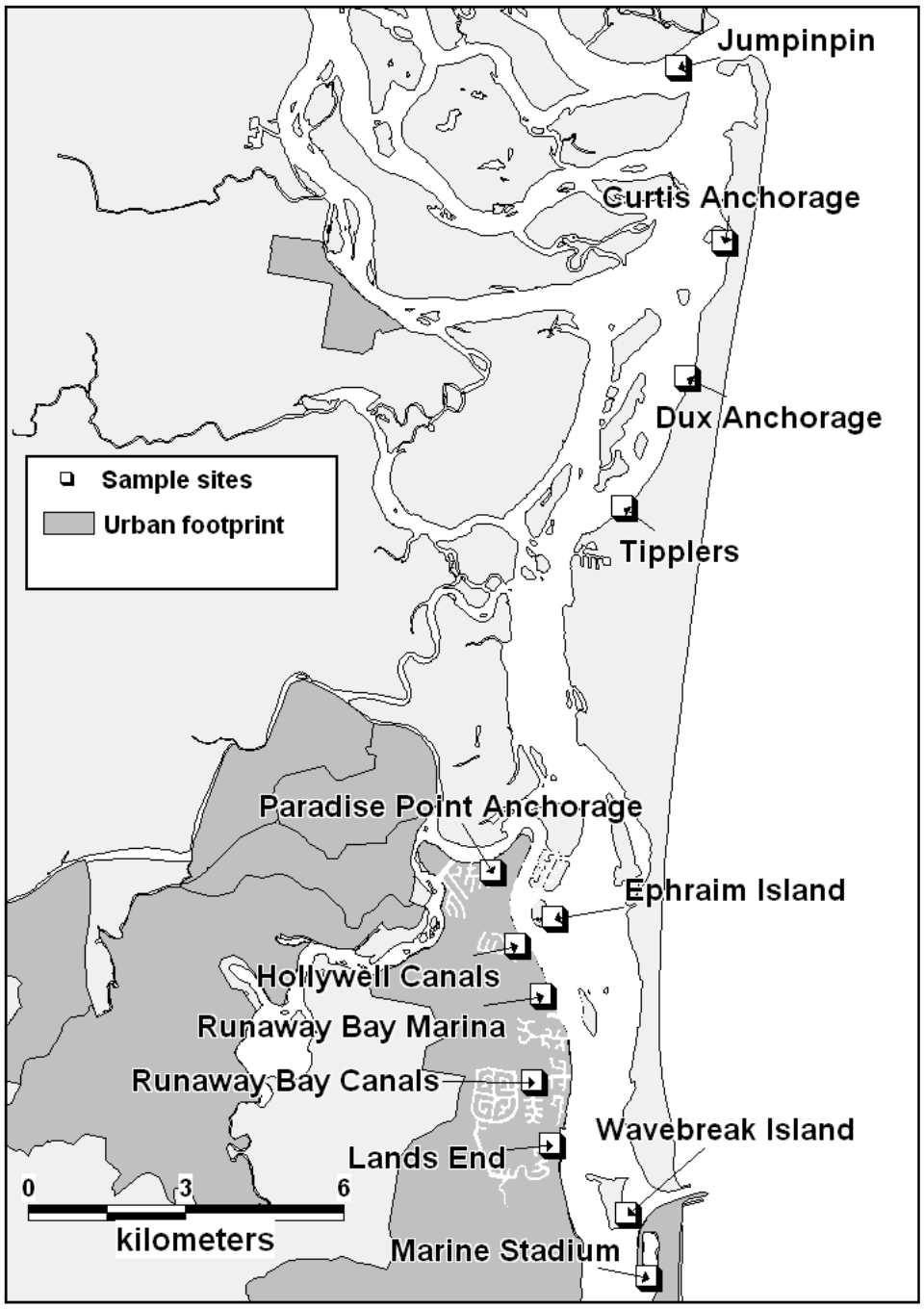

Jumpinpin
Curtis Anchorage
Dux Anchorage
Tipplers
Sample sites
Urban footprint
Paradise Point Anchorage
Ephraim Island
Hollywell Canals
Runaway Bay Marina
Runaway Bay Canals
Wavebreak Island
Lands End
0
3
6
kilometers
Marine Stadium

Figure 3

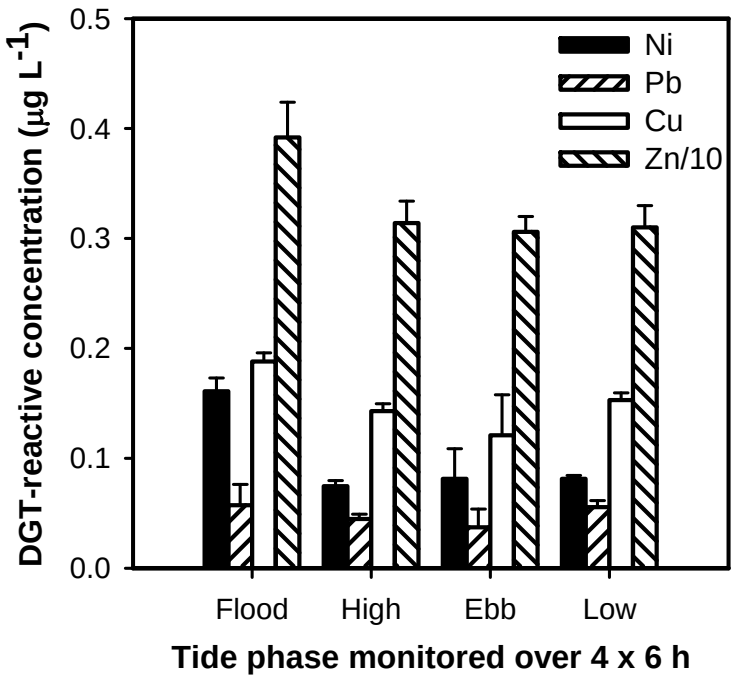
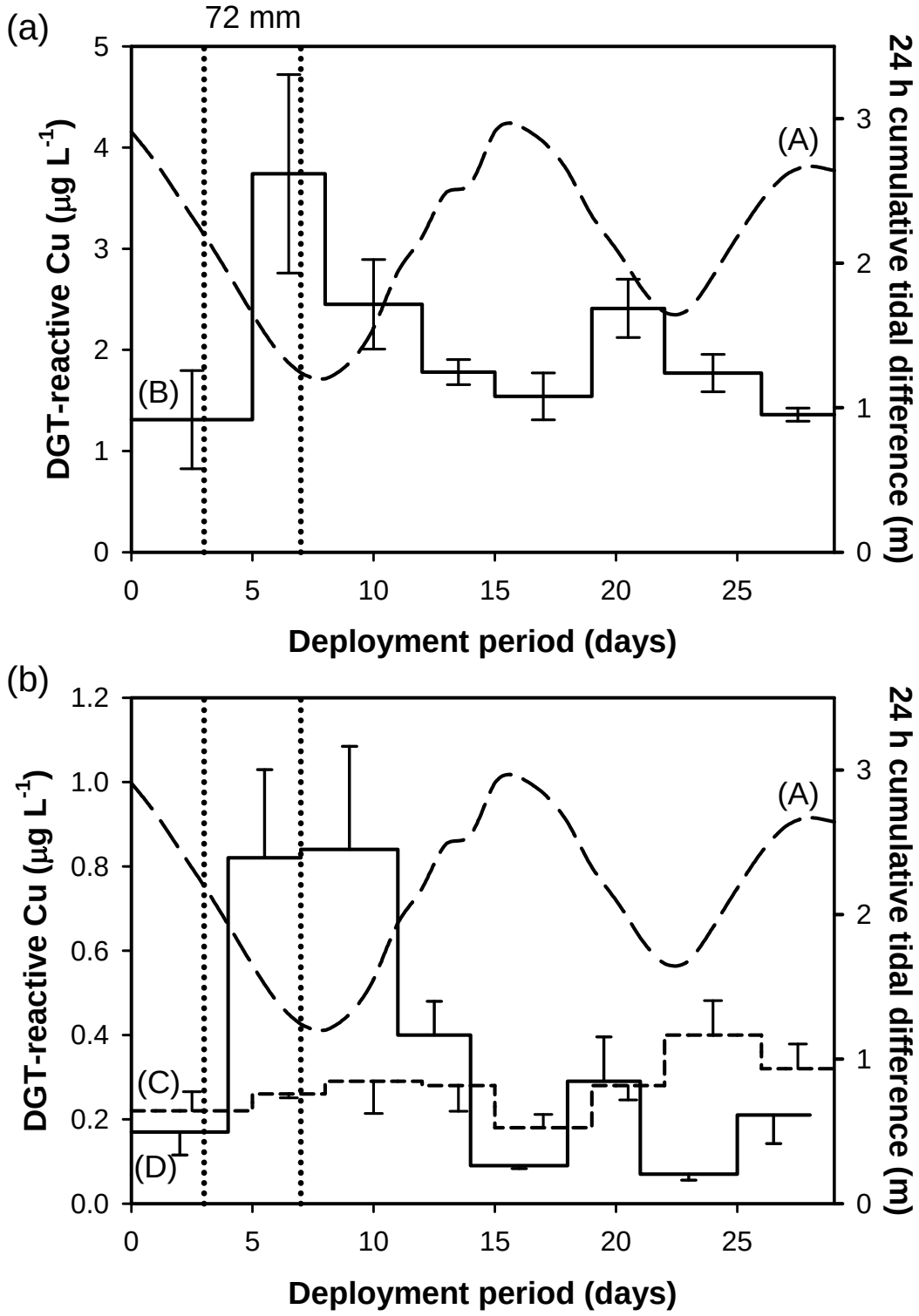

DGT-reactive concentration (µg L-1)
0.5
0.4
0.3
0.2
0.1
0.0
Ni
Pb
Cu
Zn/10
Flood
High
Ebb
Low
Tide phase monitored over 4 x 6 h

Figure 4


(a)
72 mm
DGT-reactive Cu (µg L-1)
24 h cumulative tidal difference (m)
(A)
(B)
Deployment period (days)
(b)
DGT-reactive Cu (µg L-1)
24 h cumulative tidal difference (m)
(A)
(C)
(D)
Deployment period (days)