The application of diffusive gradients in thin films (DGT) for improved understanding of metal behaviour at marine disposal sites

Ruth Parker[1], Thi Bolam[1*], Jon Barry[1], Claire Mason[1], Silke Kröger[1], Lee Warford[1], Briony Silburn[1], Dave Sivyer[1], Silvana Birchenough[1], Andrew Mayes[2] and Gary R. Fones[3]

[1] Centre for Environment, Fisheries and Aquaculture Science, Lowestoft Laboratory, Pakefield Road, Lowestoft, Suffolk, UK, NR33 0HT.

[2]School of Chemistry, University of East Anglia, Norwich Research Park, Norwich, UK, NR4 7TJ

[3]School of Earth and Environmental Sciences, University of Portsmouth, Burnaby Building, Burnaby Road, Portsmouth, UK, PO1 3QL.

* Corresponding author. Tel.: +44 1502 524525; E-mail address: thi.bolam@cefas.co.uk

Abstract:

Assessment of the effects of sediment metal contamination on biological assemblages and function remains a key question in marine management, especially in relation to disposal activities. However, the appropriate description of bioavailable metal concentrations within pore-waters has rarely been reported. Here, metal behaviour and availability at contaminated dredged material disposal sites within UK waters were investigated using Diffusive Gradient in Thin films (DGT). Three stations, representing contrasting history and presence of dredge disposal were studied. Depth profiles of five metals were derived using DGT probes as well as discrete analysis of total metal concentrations from sliced cores. The metals analysed were: iron and manganese, both relevant to sediment biogeochemistry; cadmium, nickel and lead, classified as priority pollutants. DGT time-integrated labile flux profiles of the metals display behaviour consistent with increasingly reduced conditions at depth and availability to DGT (iron and manganese), subsurface peaks and a potential sedimentary source to the water column related to the disposal activity (lead and nickel) and release to pore-water linked to decomposition of enriched phytodetritus (cadmium). DGT data has the potential to improve our current understanding of metal behaviour at impacted sites and is suitable as a monitoring tool. DGT data can provide information on metal availability and fluxes within the sediment at high depth-resolution (5 mm steps). Differences observed in the resulting profiles between DGT and conventional total metal analysis illustrates the significance of considering both total metals and a potentially labile fraction. The study outcomes can help to inform and improve future disposal site impact assessment, and could be complemented with techniques such as Sediment Profile Imagery for improved biologically relevance, spatial coverage and cost-effective monitoring and sampling of dredge material disposal sites. Additionally, the application of this technology could help improve correlative work on biological impacts under national and international auspices when linking biological effects to more biologically relevant metal concentrations.

***Key words*:** Dredge material, disposal, metal profiles, sediments, DGT (Diffusive Gradient in Thin-films), labile, bioavailability.

1.0 Introduction:

Dredging operations are conducted to remove sediments in order to maintain harbour berths, marinas and channels. The amount of dredging and disposal undertaken worldwide varies depending on a combination of economic, social and legislative needs. This activity is controlled under national and international legislations via licensing authorities, which also have a duty to comply with international conventions on dredging, disposal and marine environmental protection to minimise any adverse environmental consequences (Birchenough et al., 2006; Birchenough et al., 2010).

There are 136 sites currently designated for dredged material disposal around the coast of England, mostly in close proximity to the coast and major ports or estuaries. Individual quantities disposed, may range from a few hundred to several million tonnes, with an approximate annual sum of 40 million tonnes (Bolam et al., 2010a and 2010b). The nature of the disposed material may vary from soft silts to boulders or even crushed rock according to origin (capital material), although the majority consists of finer material (maintenance dredge material). Disposed material may have differing sediment types, higher loads of organic material and, although regulated, a higher associated loads of various contaminants such as organics or metals, from background or reference sediments. Disposal sites within the UK are selected for annual monitoring based on a tier-based approach that classifies the number of possible issues or environmental concerns that may be associated with dredged material disposal to sea at certain sites (Bolam et al., 2010b). In licensing the disposal of dredged material at sea, several national and international agreements (e.g., the London Protocol of 1996 (LP96), the OSPAR Convention, the Habitats and Species Directive (92/43/EEC), the Wild Birds Directive (79/409/EEC), the Water Framework Directive (2000/60/EC) and the Waste Framework Directive (2008/98/EC)), must be taken into account, to determine whether likely impacts arising from the dredging and disposal are acceptable (MEMG, 2003). Criteria considered under the various conventions and directives include the presence and levels of contaminants in the materials to be disposed of, along with perceived impacts on any sites of conservation value in the vicinity of disposal.

A number of different substances are determined as part of the monitoring of disposal sites, such as tributyltin, polycyclic aromatic hydrocarbons, organohalogens (e.g. PCBs) and metals measured as total metal concentrations in bulk sediments. Additional physico-chemical information, such as sediment particle size, organic carbon and nitrogen content, and sediment profile imagery (SPI), is obtained to further characterise sediment status (Birchenough et al., 2006; Bolam et al., 2010a and b).

Existing monitoring programmes are designed to address important questions such as: what is the fate of contaminants (including metals) imported to the site with the disposed material and what effect does this have on ecological components? Associated questions are those relating to the disposed sediments as sources and sinks of metals to the water column, either by diffusion or due to disturbance

by storms. At present, the analysis of total metals is the traditional technique used to assess the metal contaminant pressure within the disposal site monitoring programmes. In comparison, little is known regarding metal speciation or detailed vertical distribution and partitioning of metal contaminants between pore-water and solid phases within the sediments at the disposal sites. As such, the impact assessment of disposed material and management accordingly can be limited by using a total metal approach alone in assessing metal pressure within the sediment.

The sediment pore-water concentrations of contaminants and hence the bioavailability of chemicals in sediments is often estimated using various techniques (Forstner and Wittman, 1981; Bufflap and Allen, 1995; Stockdale et al., 2009). Pore-water can be obtained by *ex-situ* (slicing, centrifuge, suction, or pressure) methods or *in situ* (probe pumping or diffusion) methods, such as passive samplers (dialysis peepers, teflon sheets, DET and DGT). *Ex-situ* methods are often difficult to control and analyse due to issues in controlling oxidation during sampling, preservation and detection limits associated with small volumes and lack of pre-concentration. Additionally, as samples are handled open to the air, whilst on the boat, issues such as clean handling techniques can be a challenge for standard monitoring conditions. There may also be limitations of sampling resolution (Bufflap and Allen, 1995). Diffusion methods such as passive samplers (Peijnenburg et al., 2014) can be useful in that they can offer high resolution and are constrained inside probes which can allow cleaner handling, without full clean trace metal provisions. Some techniques can also pre-concentrate chemicals which can facilitate analysis success by lowering detection limits. Deployment times are typically ≥24 h, but deployments for this length of time can also minimise the effect of disturbances caused by deployment (Davison et al. 2007). Passive sampling methods can provide 'dissolved' concentrations in sediment porewater (C_{free}) thus providing a more relevant exposure metric for risk assessment than do total concentrations (Peijnenburg et al. 2014). Other information that can be obtained from passive samplers in sediments includes estimates of metal sources, sinks and time-integrated measurements.

Passive samplers such as Diffusive Gradient in Thin Films (DGT) have been used increasingly in sediments to determine pore-water metal 'dissolved' concentrations (C_{DGT}) and time-integrated labile metal fluxes (Zhang et al. 1995; Davison et al. 2000; Fones et al. 2001; Fones et al 2004; Peijnenburg et al. 2014; Amato et al. 2015). DGT is a passive sampling technique that has been used for determining metal concentrations in natural waters for more than 20 years (Davison and Zhang; 1994). A typical DGT device for common divalent metal ions consists of Chelex®-100 resin embedded within a hydrogel, overlaid with a diffusive layer of hydrogel and a filter membrane. These devices have been successfully employed in the sampling of metals prior to analysis of their concentrations in surface waters (Schintu et al. 2010; Shiva et al. 2016), soils (Oporto et al. 2009; Ernstberger et al. 2005) and sediments (Davison et al. 1997; Fones et al. 2004; Tankere-Muller et al. 2007; Teal et al., 2009; Teal et al., 2013) and by using different binding agents the range of determinands has been extended to include

other cations (Dahlqvist et al. 2002), oxyanions (Panther et al. 2014) and targeted species including sulphide (Teasdale et al. 1999) and uranium (Turner et al. 2012; Turner et al. 2015).

DGT is a well-developed technique for sampling metals in bulk water, with deployments from 6 to 72 h being typical, with the rate of metal uptake by the resin gel controlled by the diffusive layer (Davison and Zhang, 2012). The diffusion coefficient in the diffusive gel is similar to that of the diffusion rate of the metal ion in pure water and can be measured accurately by experiment (Zhang and Davison 1999). Diffusion coefficients for many metals including different species (Metal-NOM complexes) in polyacrylamide gels are available in the literature (Zhang and Davison, 2000; Scally et al. 2006; Shiva et al. 2015). The concentration in the water can then be calculated using the previously published DGT equation (Davison and Zhang, 1994; Davison and Zhang, 2012). One problem associated with this is the potential for metal species and complexes operationally defined as 'labile' to be sorbed onto the resin gel, this thus depends on the relative diffusion rates of the species that pass through the gel (Zhang and Davison, 2000).

DGT has also been fully characterized for use in sediments (Zhang et al. 1995; Fones et al. 2004; Amato et al. 2014). When used in sediments it is an in-situ technique that provides time-integrated measurements of the combined labile metal fluxes from the sediment pore water and particulate phases (Zhang et al. 1995). Upon deployment of the DGT probe in the sediment, metals dissolved in the pore water are rapidly accumulated on the resin in the binding gel. This generates a localized zone of depletion in the pore waters and induces a release of labile, weakly bound metals absorbed onto sediment particles (Harper et al. 1998; Ciffroy et al. 2011). The DGT device thus acts as a localised sink, removing labile metal species permanently from solution. The metal continuously accumulates in the DGT device while it is deployed in the sediment (Harper et al. 1999) and therefore measures a time-averaged flux from the pore water to the resin (Harper et al 1998 and 1999).

Harper et al. (1998) and Zhang et al. (1995) both showed that DGT fluxes can be interpreted as pore water concentrations using Fick's law of diffusion along with metal diffusion coefficients, deployment time and diffusive gel thickness if the metal concentrations at the interface between the DGT device and sediment are well buffered by metal resupply from the sediment sold phase. However, in most cases there is only partial resupply or resupply by metal diffusion so DGT measurements are the result of dynamic equilibriums between the binding strength of the DGT resin and that of the sediment (Davison and Zhang, 2012). Amato et al. (2015) suggested that interpreting DGT measurements as fluxes ($\mu g/h/m^2$) is the most suitable approach for sediment deployments. The DGT metal flux will differ depending on sediment properties and also the chemical behaviour of the metals. These differing release rates will influence accumulation of metals by benthic organisms thus providing the use of DGT-metal fluxes for assessing metal bioavailability in sediments (Simpson et al., 2012; Amato et al. 2014; Amato et al. 2015). However, only a few studies have utilised DGT sediment

144 measurements in the context of contamination studies at capping (Knox et al., 2012; Knox et al., 2016)
145 or disposal sites.

146 While the established practise of analysing total trace metals in bulk sediment samples gives
147 important information about absolute concentrations and so potential hazards, looking at depth resolved
148 profiles of metal fluxes as measured by DGT improves our understanding of how mobile and thus
149 available these metals are from a total disposal reservoir. In other words, what actual risk disposed
150 sediments pose. The bioavailability of heavy metals has been more closely linked to levels of dissolved
151 contaminants in pore-waters than to bulk sediment concentrations (Calmano et al., 1993; Ankley et al.,
152 1996b; Chapman et al., 1998; Eggleton and Thomas, 2004) as bioavailability and toxicity of metals in
153 sediments was not well predicted by sediment metal concentrations only (Lee and Lee, 2005).
154 The aim of this work was to apply therefore a passive sampling approach, diffusive gradient in
155 thin films (DGT) technology, as a complementary tool to the routine monitoring conducted at an UK
156 disposal site and thus assess the additional insight and understanding of metal behaviour and fate gained
157 by including this technique in a monitoring programme. Some of the metals examined (lead, nickel and
158 cadmium) are on the EU Water Framework Directive (WFD) list of priority substances and OSPAR list
159 of priority pollutants while others have mainly ecological relevance (iron and manganese).
160

161 **2.0 Materials and methods**

162 *2.1 Study site*

163 The Souter Point disposal site is located off the North East coast of the UK (Figure 1). This site has
164 been used for the disposal of dredged material since 1952 and selected stations have been monitored
165 annually since the early 1970s (Bolam et al., 2010a; Bolam et al., 2010b). The site is located at a depth
166 of approximately 40-50 m, shallowing by up to 5m towards the western boundary due to historical
167 accumulations of minestone and fly-ash deposits (Rees et al., 2006). Tidal currents in the vicinity of
168 the disposal site are moderate in strength and run generally parallel to the coastline, with a southerly
169 net residual drift. The sediments within the vicinity of this disposal site are muddy sands. However,
170 sediments may vary to a large extent following dredged material disposal and in relation to a sites earlier
171 history of solid industrial wastes and other discharges inshore (Rowlatt, et al., 1989; Rowlatt and
172 Ridgeway, 1997; Birchenough et al., 2007). The results of this work summarises results obtained during
173 a research cruise conducted in June 2011. Observations and measurements were made during the cruise
174 and on recovered samples back at the laboratory.

175 *2.2 Sampling approach*

176 A 0.1 m^2 NIOZ box-core was used to collect sediment at 3 stations: 4 core replicates were collected
177 from the Reference station (located to the south of the disposal site) and 3 core replicates were taken
178 from each of stations C and S, both located within the disposal site (Figure 1).

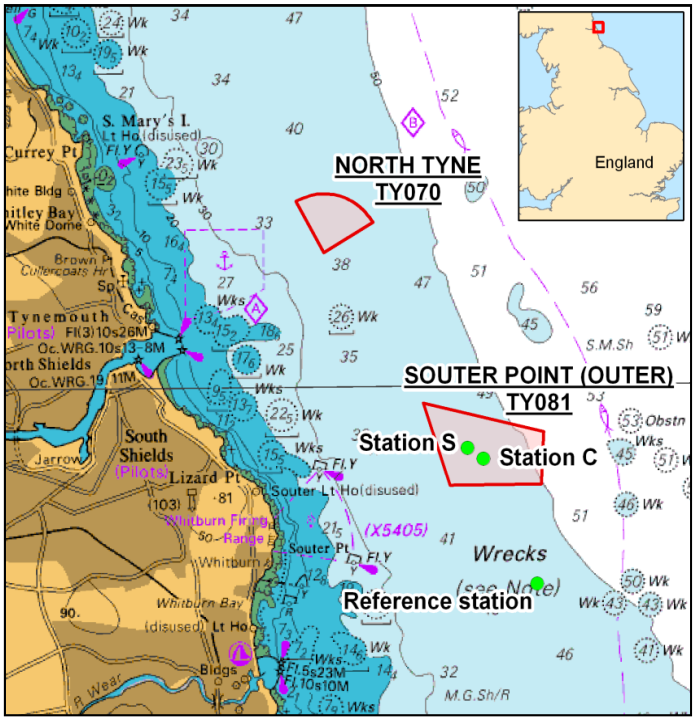

Figure 1. Souter Point disposal and sampling stations on the disposal stations (S, C) and reference station (R).

The DGT devices for metals in sediments were purchased as complete assembled probes from DGT Research (Lancaster, UK). The overall dimensions are 5 x 240 x 40 mm, with an exposure window of 18 x 150 mm and the device consists of a 0.8 mm APA diffusive gel, polyethersulphone filter membrane and Chelex binding layer. Probes and procedural blanks were de-oxygenated in a 0.01M NaCl solution overnight using oxygen free-nitrogen. The cores were placed in an incubating tank (in the dark and filled with oxygenated seawater) on-board ship and were stabilised for 2 hours before deployment of the probes. For each core, two probes were used: the Chelex gel probe (for metals determination) and the silver-iodine (AgI) gel probe (for sulphide determination). The probes were inserted into the sediment core, leaving 1 - 2 cm between the top of the probe window and the sediment/water interface. Furthermore, Chelex gel discs and AgI gel discs were deployed in the incubating tank in parallel with the probes to determine concentrations in the overlying water column. The probes and discs were deployed for 24 - 28 hrs. The time and temperature were recorded at the deployment and retrieval points. On removal, nanopure water (resistivity of 18.2 MΩ·cm) was used to rinse off any sediment traces that remained on the surface of the probes/discs. These were stored in a labelled bag and kept in the refrigerator prior to transfer to the laboratory for analysis.

Five replicate Sediment Profile Imagery (SPI) images were taken at each of the sites where the DGT technique was employed. Sediment Profile Imagery is a rapid, *in-situ* technique, which takes vertical profile pictures of the upper 20cm of the sediment system. The SPI camera works like an

201 'inverted periscope', the camera possesses a wedge-shaped prism with a Plexiglas faceplate and an
202 internal light provided by a flash strobe. The back of the prism has a mirror mounted at a 45° angle
203 which reflects the image of the sediment-water interface at the faceplate up to the camera. The imaging
204 system (a Nikon D-100 camera) provides *in-situ* visualisation of sediment characteristics (layers,
205 structure) and the interaction of the sediment and succession of large in-fauna (Rhoads and Germano,
206 1982; Germano et al., 2011). Visual assessment of sediment colour can be used to assess sediment redox
207 state, in particular iron reduction (loss of brown), manganese reduction (grey) and pyrite formation
208 (black), (Lyle, 1983; Bull and Williamson., 2001; Teal et al., 2009; Teal et al., 2010).
209
210 *2.3 Analysis of passive samplers*
211 *Chelex gel:* The DGT probes were rinsed with nano-pure water once retrieved. After opening the
212 window frame, the filter and diffusive gel layer were removed and discarded. The remaining resin gel
213 layer was carefully placed on a flat surface and the gel was sliced at 0.5 cm resolution. Each slice was
214 then placed in a sample tube and 1 ml of 1M HNO_3 was added to the tube, ensuring that the resin gel
215 layer was fully immersed in the HNO_3 solution. The sample was left to elute for at least 24 hours before
216 analysis (Davison *et al.,* 2007). The eluted solution was then diluted prior to analysis by Inductively-
217 Coupled Plasma-Mass Spectrometry (ICP-MS) using an Agilent 7500ce (Agilent Technologies,
218 Waldbronn, Germany), and by Inductively-Coupled Plasma-Atomic Emission Spectroscopy (ICP-
219 AES) using a Varian Ax Vista Pro (Agilent Technologies, Waldbronn, Germany). Quantification of
220 Cd, Fe, Mn, Ni, and Pb was performed by external calibration and deploying eight levels (0, 0.5, 1, 5,
221 10, 20, 100 and 500µg/L) of working standard solutions which were prepared from a customised mixed
222 metal standard solution of 100mg/L (SPEX Certiprep Ltd, Middlesex, UK). The limits of quantification
223 (LOQ) for each metal DGT analysis (24hr deployment) are (nmol/cm^2/s): Cd; 2.8x10^{-8}, Pb: 1.14x10^{-8},
224 Ni: 5.7x10^{-8}, Fe: 9.7x10^{-6}, Mn: 1.6x10^{-7}.
225
226 *AgI gel:* The AgI gels were removed from the probes and covered with a polyester film. The gels were
227 then scanned while wet in a flat-bed scanner. The greyscale intensity of the scanned images was
228 analysed with the software Image J (http://rsb.info.nih.gov/ij/). Using the calibration curve derived by
229 Teasdale *et al.,* 1999, total dissolved sulphides can be quantitatively measured in the gel.
230
231 *Metal flux calculations:* The measured concentrations, *Cg* (µg kg^{-1}) of the DGT gel solutions were
232 converted to molar concentrations and used to calculate the mass, *M* (nmol cm^{-2}), accumulated in the
233 resin layer of each gel strip:
234
235 $$M = \left(\frac{C_g (v+V)}{0.8 \times A} \right) \frac{1}{x} \qquad (1)$$

where V is the volume of gel (mL), v the extractant volume (mL) and x the atomic mass of the element in question. The factor 0.8 accounts for the fact that only 80% of the bound metal is released (Davison et al. 2000). Knowing the time of gel deployment, t (sec), allowed calculation of the time averaged Flux F (nmol cm^{-2} s^{-1}) of metal from the porewaters to the resin strip,

$$F = \frac{M}{t \times A} \qquad (2)$$

where A is the area of exposed gel (cm^2). The term 'flux' used from here onwards thus refers to the flux of reduced metal forms from the pore water to the resin gel of the DGT device, here onwards refered to as 'resin gel' (i.e. not reduction fluxes or process rates) and serves as a proxy for metal availability.

2.4 Supporting sediment analysis

Supporting measurements to complement the DGT probes and characterise the sediment at each of the stations were also collected. Oxygenation of the upper sediments layer was measured using oxygen pore water profiles obtained on intact cores and using oxygen microelectrodes (Unisense, Denmark) and a method adapted from Rabouille et al. (2001). Sediment characteristics were derived from vertical slices of sub-cores from a NIOZ box-corer at resolutions 0 to 0.5 cm, 0.5 to 1 cm and then at 1 cm intervals, stored at -20° C or analysed immediately. These sample slices were analysed for particle size, porosity, chlorophyll/phaeopigment and total organic carbon content.

Particle size analysis (PSA) was conducted using a method developed by Mason et al. (2011). In short, a subsample of each sediment was screened at 1 mm and laser sized using a Malvern Mastersizer 2000 (Malvern, Worcestershire, UK). The remaining sample was wet split at 1 mm, and the > 1 mm sediment was oven dried and then dry sieved over a range of test sieves down to 1 mm. Sediment < 1 mm was oven dried and weighed. The results from these analyses were combined to provide a full particle size distribution. Summary statistics, including %gravel, % sand and % mud, were derived from the full distribution dataset. Total Organic Carbon (TOC) was analysed using broadly similar methodology to that described by Verardo et al., 1990. Samples were freeze-dried and then ground to homogenise the sample. Inorganic carbonate was removed from a 1.3 g subsample using sulphurous acid to excess. Sub-samples (~0.5 g) were then weighed into tin cups and analysed using a Carlo Erba EA1108 Elemental Analyser. Chlorophyll a and phaeopigments were extracted in 90% acetone (Fisher Scientific, Leicestershire, UK) and refrigerated before analysis. A Turner Designs Model 10AU filter fluorometer (Turner Designs, Sunnyvale, California, USA) was used to measure extracted chlorophyll a by fluorescence before and after acidification, as described in Sapp et al. 2010. The fluorometer was calibrated using a solution of pure chlorophyll a (Sigma-Aldrich, St. Louis) with the concentration being determined spectrophotometrically. The percentage error of chlorophyll a analyses was < 2 % relative to Turner-certified reference material. Porosity was calculated using the

dry weights and wet weights of known volumes of sediment slices assuming a sediment particle density of 2.7 g cm^{-3} and a seawater density of 1.035 g cm^{-3} (Sapp et al. 2010).

2.5 Total Metals

A sub-core from each station was taken and sliced according to its visual description. Each slice was subsequently analysed for total metals on the < 63 µm sediment fraction. Typically, 0.2 g of the sieved and freeze-dried sediment sample was digested in a mixture of hydrofluoric (HF), hydrochloric and nitric acids using enclosed vessel microwave heating. The HF was then neutralised by the addition of boric acid and the digest made up in 1 % nitric acid and further diluted prior to analysis by ICP-MS and ICP-AES. Quantification of Cd, Fe, Mn, Ni, and Pb used external calibration with Indium as internal standard. A method blank and a certified reference material (CRM) PACS-2 (a marine sediment produced by the National Research Council Canada) were run within each sample batch so that the day-to-day performance of the method could be assessed. Shewhart control charts were derived from the CRM data and monitored using (upper/lower) warning and control limits set at ± 2 and 3 standard deviations from the mean value, respectively. Any batches with results outside these control limits were rejected and the samples re-analysed. The mean recoveries of all elements of interest range from 94% to 116% with a % relative standard deviations ranging from 2.8% to 12.2%.

2.6 Statistical approaches and analysis

To aid in comparing and contrasting features of DGT profiles within and between sites, a statistical model was fitted to each of the metal profiles. Before the main analysis, mean values were taken over the replicates to avoid statistical complications caused by spatial correlations between the cores. When examining the profiles, natural logs (Ln) were taken to reduce the visual impact on the profile of large readings. The Ln data also better fitted the assumptions behind the modelling which followed.

Initially, Ln profile plots of all eight metals were completed at all sites. For metals exhibiting the biggest differences between sites (Pb, Ni, Mn and Fe), further modelling was conducted to tease out the statistical evidence for these differences. We describe this modelling below.

The depth profiles for each of the metals at the three stations was smoothed using a Generalised Additive Model (GAM) (Wood, 2006) using the R package mgcv (R Development Core Team, 2010). Thin plate regression splines were used to smooth the data and the degree of smoothing (number of degrees of freedom (df) for the model parameters) was set to the minimum needed to explain the main fluctuations in the profile: we used 5 df for Pb and Mn and 4 df for Ni and Fe. The residuals (data minus the smoothed value) were calculated at each of the observed depths. For Pb and Ni, autocorrelation plots suggested that neighbouring residuals were independent; however, residuals from the Mn and Fe profiles were correlated. Thus, two different kinds of models, one assuming independence and one assuming one-lag auto correlation were required to model the depth profiles.

For the independent residuals, for a particular site and at each depth i, we assume that data arises from the model:

$$\ln(M_i) = s_i + e_i \quad (3)$$

where s_i is the smoothed value from the GAM model of metal M_i, and e_i is an independent error term which we assume to be distributed $N(0, \sigma^2)$, where σ^2 is the variance of points around the smoothed line σ^2 is estimated by the sum of the squared residuals divided by $(n-k)$, where n is the number of points and k is the number of degrees of freedom used in fitting the GAM model.

For the autocorrelated models, an autoregressive model of order 1 was used to the model the residuals:

$$r_i = \alpha r_{i-1} + e_i \quad (4)$$

where r_i is the i th residual, α is a parameter (estimated by maximum likelihood using the ar function in R) and e_i is an independent error term as in model (3). Simulated realisations of M_i were generated from (4) by adding on the smoothed surface s_i.

One thousand realisations were then simulated from the model in (3) or (4) and the mid 95% envelope taken. This is equivalent to a 95% confidence interval for the profile at each depth (Manly, 2008).

3.0 Results and discussion

3.1 Bulk metal and sediment characteristics

A summary of station sediment characteristics is shown in Table 1a and b and Figure 2 and bulk sediment metal profiles are illustrated in Figure A.1 (Appendix 1).

Table 1a: Mean sediment characteristics from sliced sediment cores (0 to ~10cm). Number in brackets is one standard deviation.

Station	Silt/clay (<63 µm, %)	Porosity	Chlorophyll (mg/m^3)	Phaeo-pigment (mg/m^3)	TOC (% mass/ mass)	Oxygen penetration (OPD) - cm
Reference	17.0 (3.7)	0.45 (0.04)	3.0 (2.3)	14.0 (7.0)	1.3 (0.3)	0.5 (0.2)
Disposal S	49.2 (20.7)	0.62 (0.05)	3.4 (2.4)	14.2 (6.9)	5.6 (1.6)	0.4 (0.2)
Disposal C	22.4 (16.9)	0.53(0.05)	4.7 (3.9)	14.7 (7.4)	5.4 (0.9)	0.4 (0.1)

340 Table 1b: Mean total metal concentration from bulk samples from core layers (full plots are in Appendix
341 1 Figure A.1)
342

Average Concentrations[#]	Ni (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Mn (mg/kg)	Fe (g/kg)
Reference (n=4)	50.0	<0.18	136	445	38.9
Disposal C (n=7)	49.6	0.50	172	510	39.6
Disposal S (n=6)	50.6	0.46*	164	475	39.1

343 *Cd at layer 8-9cm <0.2mg/kg
344 [#]SD not available as single measurement at each layer.

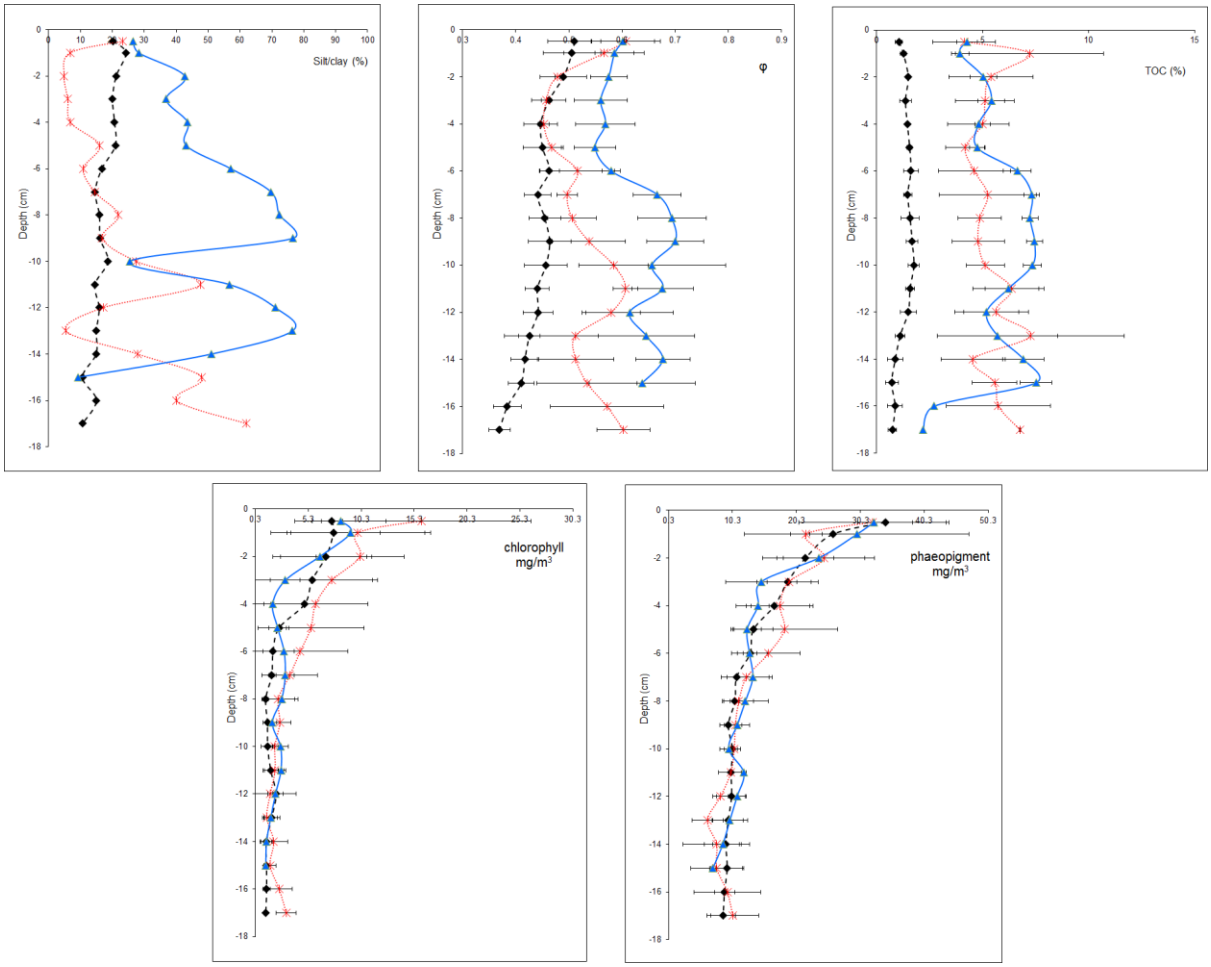

Figure 2: Vertical profiles of sediment properties at the three stations (reference, station C and station S) Silt/clay (%, single measurement), Porosity, Total Organic carbon (%m/m), Chlorophyll and Phaeopigment. Error bars are +/- 1 standard deviation, n=3

All stations were composed of either muddy sands where the sand:mud (mud being defined as the sediment fraction <63µm, and sand between 63µm and 2mm) ratio is >1:1 and <9:1; or to a lesser extent sandy muds, where the sand:mud ratio is >1:9 and <1:1; as defined in Folk classification (Folk, 1954). Note all bulk samples contained <2% gravel and therefore for the purposes of these descriptions this has been ignored. Porosity in the upper layers of the sediment at the reference station was lowest (0.45) and elevated at the disposal stations, especially in the deeper sediment layers. Total organic carbon was lowest at the Reference station with higher total organic carbons (> 5 % m/m) at the two disposal stations. The sediment characteristics depth profiles (Figure 2) illustrate the differences between the reference and disposal stations. The reference station showed a gradual decrease in porosity and organic carbon with depth whilst the disposal stations exhibited complex porosity and carbon signatures down-core probably related to disposal events. The heterogeneous structure in vertical profiles illustrated the contrasting disposal events at the impacted stations at different depths and with differing % silt/clay, TOC and porosity signatures. Station C in particular exhibited a low % silt/clay level in the upper parts of the sediment. The pigment profiles are similar across the stations and illustrate the water column

source with similar degradation profiles with depth. The oxygen profiles and penetration depth were similar for all the stations, with diffusion-type profiles and with oxygen consumed within the upper 1cm of the sediment. Observations conducted on the SPI images using Fe^{3+} colour also showed that more reduced sediment conditions were found deepest at the reference station, and shallowest at the disposal stations (Figure 3). The SPI images also showed the occurrence of sulphide formation (black colouration) to be more intense and shallower in the disposal station sediments when compared to the reference station and this supports an assessment of increased reducing conditions at these sites.

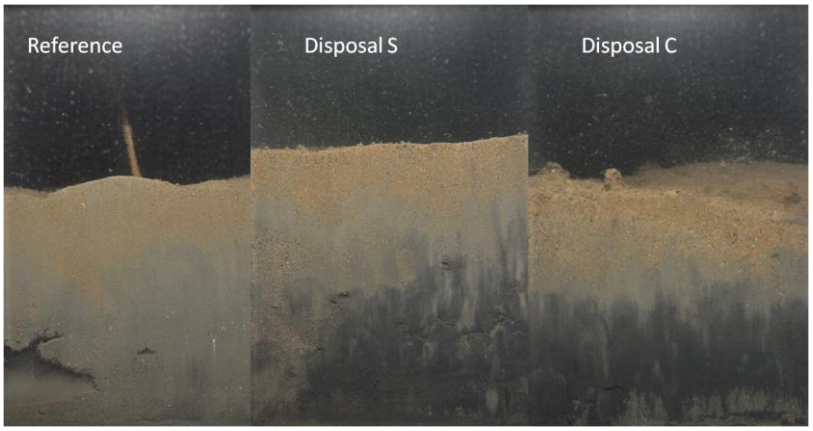

Figure 3: Example Sediment Profile Images (SPI) from the three stations at Souter Point (size of SPI optical window is 15 cm wide by 20 cm deep).

3.2 DGT fluxes and profiles

DGT metal fluxes were calculated for each of the deployed DGT probes at each station according to the method described in Davison and Zhang (1994) and the average flux profiles (±sd) were plotted for each metal at the 3 stations (Figure 4).

3.3 Metal sediment behaviour

Iron and Manganese: The DGT flux profiles showed high resolution information of iron (Fe) and manganese (Mn) remobilisation behaviours. Both metals are redox sensitive and are used as successive Terminal Electron Acceptors (TEAs) during the remineralisation of organic matter, Mn before Fe (Burdige, 2006). Their supply to the resin gel increased as they became reduced in the sediments (Fe^{3+} to Fe^{2+}, Mn^{4+} to Mn^{2+}). Consistent with this, Fe and Mn DGT flux profiles (Figure 4) showed the start of sub-surface remobilisation at about 1 – 2 cm and < 1 cm, respectively. Mn release occurred as oxygen was depleted within the upper centimetre of the sediment. Iron supply to the resin gel rapidly increased near the surface, but below the oxic zone. This close linkage between Fe and Mn behaviour and oxic/suboxic carbon remineralisation processes is usual in marine sediments (Burdige, 2006; Gao et al., 2009; Teal et al., 2009; 2013). Increasing DGT-iron fluxes near the sediment surface occurred at all

stations and there was continued supply to the resin gel at increasing depths. The rate of increase of iron supply with depth at the disposal stations was greater than at the reference station and is likely to be driven by the more reducing conditions found at these locations. Iron showed continued supply to depth whilst Mn showed a subsurface peak.

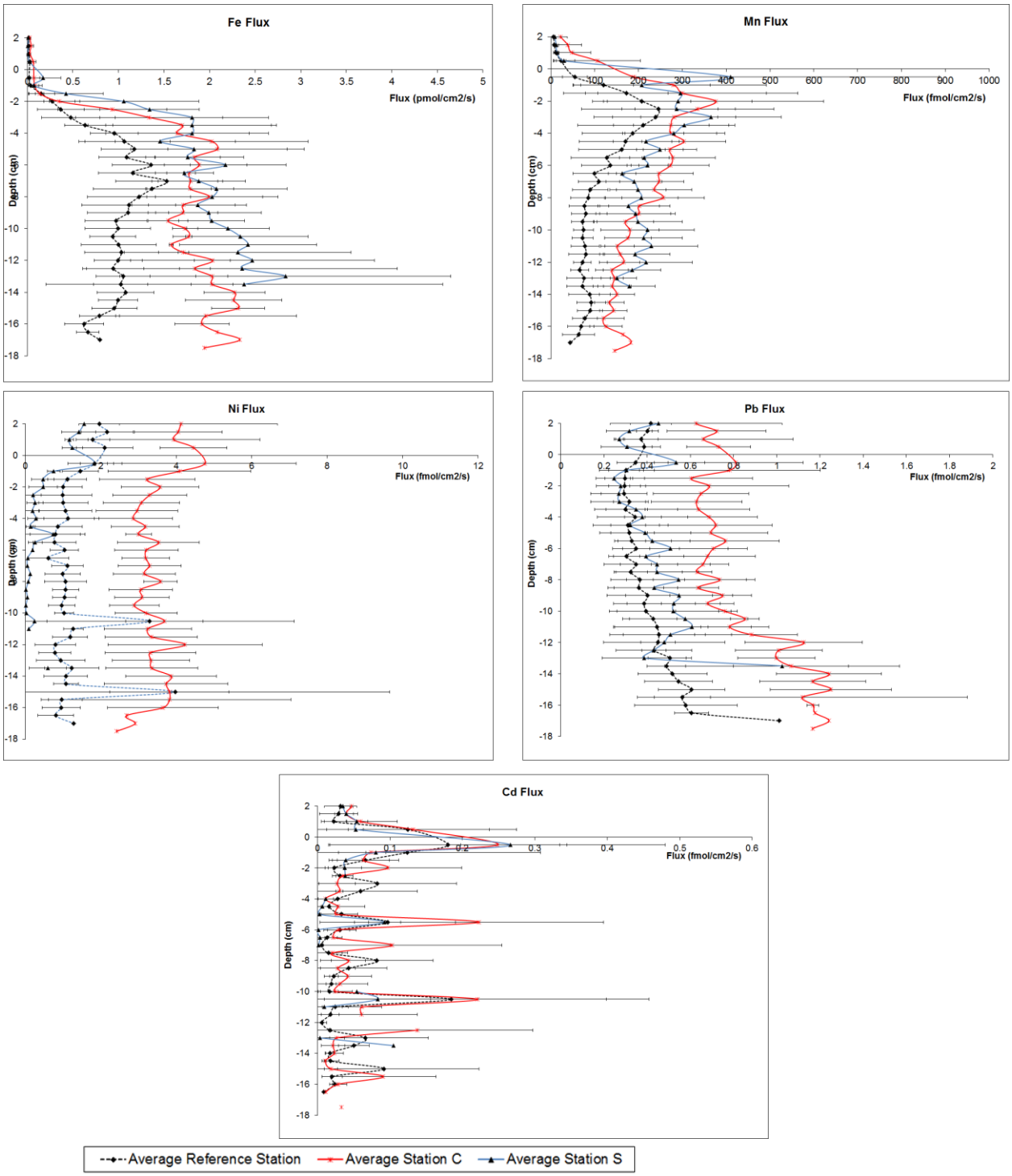

Figure 4: Vertical profiles of metal flux to the DGT probes at the three stations (reference, station C and station S) - Fe, Mn, Ni, Pb, Cd. Error bars are +/- 1 standard deviation, n=3

405 The peak in the Mn concentration in the subsurface layer is often observed in coastal systems (Gao et
406 al., 2009; Teal et al., 2013), however, the continued supply of iron to the resin gel with increasing depth,
407 found in this study, is in contrast to others which show an iron peak (Gao et al., 2006; Merritt and
408 Amirbahman; 2007). This continued supply at depth could be linked to very low sulphide
409 concentrations which allow reduced iron to be readily available for uptake by the DGT probes. The
410 supply rates for Fe and Mn to the resin gel from sediments at the disposal stations were higher than at
411 the reference station. This is consistent with the higher organic matter loads at the disposal sites and
412 thus the increased reducing conditions found there. This is also corroborated by the SPI images at the
413 disposal sites, which show more reducing conditions closer to the sediment surface. The Fe fluxes were
414 one order of magnitude higher than Mn fluxes. The profile shapes indicate a supply of dissolved Mn
415 across the Sediment – Water Interface (SWI) into the water column, but this was not observed for iron,
416 which is probably oxidised within the upper cm of the sediment where oxygen is present. The DGT flux
417 profiles indicate that the resupply to the resin gel is higher at the disposal sites, despite similar bulk Fe
418 and Mn levels across the sites.
419
420 **Cadmium:** All 3 stations showed a peak of DGT available cadmium at the SWI. Below the SWI, levels
421 of Cd supply were low at all stations, apart from distinct peaks of higher Cd supply at discrete depths
422 (0.1 to 0.2 fmol/cm^2/s). This release of Cd across the SWI and the maximum in the sediment surface
423 layer can be attributed to the mobilisation of metal from particles having recently been deposited on the
424 sediment surface, mainly through the rapid degradation of organic matter accumulated on the surface
425 of the sediment. This process can be related to break-down of deposited phytodetritus (Fones et al.,
426 2004; Sakellari et al., 2011) and can also be associated with other metals such as Cu and Zn. There was
427 no trend of Cd release with increasing depth at any of the stations. The low Cd particulate concentrations
428 and lack of difference in Cd supply between the reference and disposal stations would imply that Souter
429 Point stations were not a significant source of Cd release into the pore-water associated with dredged
430 material disposal, but that it is likely that the SWI Cd source was seasonal deposition and burial of
431 phytodetrital material.
432
433 **Lead:** Lead (Pb) profiles showed increasing flux to the resin gel with depth, with the flux rate increasing
434 at all stations in the deeper sediment layers. The fluxes at the reference station and at the disposal station
435 S were similar, whilst disposal station C showed the highest Pb fluxes (Figure 4).
436 The variability (relative SD) in Pb flux with depth was lower at the reference station and highest at the
437 disposal stations. This variance was similar to other metals, illustrating the heterogeneity in sediment
438 conditions and hence metal cycling introduced by dredged material disposal operations. The levels of
439 total Pb were highest at the disposal station C, but not directly proportionate to the much higher supply
440 rates observed. This discrepancy showed that mechanisms of metal release could be complex and
441 therefore cannot be determined from total sediment metal content alone. Indeed, studies have shown

that Pb could respond much more to concentrations of organic matter and Acid Volatile Sulphide (AVS) (Duran et al., 2012) rather than other sediment variables. Both disposal stations show a surface peak in Pb supply to the resin gel close to the SWI which means that these sites could be acting as sources of pore-water Pb to the water column. This is not the case at the reference station. It is possible that this release of Pb (a metal with a high partition co-efficient, K_d) within the upper layers of the sediment could be linked to Fe/Mn particulate reduction. In sub-oxic zones within estuarine sediments, Fe and Mn can act as master variables controlling the distribution and speciation of other trace elements (Forstner et al., 1986; Butler et al., 2005).

Nickel: All 3 stations showed an increase in nickel (Ni) supply to the DGT device in the upper few cm of the sediment, with consistent supply rates at depths greater than 5 cm. This increase is likely to be linked to the reduction of Fe and Mn oxyhydroxides and degradation of organic material as shown by the Fe/Mn flux and labile carbon (chlorophyll/phaeopigment) profiles. This behaviour has also been observed in other DGT studies (Tankere-Muller et al., 2007). The overall supply of Ni to the sediment pore-water throughout the profile at disposal station C was higher than at the other two stations. It is likely that the presence/absence of other complexing species (not sulphides) must be creating this between station heterogeneity of supply to the resin gel, given the consistent total Ni particulate pool.

Similar to the observed Pb behaviour, the release of Ni near the SWI can be a source of Ni to the water column. This was observed at both disposal stations, in contrast to the reference station. For Ni this could be driven by local release to pore-waters in the upper layers of the sediment (0 to 5 cm depth).

Sulphide: Metal availability and mobility can be closely linked to the amount of free sulphide ions in sediments, especially at depth (Gao et al., 2009). Deployment of AgI gel probes into the sediments cores revealed that free sulphide was at or below the limit of detection for the DGT based method evaluated through colour scanning. The sulphide detection limit for the AgI gels was 0.25 µmol/L for a 24 hour deployment which equates well to previous studies (Teasdale et al., 1999). This correlated well with the high concentrations of free Fe and Mn ions observed in the metal profiles, as any free sulphide would have reacted with the Fe and Mn to form insoluble iron/manganese-sulphide complexes.

3.4 Statistical analysis and comparison of the DGT profiles

Figure A.2 (Appendix 1) shows natural log depth profile plots for all five metals. For Cd, it is difficult to statistically distinguish the profiles between the stations. For the remaining four metals (Pb, Ni, Mn and Fe), we used the 95% envelope plots in Figure 5 to further explore differences between the sites.

For Mn and Fe we used the 1-lag autocorrelation models (equation (4)) for the residuals to create these envelopes (see Figure A.3, as an example, to see the autocorrelated residuals for Mn). Note that these

models did successfully remove the autocorrelation. For Pb and Ni we used the independence model in equation (3).

For Fe, the envelopes overlap throughout the profile and it is impossible to distinguish the stations from each other. In contrast, the Ni reference and station C profiles are consistently different, whereas the station S profile diverges from the other two with increasing depth. Stations S and C (the disposal stations) have similar profiles for Mn, but the reference station profile separates off slightly from the other two at depths below about 8cm. The reference and station C profiles are very different for Pb. However, the large amount of variation for station S makes it difficult to distinguish this station from the other two statistically.

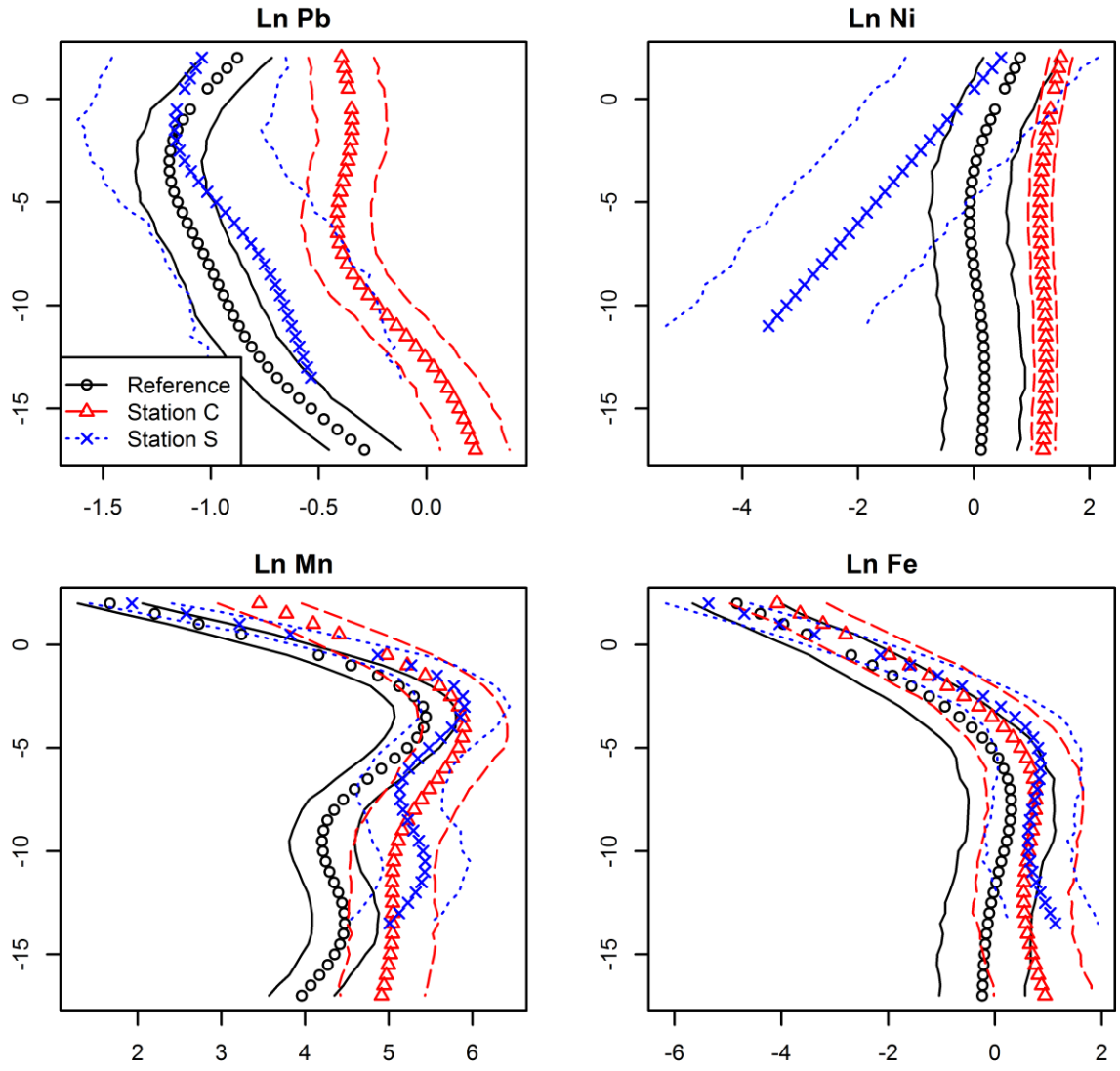

Figure 5: 95% confidence envelopes for the profiles of Ln metal flux to the passive sampler at each station for Pb, Ni, Mn and Fe

In summary, for Mn and Fe the reference station profile is statistically different from the other two stations, especially at depth, whereas it is difficult to distinguish between the profiles for the other

two disposal stations (S and C). For Pb, as previously seen, station C is distinctly different from the other two stations whereas there is only an obvious difference between profiles for site S and the reference station at mid depths. For Ni all three stations are different for almost the whole profile with the reference fluxes lying between lowest fluxes at station S and highest fluxes to the resin gel at site C. The only exception is near the surface, where station C and the reference station have similar profiles.

This analysis is designed to introduce some statistically defensible method to describe and test differences between DGT profiles in relation to different metals, sites and the impact of an activity such as dredge material disposal. This can be very useful for regulatory or licensing purposes in comparing spatial or temporal changes in metal behaviour. The work here illustrates that given the high variability within some sites it can be difficult to determine statistically the difference between disposal and reference stations for some metal fluxes. Greater replication (here n = 3 at each station) would improve the power of such a technique, helping to distinguish reference and impact changes in sediment conditions for improved disposal site monitoring (over different depth or spatial and temporal resolutions).

3.5: Summary of findings and discussion

Dredging and disposal are major activities for sustainable port development and expansion worldwide. The assessment of the effects of sediment metal contamination, associated with dredging and disposal, on biological assemblages and function remains a key question in marine management. However, the appropriate description of bioavailable metal concentrations within pore-waters has rarely been reported, as routinely only total metal concentrations are monitored. In the majority of targeted monitoring programmes, where cost-effectiveness and increasing complexity of regulatory questions is an ever increasing demand, there is an opportunity to incorporate novel approaches which can improve the information and understanding provided. For example, changing regulatory demands from understanding metal contamination levels towards biological effects/toxicity and impact assessment and human activity management. In this work we have attempted to test the use of DGT passive sampler as means of generating cost-effective (compared to conventional porewater sampling, total metal analysis at an equivalent resolution or specific bioavailability studies), targeted and novel information on metal release (sources and sinks) and behaviour within marine sediments.

Traditional monitoring of disposal sites within the UK provides the quantitative analysis of total metal within bulk sediments with limited depth resolution (see Appendix 1 Figure A.1). This is used to undertake assessments of metal risk posed from a total pool. Many papers have illustrated the lack of agreement between total metal concentrations and metal availability in the pore-waters and hence bioavailability and ecotoxicological risk (Di Toro 1992; Lee and Lee, 2005; U.S. EPA, 2005; Roullier et al., 2008). In comparison, the DGT technique applied in this study has provided higher resolution depth information on comparative fluxes of metals to the pore-water (primarily via dissolution and/or desorption of weakly bound metals from the solid phase), and hence potential bioavailability (via

529 various solute pathways). This type of information can describe areas of metal loss/remobilisation with
530 depth, contrast the release/resupply of metals between sites and can also illustrate the presence,
531 magnitude and direction of metal fluxes across the sediment-water interface. Table 2 summarises each
532 of these information types supplied by the DGT (namely, metal behaviours observed at the three sites
533 with respect to DGT, Sediment-Water Interface fluxes, and additional information supplied by DGT)
534 in comparison to the total metal enrichment information. The implications of these findings are
535 discussed further in subsequent sections.
536
537 Table 2. Summary metal behaviour at the 3 disposal site stations as derived by DGT profiles and
538 comparison to total bulk metal reservoir (SWI = sediment-water interface)
539

Metal	Enriched in disposal sediments	Depth profile shape and flux to DGT	Flux across SWI	Insight given by DGT profiles
Ni	No	Shallow sub-surface peak of Ni release at disposal sites only. Supply to resin gel consistent with depth across all sites. Flux to resin gel higher at station C.	Flux to water column at disposal sites, associated with a shallow sub-surface peak.	Supply of Ni to water column at disposal sites. Pore-water chemistry controls supply to resin gel at station C.
Cd	Yes	Shallow subsurface peak (<1cm) at all sites. Distinct peaks of remobilisation and flux to resin gel. Some LOQ issues. Not coupled to total sediment metal (bulk or profile).	Flux to the water column at all stations, associated with shallow sub-surface peak.	Release not linked to disposal source. Likely phytodetritus source but controls related to redox (Fe/Mn).
Pb	Yes	Increased supply to resin gel with depth. Flux to resin gel significantly higher at station C.	Flux to water column at disposal sites, associated with a shallow sub-surface peak (Pb release from Mn/Fe reduction.	Higher disposal total metal only released at station C. Other factors controlling DGT uptake (S^{2-} , DOC). Link to Mn or Fe particulate reduction ~ high Pd Kd
Fe	No	Increased Fe supply to resin gel below oxic layer (>1cm). Rate of increase and flux greater at disposal sites. Flux is maintained or increases with depth.	None – oxic layer prevents release.	Higher iron release at disposal sites – linked to increased reducing conditions at depth & elevated TOC. No SWI exchange limited by oxic layer
Mn	Yes	Increased resupply as oxygen saturation decreases.	Flux to the water column at all sites	Release governed by increasingly reducing

		Peak resupply in upper 4 cm and then decline to depth. Flux to the resin gel and depth/rate of increase with depth is higher at the disposal sites.	but higher at disposal sites.	conditions at disposal sites (fines and TOC).

Metal behaviour (release, availability, cycling) information provided by DGT:

Firstly, DGT provides high resolution information with depth DGT flux data inferred to be DGT-labile metal (dissolved metal present in the pore-water as well as "weakly" bound to the solid phase), its production within the sediment, release and behaviour, and associated site differences. Iron and manganese display behaviour consistent with increasingly reducing conditions at depth, i.e. increased release to the pore-water and availability to DGT. Two of the metals (Pb, Ni) illustrate subsurface DGT-labile (C_{DGT}) peaks (close to the SWI ~ <1cm) which can be a result of increased metal release from degradation of organic material and/or reduction of Fe and Mn oxyhydroxides associated with elevated TOC loading associated with disposal activity (i.e. only present or elevated at the disposal sites). Thus, these disposal sediments represent a source of metal to the overlying water column. Additionally, the overall increase of metal fluxes observed across the whole sediment profile for Ni and Pb in the disposal sites (especially in site C) could be evidence that the disposed sediment material may release larger amounts of DGT-labile (and hence bioavailable) metals in the pore water.

Although Cd exhibits similar peaks of DGT flux (DGT-labile metal), the magnitude and depth distributions of the DGT-Cd fluxes are similar across all sites, despite the elevated bulk total Cd levels reported at the disposal sites. It is therefore likely that this Cd supply to the pore-water is not related to disposal activities, but decomposition of Cd enriched phytodetritus, either at the surface, as supported by the SWI associated peaks (<1cm) or regular peaks of DGT-Cd flux with depth across all of the sites (reference and disposal) and consistent with frequent and regional bloom deposition and burial events. Metals such as Cu and Zn have also been shown to exhibit this behaviour (Lee and Morel, 1995; Wang and Dei, 2001).

Linking total metal pool (particulate) and pore-water behaviour:

DGT use also illustrates the lack of agreement between total metal pool determined during routine monitoring of the disposal activity and the metal concentrations/DGT-labile (C_{DGT}) found in pore-waters as highlighted by the DGT flux. There is clear contrast between the total metal particulate reservoir and the release for certain metals. The differences in both DGT profile shape and release of metals in relation to total sediment metal can be seen in Appendix 1, Figure A.1. This is observed in particular for Cd, which is enriched in bulk sediments at the disposal sites but whose source is likely to be linked to phytodetrital decomposition (Fones et al., 2004; Sakellari et al., 2011). Pb and Mn also show enrichment in disposed sediments, but elevated release into the pore-waters is only seen for Mn.

For other metals, the DGT data illustrates that release to the pore-waters is controlled by a combination of redox levels (Fe, Mn) and links to Fe/Mn particulate control on partitioning (Pb).

Concentrations of metals in the pore-water can also be controlled by other pore-water phases such as the presence of Dissolved Organic Carbon (DOC) or Acid Volatile Sulphides (AVS) (especially Pd, but not Ni) (Lee and Lee, 2005; Duran et al., 2012). It is this control of metal release by and from pore-water particulate compounds (solid phases / colloidal material) and associated within pore-water chemistry that will ultimately control the availability of metal to the resin gel as supplied from the particulate sediment pool (Chifroy et al., 2011). At these sites, free sulphide was below detection limits in the upper parts of the sediment. The controlling behaviour of S^{2-} species on metal pore-water supply is complex and could inhibit/restrict metal release fluxes to a DGT sampler depending on solubility and the prevailing redox or pH conditions (Ankley et al., 1991; Ankley, 1996a; Lee and Lee 2005; Teal et al., 2009; Duran et al., 2012). This control of pore-water chemistry on DGT-metal flux can be seen in the increased release of Pb and Ni to the DGT device at Station C despite no clear relation to drivers such as the total sediment metal pool. This change is also highlighted in the differing behaviour of Ni across all three stations despite an equivalent Ni total sediment pool at all sites.

The metal pore-water flux profiles determined in this study illustrate the comparative differences and balance between the metal release from the total particulate pool, pore-water metal chemistry and hence availability to a pore-water sampler such as DGT. The controls on this release are complex and relate to dynamic equilibrium interactions between the total metal particulate pool, the impact of reduction chemistry with depth, and the complexation of released metal ions by pore-water ligands such as sulphur species or organic matter (Chifroy et al., 2011). These chemical interactions within the pore-water will ultimately control metal availability to the DGT and hence metal release within or from the sediment. The understanding of these complex processes is still challenging though the status information provided by the DGT, as a description of labile/bioavailable metal is useful, even without a full understanding of the mechanistic drivers.

DGT, bioavailability, bioaccumulation and ecotoxicology:

DGT has often been described as a tool capable of describing the bioavailable fraction of metals in comparison to total metals (Simpson et al., 2007; Simpson et al., 2012; Amato et al., 2015; Ren et al., 2015). This study has illustrated the capacity for DGT to provide vertically resolved metal fluxes to a passive sampler, which could be used as a proxy for a bioavailable fraction. The potential disconnection between total metals and DGT-metal flux observed here has been observed in other studies (see Di Toro 1992; Roulier et al., 2008), although total metals in sediments were the best predictors of bioaccumulation in other studies (Roulier et al., 2008 and references there-in). Some studies have started investigating the links between metal phases (particulate totals, acid extractable, dissolved, DGT fractions) and biological response/load (Simpson et al., 2012). However, further development to demonstrate dose/response from DGT fractions and benthic organisms / effects and appropriate solid

phase – pore-water phase modelling would be beneficial. In particular, the complex controls on metal bioavailability created by the interactions within the pore-water chemistry inhibit a mechanistic understanding of the conditions that will promote metal release from a similar total metal pool. The best descriptors of bioavailable metal are still being discussed and evaluated under controlled experimental conditions. An enhanced understanding through combined pore-water metal observational and modelling approaches is needed to enable predictions or risk assessments of metal bioavailability and toxicity to be undertaken in the marine environment under contaminated conditions, including disposal sites.

The dynamics between metal supply (particles), metal release and complexation (pore-water) and uptake (bioavailability or bioaccumulation) is a complex one but can be linked to key variables (Dissolved Organic Carbon - DOC, Acid Volatile Sulphide - AVS) in future to further understand release mechanisms and controls. DGT defined fractions may have a role to play here in describing the potential availability and toxicity of a sediment in a similar way to Simultaneously Extractible Metal (SEM) : AVS information (Di Toro et al., 1990; 1992; US EPA , 2005; Simpson et al., 2007; Knox et al., 2012; Simpson et al., 2012). A rapid, depth and space integrated imaging technique such as SPI, which describes iron reduction or sulphide precipitation depths, further aids understanding.

The knowledge of the metal release dynamics provided by DGT enhances our ability to describe and explain different biological uptake or impacts observed in sediments of similar total metal concentrations and improves the understanding of the links between total metal, pore-water and biological effects. This description of metal concentration beyond a traditional total measurement is largely missing in local regulatory or regional scale impact or status assessments within the UK or Europe such as OSPAR Quality Status Reports (OSPAR QSR 2010) or ICES reports (ICES WGMS). And yet, improved understanding of the link between hazardous substances and biological responses in sediments is also required as management regulations increasingly require an ecosystem approach. For example, the European Union Marine Strategy Framework Directive (2008/58/EC) includes Descriptor 8, which considers the management of sediment contaminant concentrations "*at levels not giving rise to pollution effects*" and requires appropriate linkages of benthic system parameters and anthropogenic pressures to invoke a management response (Van Hoey et al., 2010; Borja et al., 2013).

Considerations for monitoring applications

A main driver of this study has been to assess the utility of a passive sampler such as DGT to provide better assessment of the risk posed of metal remobilisation from sediments and therefore to aid future sediment activity management. The case study has demonstrated the feasibility by which such relatively cost-effective, easy to use techniques can be built into a monitoring programme alongside the other measures already being sampled. Such a technique can be focused towards site specific contaminant or management (e.g. capping strategies) issues whilst more rapid techniques such as SPI can provide wider spatial context (Germano et al., 2011; Birchenough et al., 2013).

In combination with monitoring of total sediment metal, DGT is capable of illustrating areas of metal release, fluxes across the interface and the potential disconnection between total particulate metal pool and pore-water metal. This is especially useful in describing and quantifying a potential pressure or risk associated with metal contamination.

Critical within a regulatory framework are also methods to demonstrate and track changes related to an activity, in space/time. This is particularly important for disposal site licensing and monitoring. It is essential to be able to describe changes in metal levels or behaviour in an auditable and defensible way. The comparison of metal profiles between sites has usually occurred by visual comparisons and descriptions, and sometimes regression analysis with depth (Fones et al., 2004). However, this is not statistically robust or makes site comparison difficult, and with higher variances induced by natural sediment heterogeneity or disturbance it is essential to have a method that can detect metal differences within and between sites or changes over time. The statistical modelling of the DGT metal profiles in this study has demonstrated a methodology that allows statistical analysis and investigation of high resolution metal profiles. This approach can provide increased confidence in an assessment of the differences between sites, the site status or processes driving changes in metal levels and distributions and how disposal is affecting them. Despite the high variance, it provides increased ability to determine status/metal flux levels statistically and detect changes over depth, time or space. This is particularly important for detecting changes as a result of a management action or tracking changes after a management action has been implemented. The power of the technique could be improved with increased replication and further investigation of variability with space and time.

These insights into metal release (by coupling the DGT measurements and statistical investigation of the profiles) can provide supporting, targeted and complimentary evidence to risk assessments of metal impact at particular locations or for specific questions. The coupling technique is compatible with existing monitoring programmes as documented here. It could be directed towards a specific condition or question highlighted by routine monitoring or total metal assessments. It could also be used to refine total metal trigger levels through improved understanding of the relationship between total metal and pore-water concentrations and resupply (flux). The depth information can also be used to make assessments of metal release risk to the water column under physical disturbances (storms, trawling). Further work would be needed though to give a greater overview of spatial and temporal variability in metal behaviour in relation to total sediment metal levels related to disposal activities and other controlling factors within the sediment matrix, which will dictate metal availability within the pore-water. Combined with rapid spatial techniques such as SPI it might be possible to investigate the disposal site signature and associated changes in metal availability and risk of release under contrasting environmental conditions.

4.0 Conclusions

The application of high resolution DGT passive samplers to the three sites in this study has improved our understanding of specific metal remobilisation behaviour, contrasting release features between metals, sites and with depth. It has also demonstrated that total particulate metal and DGT-metal flux are not always in agreement, indeed, elevated total particulate metal concentrations do not necessarily lead to high metal release into the sediment pore-waters. This initial application of DGT passive sampler technology, alongside sediment bulk metal analysis, to evaluate metal behaviour at the Souter Point disposal site has highlighted the complex relationship between contaminant disposal load from particulates and metal availability to the pore-water. Furthermore, it has underlined the metal heterogeneity found in the sediments at this disposal site, both between stations and with depth.

While bulk sediment analysis for metals gives important information about the quantity of metals present, i.e. the size of the benthic reservoir, and is indicative of the potential hazard, it does not give information about the availability of these metals to the various components of the ecosystem and thus the actual risk posed – either to the benthic community or by flux into the overlying water column and so into the pelagic system. This is where complementary methodology such as DGT enables additional insights. The clear differences in metal flux profiles recorded at different stations, which do not strictly correlate with total metal concentrations in the corresponding slices, illustrate that environmental parameters are influential in regulating fluxes and, by implication, availability of metals. Statistical modelling approaches, as documented here, could be developed in future to describe and track changes in metal behaviour and release across areas and also mechanistically with other metal (metal:metal couples) or environmental controls.

In summary, the use of depth resolving passive samples such as DGT is compatible with routine monitoring of disposal sites and can provide valuable additional information. Further work to improve understanding of the controlling factors of metal release to pore-waters, and the likely exposure routes of biota (linked to faunal traits such as feeding modes or sediment location) within the receiving ecosystem as well as corresponding ecotoxicological implications would be beneficial to inform management decisions. Such an increased understanding would not only enable more robust assessments of risks posed by disposal of sediments with high contaminant loads, but could also be used when assessing likely impacts arising from natural events, such as storms, and human activities, such as fishing and changes in controlling parameters under predicted future climate scenarios.

Acknowledgements:

This work was supported by Defra and MMO (contract E5403). The views expressed are those of the authors and do not reflect the policies of the funding departments. We gratefully acknowledge the valuable contributions made by the scientific staff and crew of the RV Cefas Endeavour. We also thank

Robin Law and three anonymous reviewers for comments to really improve the manuscript and insights our data provided.

References:

Amato, E.D., Simpson, S.L., Jarolimek, C.V., Jolley, D.F. Diffusive Gradients in Thin Films Technique Provide Robust Prediction of Metal Bioavailability and Toxicity in Estuarine Sediments. Environ. Sci. Technol., 2014; 48 (24), 4485–4494.

Amato, E.D., Simpson, S.L., Belzunce-Segarra, M.J., Jarolimek, C.V., Jolley, D.F. Metal Fluxes from Porewaters and Labile Sediment Phases for Predicting Metal Exposure and Bioaccumulation in Benthic Invertebrates. Environ. Sci. Technol., 2015; 49, 14204–14212.

Ankley, G.T., Phipps, G.L., Leonard, E.N., Kosian, P.A., Cotter, A.M., Dierkes, J.R. Acid-volatile sulfide as a factor mediating cadmium and nickel bioavailability in contaminated sediments. Environ Toxicol Chem 1991; 10:1299– 307.

Ankley, G.T. Evaluation of metal/acid-volatile sulfide relationship in the prediction of metal bioaccumulation by benthic macroinvertebrates. Environ Toxicol Chem 1996a; 15:2138– 46.

Ankley, G.T., Di Toro, D.M., Hansen, D.J., Berry, W.J. Technical basis and proposal for deriving sediment quality criteria for metals. Environ Toxicol Chem 1996b; 15:2056– 66.

Birchenough, A., Bolam, S.G., Bowles, G.M., Hawkins, B. Whomersley, P., Weiss, L. Monitoring of dredged material disposal sites at sea and how it links to licensing decisions. Proceedings from PIANC MMX, Liverpool, May 2010.

Birchenough, S.N.R, Boyd, S.E., Coggan, R.A., Limpenny, D.S., Meadows, W.J., Rees, H.L. Lights, camera and acoustics: Assessing macrobenthic communities at a dredged material disposal site off the North East coast of the UK. Journal of Marine Systems 2006; 62 (3): 204-216.

Birchenough, S.N.R., Blake, S.J., Rees, J., Murray, L.A., Mason, C.E., Rees, H.L., Vivian, C., Limpenny, D.S. Contaminated dredged material: monitoring results from the first capping trial in the U.K. In: 4th International Conference: Proceedings of the Port Development and Coastal Environment. 25–28 September 2007, Varna Bulgaria.

753 Birchenough, S.N.R., Bolam, S.G., Parker, E.R. SPI-ing on the seafloor: characterising benthic systems
754 with traditional and in situ observations. Biogeochemistry 2013; 113 (1-3): 105-11
755
756 Bolam, S.G., Rees, H.L., Somerfield, P., Smith, R., Clarke, K.R., Warwick, R.M., Atkins, M.,
757 Garnacho, E. Ecological consequences of dredged material disposal in the marine environment: a
758 holistic assessment of activities around the England and Wales coastline. Marine Pollution Bulletin
759 2010a; 52: 415-426.
760
761 Bolam, S.G., Mason, C., Bolam, T., Whomersley, P., Birchenough, S.N.R, Curtis, M., Birchenough,
762 A., Rumney, H., Barber, J., Rance, J., McIlwaine, P., Law, R.J., Dredged material disposal site
763 monitoring around the coast of England: results of sampling. SLAB5 Project Report, Cefas, UK. 2010b.
764
765 Borja, A., Elliott, M., Marine monitoring during an economic crisis: the cure is worse than the disease.
766 Mar. Pollut. Bull. 2013; 68: 1–3.
767
768 Bufflap, S. E., Allen, H. E. Sediment pore water collection methods for trace metal analysis: A review.
769 Wat. Res. 1995; 1: 165-177
770
771 Bull, D.C., Williamson, R.B. Prediction of principal metal-binding solid phases in estuarine sediments
772 from colour image analysis. Environ. Sci.Technol. 2001; 35:1658-1662.
773
774 Burdige, D.J. Geochemistry of marine sediments. Princeton University Press. 2006.
775
776 Butler, E., Leeming, R., Watson, R., Armand, S., Green, M., Final Report on Sediment Resuspension
777 Experiment for Derwent CCI Project. CSIRO Marine Research, Hobart, Tasmania, Australia.
778 http://www.derwentestuary.org.au/file. 2005.
779
780 Calmano, W., Hong, J., Forstner, U. Binding and mobilisation of heavy metals in contaminated
781 sediments affected by pH and redox potential. Water Sci Technol 1993; 28: 223–35.
782
783 Chapman, P.M., Wang, F., Janssen, C., Persoone, G., Allen, H.E. Ecotoxicology of metals in aquatic
784 sediments: binding and release, bioavailability, risk assessment, and remediation.
785 Can J Fish Aquat Sci 1998; 55: 2221–43.
786
787 Ciffroy, P., Nia, Y., Garnier, J.M. Probabilistic Multicompartmental Model for Interpreting DGT
788 Kinetics in Sediments. Environ Sci Technol 2011; 45: 9558–9565.
789

790 Dahlqvist, R., Zhang, H., Ingri, J. and Davison, W. Performance of the diffusive gradients in thin films
791 technique for measuring Ca and Mg in freshwater. Anal Chim Acta 2002; 460(2): 247-256.
792
793 Davison, W., Zhang, H. In situ speciation measurements of trace components in natural waters using
794 thin-film gels. Nature 1994; 367: 546–8.
795
796 Davison, W., Fones, G. R. & Grime, G. W. Dissolved metals in surface sediment and a microbial mat
797 at 100-mu m resolution. Nature 1997; 387, 885-888.
798
799 Davison, W., Zhang, H. Progress in understanding the use of diffusive gradients in thin films (DGT) –
800 back to basics. Environ. Chem. 2012; 9: 1–13.
801
802 Davison, W., Fones, G.R., Harper, M., Teasdale, P., Zhang, H. Dialysis, DET and DGT: in situ
803 diffusional techniques for studying water, sediments and soils. In: Buffle, J., Horvai, G. (Eds.), In-Situ
804 Monitoring of Aquatic Systems: Chemical Analysis and Speciation. IUPAC. Wiley, New York, 2000;
805 495–569.
806
807 Davison, W., Zhang, H., Warnken, K.W. Theory and applications of DGT measurements in soils and
808 sediments. In: Greenwood, R., Mills, G., Vrana, B. (Eds.), Comprehensive Analytical Chemistry.
809 Passive Sampling Techniques in Environmental Monitoring, Elsevier, 2007; 48: 353–378.
810
811 Di Toro, D.M., Mahony, J.D., Hansen, D.J., Scott, K.J., Hicks, M.B., Mayer, S.M., Redmond, M.S.
812 Toxicity of cadmium in sediments: the role of acid volatile sulfide. Environ Toxicol Chem 1990;
813 9:1489– 504.
814
815 Di Toro, D.M., Mahony, J.D., Hansen, D.J., Scott, K.J., Carlson, A.R., Ankley, G.T. Acid volatile
816 sulfide predicts the acute toxicity ofcadmium and nickel in sediments. Environ. Sci. Technol. 1992; 26:
817 96–101.
818
819 Duran, I., Sanchez-Marin, P., Beiras, R. Dependence of Cu, Pb and Zn remobilization on
820 physicochemical properties of marine sediments. Mar Environ Res 2012; 77: 43-49.
821
822 Directive 2008/56/EC of the European Parliament and of the Council of 17 June 2008 establishing a
823 framework for community action in the field of marine environmental policy (Marine Strategy
824 Framework Directive).
825

826 Eggleton, J., Thomas, K.V. A review of factors affecting the release and bioavailability of contaminants
827 during sediment disturbance events. Environ Int 2004; 30: 973–980.
828
829 Folk, R.L., 1954. The distinction between grain size and mineral composition in sedimentary rock
830 nomenclature. Journal of Geology 62 (4), 344-359
831
832 Fones, G.R., Davison, W., Holby, O., Jorgensen, B.B. and Thamdrup, B. High-resolution metal
833 gradients measured by in situ DGT/DET deployment in Black Sea sediments using an autonomous
834 benthic lander. Limnol Oceanogr 2001; 46(4): 982-988.
835
836 Fones, G.R, Davison W., Hamilton-Taylor, J. The fine-scale remobilization of metals in the surface
837 sediment of the North-East Atlantic. Cont Shelf Res 2004; 24: 1485–1504
838
839 Forstner, U., Wittman, G.T.W. Metal pollution in the aquatic environment. Berlin:
840 Springer-Verlag; 1981.
841
842 Forstner, U., Ahlf, W., Calmano, W., Kersten, M., Salomons, W. Mobility of heavy metals in dredged
843 harbour sediments. In: Sly PG, editor. Sediments and Water Interactions.
844 New York: Springer-Verlag. 1986; 371–80.
845
846 Gao, Y., Leermakers, M., Gabelle, C., Divis, P., Billon, G., Ouddane, B., High resolution profiles of
847 trace metals in the pore waters of riverine sediment assessed by DET and DGT. Sci Total Environ 2006;
848 362: 266-277.
849
850 Gao, Y., Lesven, L., Gillan, D., Sabbe, K., Billon, G., De Galan, S., Elskens, M., Baeyens, W.,
851 Leermakers, M. Geochemical behaviour of trace elements in sub-tidal marine sediments of the Belgian
852 coast. Mar Chem 2009; 117: 88-96.
853
854 Germano JD, Rhoads DC, Valente RM, Carey DA, Solan M. The use of sediment profile imaging (SPI)
855 for environmental impact assessment and monitoring studies: lessons learned from the past four
856 decades. Oceanogr Mar Biol 2011; 49:235–298
857
858 Harper, M.P., Davison, W., Zhang, H. and Tych, W. Kinetics of metal exchange between solids and
859 solutions in sediments and soils interpreted from DGT measured fluxes. Geochim Cosmochim Ac 1998;
860 62(16): 2757-2770.
861

Harper, M.P., Davison, W. and Tych, W. Estimation of pore water concentrations from DGT profiles: A modelling approach. Aquat Geochem 1999; 5(4): 337-355.

ICES Reports from WGMS, accessed on 22nd April 2016, URL: http://www.ices.dk/community/groups/Pages/WGMS.aspx

Knox, A., Paller, M., Roberts, J. Active Capping Technology—New Approaches for *In Situ* Remediation of Contaminated Sediments. Remediation 2012; DOI: 10.1002/rem.21313.

Knox, A. S., Paller, M. H., Milliken, C. E., Redder, T. M., Woolfe, J. R., Seaman, J. Environmental impact of ongoing sources of metal contamination on remediated sediments. Sci Total Environ 2016; 563-564: 108-117.

Lee, J., Morel, F.M. Replacement of zinc by cadmium in marine phytoplankton. Mar Ecol Prog Ser 1995; 127: 305-309.

Lee, J.-S., Lee, J.-H. Influence of acid volatile sulfides and simultaneously extracted metals on the bioavailability and toxicity of a mixture of sediment-associated Cd, Ni, and Zn to polychaetes Neanthes arenaceodentata. Sci Total Environ 2005; 338: 229– 241

Lyle, M. The brown-green colour transition in marine sediments: A marker of the Fe(III)–Fe(II) redox boundary, Limnol. Oceanogr 1983; 28, 1026–1033.

Manly, F. J. Randomization, Bootstrap and Monte Carlo Methods in Biology: 2nd edition. Chapman and Hall, London. 2008

Mason, C. NMBAQC's Best Practice Guidance. Particle Size Analysis (PSA) for Supporting Biological Analysis. National Marine Biological AQC Coordinating Committee, 72pp, Dec. 2011.

Merritt, K.A., Amirbahman, A. Mercury dynamics in sulfide-rich sediments: Geochemical influence on contaminant mobilization within the Penobscot River estuary, Maine, USA Geochim Cosmochim Acta. 2007; 71: 929–941.

MEMG Group Co-ordinating Sea Disposal Monitoring. Final Report of the Dredging and Dredged Material Disposal Monitoring Task Team. Science Series Aquatic Environmental Monitoring Reports, CEFAS, Lowestoft, (55): 52pp. 2003

899 Oporto, C., Smolders, E., Degryse, F., Verheyen, L. and Vandecasteele, C. DGT-measured fluxes
900 explain the chloride-enhanced cadmium uptake by plants at low but not at high Cd supply. Plant Soil
901 2009; 318(1-2): 127-135.
902
903 OSPAR. Quality Status Report (QSR) 2010. OSPAR Commission, London, 2010: 176 pp.
904
905 Panther, J.G., Bennett, W.W., Welsh, D.T. and Teasdale, P.R. Simultaneous Measurement of Trace
906 Metal and Oxyanion Concentrations in Water using Diffusive Gradients in Thin Films with a Chelex-
907 Metsorb Mixed Binding Layer. Anal Chem 2014; 86(1): 427-434.
908
909 Peijnenburg, W. J. G. M., Teasdale, P. R., Reible, D., Mondon, J., Bennett, W. W., Campbell, P. G. C.
910 Passive sampling methods for contaminated sediments: State of the science for metals. Integrated
911 Environmental Assessment and Management. 2014; 10(2): 179–196.
912
913 R Development Core Team. R: a language and environment for statistical computing. R Foundation
914 for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0, http://www.R-project.org. 2010
915
916 Rabouille, C., Denis, L., Dedieu, K., Stora, G., Lansard, B., Grenz, C. Oxygen demand in coastal marine
917 sediments: comparing in situ microelectrodes and laboratory core incubations J Exper Mar Biol Ecol
918 2001; 285/286: 49–69.
919
920 Rees, H.L., Pendle, M.A., Limpenny, D.S., Mason, C.E., Boyd, S.E., Birchenough, S., Vivian,
921 C.M.G. Benthic responses to sewage-sludge disposal and climate events in the Western North Sea. J.
922 Mar. Biol. Assoc. UK. 2006; 86: 1–18.
923
924 Ren, J., Williams, P.N., Luo, J., Ma, H., Wang, X. Sediment metal bioavailability in Lake Taihu, China:
925 evaluation of sequential extraction, DGT, and PBET techniques. Environmental Science and Pollution
926 Research. 2015; 22 (17), 12919-12928.
927
928 Rhoads, D.C., Germano, J.D. Characterization of organism-sediment relations using sediment profile
929 imaging: an efficient method of remote ecological monitoring of the seafloor. Mar Ecol Prog Ser 1982;
930 8:115-128
931
932 Roulier, J.L., Tusseau-Vuillemin, M.H., Coquery, M., Geffard, O., Garric, J. Measurement of dynamic
933 mobilization of trace metals in sediments using DGT and comparison with bioaccumulation in
934 Chironomus riparius: First results of an experimental study. Chemosphere 2008; 70: 925–932.
935

936 Rowlatt, S.M., Rees, H.L., Limpenny, D.S. & Allen, J. Sediment quality of the north-east coast of
937 England. International Council for the Exploration of the Sea (CM Papers and
938 Reports) 1989; CM1989/E:16, 21pp.
939
940 Rowlatt, S.M., Ridgeway, I.M. Final reports of the metals task team and the organics task team. Science
941 Series, Aquatic Environment Monitoring Report, Cefas, Lowesoft, 1997; No. 49,
942 51 pp.
943
944 Sakellari, A., Plavsi, M., Karavoltsos, S., Dassenakis, M., Scoullos, M. Assessment of copper,
945 cadmium and zinc remobilization in Mediterranean marine coastal sediments. Estuar Coast Shelf Sci
946 2011; 91: 1-12.
947
948 Sapp, M., Parker, E.R., Teal, L.R., Schratzberger, M. Advancing the understanding of biogeography-
949 diversity relationships of benthic microorganisms in the North Sea. FEMS Microbiol Ecol 2010; 74:
950 410-429.
951
952 Scally, S., Davison, W., Zhang, H. Diffusion coefficients of metals and metal complexes in hydrogels
953 used in diffusive gradients in thin films, Anal. Chim. Acta 2006; 558: 222-229.
954
955 Schintu, M., Marras, B., Durante, L., Meloni, P. and Contu, A. Macroalgae and DGT as indicators of
956 available trace metals in marine coastal waters near a lead-zinc smelter. Environ Monit Assess 2010;
957 167(1-4): 653-661.
958
959 Shiva, A.H., Teasdale, P.R., Bennett, W.W. and Welsh, D.T. A systematic determination of diffusion
960 coefficients of trace elements in open and restricted diffusive layers used by the diffusive gradients in
961 a thin film technique. Anal Chim Acta 2015; 888: 146-154.
962
963 Shiva, A.H., Bennett, W.W., Welsh, D.T. and Teasdale, P.R., 2016. In situ evaluation of DGT
964 techniques for measurement of trace metals in estuarine waters: a comparison of four binding layers
965 with open and restricted diffusive layers. Environ Sci Proc Imp 2016; 18(1): 51-63.
966
967 Simpson, S. L., Batley, G. E. Predicting metal toxicity in sediments: A critique of current approaches.
968 Integr. Environ. Assess. Manage. 2007; 3, 18−31.
969
970 Simpson, S. L., Yverneau, H., Cremazy, A., Jarolimek, C. V., Price, H., Jolley, D. F. DGT-induced
971 copper flux predicts bioaccumulation and toxicity to bivalves in sediments with varying properties.
972 Environm Sci Technol 2012; 46 (16): 9038-9046.

973 Stockdale, A., Davison, W., Hao, Z. Micro-scale biogeochemical heterogeneity in sediments: A review
974 of available technology and observed evidence. Earth-Sci Rev 2009; 92: 81-97.
975
976 Tankere-Muller, S., Zhang, H. Fine scale remobilisation of Fe, Mn, Co, Ni, Cu and Cd in contaminated
977 marine sediment. Mar Chem 2007; 106 (1-2): 192-207.
978
979 Teal, L. R., Parker, R., Fones, G., Solan, S. Simultaneous determination of in situ vertical transitions of
980 color, pore-water metals, and visualisation of infaunal activity in marine sediments. Limol Oceanol
981 2009; 54 (5): 1801-1810.

982 Teal, L.R., Parker, E.R., Solan, M. Sediment mixed layer as a proxy for benthic ecosystem process and
983 function Mar. Ecol. Prog. Ser 2010; 298: 79–94.
984
985 Teal, L.R., Parker, E.R.; Solan, M. Coupling bioturbation activity to metal (Fe and Mn) profiles in situ.
986 Biogeosciences 2013; 10: 2365 – 2378.
987
988 Teasdale, P.R., Hayward, S., Davison, W. In situ, high-resolution measurement of dissolved sulfide
989 using diffusive gradients in thin films with computer-imaging densitometry. Anal Chem 1999; 71:
990 2186–2191.
991
992 Turner, G. S. C., Mills, G. A., Teasdale, P. R., Burnett, J. L., Amos, S. & Fones, G. R. Evaluation of
993 DGT techniques for measuring inorganic uranium species in natural waters: Interferences, deployment
994 time and speciation. Anal Chim Acta 2012; 739: 37-46.
995
996 Turner, G. S. C., Mills, G. A., Bowes, M. J., Burnett, J. L., Amos, S. & Fones, G. R. Evaluation of DGT
997 as a long-term water quality monitoring tool in natural waters; uranium as a case study. Environ Sci
998 Proc Imp 2014; 16(3): 393-403.
999
1000 U.S. EPA. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks
1001 (ESBs) for the Protection of Benthic Organisms: Metal Mixtures (Cadmium, Copper, Lead,
1002 Nickel, Silver and Zinc). EPA-600-R-02-011. Office of Research and Development. Washington,
1003 DC 20460 2005.
1004
1005 Van Hoey, G., Borja, A., Birchenough, S., Buhl-Mortensen, L., Degraer, S., Fleischer, D., Kerckhof,
1006 F., Magni, P., Muxika, I., Reiss, H., Schroder, A. & Zettler, M. L. The use of benthic indicators in
1007 Europe: From the Water Framework Directive to the Marine Strategy Framework Directive. Mar Poll
1008 Bull 2010; 60, 2187-2196.

Verardo, D.J., Froelich, P.N., McIntyre, A. Determination of organic carbon and nitrogen in marine sediments using the Carlo Erba NA-1500 analyzer. Deep-Sea Res 1990; 37: 157–165.

Wang, W.-X., Dei, R.C. Metal uptake in a coastal diatom influenced by major nutrients (N, P and Si) Wat Res 2001; 35 (1): 315-321.

Wood, S.N. Generalized Additive Models: An Introduction with R. Chapman and Hall/CRC, London. 2006.

Zhang, H., Davison, W., Miller, S. and Tych, W. In-situ high-resolution measurements of fluxes of Ni, Cu, Fe, and Mn and concentrations of Zn and Cd in porewaters by DGT. Geochim Cosmochim Ac 1995; 59(20): 4181-4192.

Zhang, H. and Davison, W. Diffusional characteristics of hydrogels used in DGT and DET techniques. Anal Chim Ac 1999; 398(2-3): 329-340.

Zhang, H. and Davison, W. Direct in situ measurements of labile inorganic and organically bound metal species in synthetic solutions and natural waters using diffusive gradients in thin films. Anal Chem 2000; 72(18): 4447-4457.