Diagenetic Cycling of Trace Elements in the Bottom Sediments of the Swan River Estuary, Western Australia

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ABSTRACT

Teflon strips were used *in-situ* in the bottom sediments at two sites in the Swan River Estuary to collect diagenetic Fe-Mn oxyhydroxides and monitor monthly changes in their morphology and trace element geochemistry. This study demonstrates that substantial concentrations of trace elements are trapped at the redox front during the accumulation of diagenetic Fe-Mn oxyhydroxides. It is likely that the Fe-Mn oxyhydroxides initially nucleate and grow on the Teflon strips via bacterial activity. Variation in trace element geochemistry of the diagenetic Fe-Mn oxyhydroxides is influenced by changes in the supply of trace elements from either the bottom sediments and/or water column or changes in the physico-chemical status of bottom and porewaters. If sufficient diagenetic Fe-Mn oxyhydroxides are preserved in the upper layer(s) of the bottom sediment it is possible that diagenetic (secondary) trace element enrichment profiles may be produced which modify the historical input of natural or anthropogenic trace element sources. Alternatively, partial or complete dissolution of the diagenetic Fe-Mn oxyhydroxides in response to temporal changes in the redox status of the bottom sediment may lead to a significant underestimate of trace element fluxes in historical bottom sediment profiles. This study highlights that considerable care must be taken when interpreting short- to long-term geochemical profiles in bottom sediments due to the possible occurrence of rapid, seasonally mediated diagenetic processes.
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1. Introduction

Diagenetic Fe-Mn oxyhydroxides formed in the (Fe-Mn) redox front play a pivotal role in the regulation of trace element concentration, speciation and vertical distribution in bottom sediments. Precipitation of diagenetic Fe-Mn oxyhydroxides may occur via a multitude of often contemporaneous scavenging, dissolution and/or coprecipitation mechanisms (e.g. Belzile et al., 1989, Belzile and Tessier, 1990, Buckley, 1989, De Vitre, 1991, Hamilton-Taylor et al., 1996, Lion et al., 1982). The presence of diagenetically formed Fe-Mn oxyhydroxides within bottom sediments, are particularly important in that they may constitute a significant proportion of total Fe and Mn, with maximum concentrations often at or near the sediment-water interface (e.g. Fortin et al., 1993).

The region near the sediment-water interface and the redox front are often coincident and are usually the site of dynamic variations in physical (e.g. porewater flux) and geochemical (e.g. bulk sediment geochemistry) gradients and biological activity. Thus, existing or newly forming diagenetic Fe-Mn oxyhydroxides occurring at the redox front may be influential in regulating the flux of trace elements into the overlying water column (e.g. Petersen et al., 1995).

Variation in physico-chemical conditions in bottom sediments and water column which lead to the vertical migration of a redox front are significant in estuaries. This variation may be caused by the opposing influences of tides and riverine flow which may exert a major short-(hours to days) to medium- term (seasonal) influence on geochemical reactivity (e.g. Morris et al., 1982a, b). These influences on bottom sediment chemistry may include coagulation of suspended material and hence deposition/incorporation into bottom sediment, sediment resuspension and changes in the direction and intensity of porewater flow and chemistry. Thus, elucidation of the mechanisms and magnitude of cycling of trace elements in the redox front in bottom sediments is important in determining changes in speciation, bioavailability and long-term fate.

Collection and analysis of diagenetic (newly-forming) Fe-Mn oxyhydroxides using Teflon strips as an integration method (i.e. over the period they remain in-situ in the bottom sediment) to record periodic changes in redox front geochemistry in aquatic environments was pioneered by Belzile et al., (1989). The use of Teflon strips to record changes in redox front geochemistry both contrasts with and compliments porewater extraction from sediment cores (e.g. Luther et al., 1996), the use of sediment porewater 'peepers' (Carignan et al., 1994, Couillard et al., 1993, Tessier et al., 1993) and recent techniques for measuring diffusive equilibrium or gradients in thin films (DET - Davison et al., 1991, Davison and Zhang, 1994, DGT - Zhang et al., 1995).
This study has used the Teflon strip method to examine monthly changes in the spatial distribution, morphology and geochemistry of newly forming diagenetic Fe-Mn oxyhydroxides associated with the redox front in bottom sediments at two sites in the Swan River Estuary. This is the first known application of the Teflon strip method in an estuarine environment and is part of a larger research program examining aspects of water quality and sediment geochemistry in the Swan River Estuary, Western Australia.
2. Sample sites and rationale for selection

Two sample sites in the Swan River Estuary of significantly different bathymetry, flushing characteristics and physico-chemical conditions were chosen for this study to highlight any differences in redox front geochemistry (Figure 1). The seasonal propagation of the salt wedge in the Swan River Estuary in spring/summer and its flushing in autumn/winter from both of the study sites leads to large variations in density (salinity) stratification. In other estuaries these variations have been demonstrated to induce large physical and chemical changes in the water column (e.g. Doering et al., 1994), bottom sediment chemistry (Ackroyd et al., 1987, Maher and De Vries, 1994) and in shallow groundwater regimes adjacent to rivers and wetlands (e.g. Smetacek et al., 1976). Indeed, research in the Swan River Estuary in the vicinity of the sample sites selected for this study have revealed large and dynamic changes on an hourly, daily and seasonal basis in shallow groundwater and porewater flow and chemistry (Campbell, 1996).

It was hypothesised that the seasonal propagation of the salt wedge may influence the morphology and geochemistry of diagenetically-formed Fe-Mn oxyhydroxides in the bottom sediments. The deep sample site (Ron Courtney Island-RCI, ca. 5-6 m) contains oxygen depleted (<2 mg/L), saline water for significant periods and is typical of isolated depressions that punctuate the relatively shallow upper Swan River Estuary. These deep sites are important as, under certain hydrological conditions the water column may become stratified for extended periods. Stratification may facilitate sustained low oxygen conditions and initiate anoxic geochemical and microbial processes. Conversely, the shallow (Tonkin Overpass-TO/P, ca. 2-3 m) sample site is typical of more extensive, relatively shallow sections of the Swan River Estuary which experience more extensive tidal or riverine flushing throughout the year (Douglas et al., 1996).
3. Methodology

3.1. Teflon strips

Strips of acid-washed Teflon (700 mm L x 1mm H x 100 mm W) were attached to a rigid backing plate of acid-washed high density polyethylene (HDPE) of similar dimensions using acid-washed nylon nuts and bolts. One end of the Teflon strip and HDPE backing plate assembly were cut to a sharp point (ca. 45°) to facilitate insertion of the strip into the bottom sediments. Two or three Teflon strip assemblies were deployed within a metre of each other into sediment to a depth of approximately 300 - 500 mm at each sample site using SCUBA divers for a period of 28-31 days. Nylon cord was used to join each Teflon strip assembly to a marker post on shore to expedite recovery. After recovery, the Teflon strips were separated from the HDPE backing plate, returned to the laboratory and allowed to air dry. The accreted Fe-Mn oxyhydroxides were removed from the Teflon strip by scraping with a pipette with an acid-washed polyethylene pipette tip. Dislodged Fe-Mn oxyhydroxide particles were recovered with the pipette using 0.5-1mL aliquots of double-distilled water. This recovery method was used as during removal, particles of dislodged Fe-Mn oxyhydroxides became charged with static electricity and adhered strongly to the pipette tip and Teflon strip surface. Dislodged particles of the Fe-Mn hydroxides suspended in double distilled water were then transferred to an acid-washed glass beaker. Due to the very small sample size, Fe-Mn oxyhydroxides from each of the 2-3 Teflon strips from each sample site were combined to yield sufficient sample for analysis. Samples were digested on hotplates (ca. 80°C) to near dryness after the addition of five mL of 70% analytical grade nitric acid. The solutions were allowed to cool and made up to 50 mL using double distilled water. A blank was included for each digest. Samples were analysed for Cu, Pb, Zn, La, Ce, Ni, Co, V, U, Mn, Al and Th, using a Fission VG Plasma Quad inductively coupled mass spectrometer (ICP-MS) and acidified standards. Blank corrections for each element were generally less than five percent of analyte concentration.

3.2. Sediment trap and bottom sediment samples

Settling sediments were collected monthly at each site using sediment traps. Three 100 mm diameter 500 mm long acid-washed polyethylene tubes were secured vertically in the bottom sediments. The sediment trap samples were recovered by SCUBA divers. A large length to diameter aspect ratio (length:diameter of 5:1) was chosen for the sediment traps as this minimizes resuspension of trapped material. All three subsamples of sediment trap material were amalgamated and homogenised immediately at the field sites and returned to the laboratory where they were dried in an oven at ca. 110°C.

Bottom sediment cores were collected by SCUBA divers who inserted ca. 40 mm diameter pre-split aluminium tubes 800 mm in length approximately 500 mm into the bottom sediments. Upon retrieval, the cores were sectioned into 20 mm intervals for the first 100 mm and in 50 mm intervals thereafter. Upon return to the laboratory the sediment cores were dried in an oven at ca. 110°C.
Figure 1. Location of sampling sites in the upper Swan River Estuary, Western Australia
Major (Fe$_2$O$_3$, MnO) and trace (Ba, Cl, Cu, Ga, Nb, Ni, Pb, Rb, S, Sr, V, Y, Zn, Zr) element geochemical analysis of sediment trap and bottom sediment samples was undertaken on samples pulverised in a manganese-steel ring mill to less than 75 microns. Fused glass discs were produced using 1.6 g of sediment and lithium borate as flux and were analysed by X-ray fluorescence (XRF) on a Phillips PW 1480 X-ray fluorescence spectrometer using the methods of Norrish and Chappell, (1977).

3.3. Water chemistry
Dissolved oxygen, salinity and pH measurements were collected _in-situ_ using a Hydrolab H20 submersible probe. Dissolved Fe was analysed by flame atomic absorption spectrometry (Varian SpectrAA 40) after filtration through a 0.2 µm membrane filter.
4. Results and Discussion

Seasonal changes in the morphology of diagenetic Fe-Mn oxyhydroxides are presented in Figure 2. A statistical summary of monthly geochemical data from the Ron Courtney Island (RCI) and Tonkin Overpass (TO/P) site are presented in Table 1 as a mean and standard deviation of the entire year and for different sampling periods (see later). Bottom water dissolved oxygen (mg/L) and salinity concentrations (parts per thousand - ppt) and dissolved Fe concentrations (mg/L) and pH for the RCI and TO/P sample sites are given in Figures 3 and 4 respectively. Monthly trace element/Fe ratios of diagenetic Fe-Mn oxyhydroxides collected using the Teflon strips for the RCI and TO/P sample sites are presented in Figures 5 and 6 respectively. Trace element concentrations for samples are expressed as a mass of the trace element per unit mass of Fe (µg/g Fe) to allow comparison of trace element concentrations independent of the amount of Fe actually deposited on the Teflon strip. A comparison of trace element/Fe ratios for different sampling periods throughout the year and for sediment trap material and bottom sediments are presented in Figure 7.

4.1. Attachment of Fe-Mn oxyhydroxides to Teflon strips

A strongly hydrophobic surface such as Teflon seems an unlikely substrate to accrete Fe-Mn oxyhydroxides. It is likely that rather than a direct adherence of the Fe-Mn oxyhydroxides, which have a variable (pH dependant) charge in natural waters, onto the hydrophobic Teflon substrate, an intermediate phase may facilitate the accretion process. Some bacteria may be able to act as an interface between hydrophobic and hydrophilic surfaces, and thus facilitate the accretion of diagenetic Fe-Mn oxyhydroxides.

Many studies have demonstrated that some bacteria can show either hydrophobic or hydrophilic properties in different circumstances which implies that the bacterial surface is non-uniform in nature (e.g. Gannon, et al., 1991). Also some freshwater bacteria such as Hyphomicrobium sp. or Pedomicrobium sp. possess a hydrophobic anchor attached via a stalk to a hydrophilic cell coating. This may allow accretion of a bacterial biofilm to the Teflon surface to create a hydrophillic surface amenable to metal adsorption and/or precipitation.

A study of fatty acid profiles in a marine microfouling community has demonstrated that Teflon may act as a substrate for the direct adherence of bacteria (Odham et al., 1985). An intimate association between bacteria and diagenetically formed Fe-Mn oxyhydroxides on Teflon strips has also been inferred from electron microscopy studies by Fortin et al., (1993) where diagenetic Fe-Mn oxyhydroxides on Teflon strips recovered from lacustrine environments contained impressions that resembled shapes of Gram-negative bacteria.
Numerous studies have demonstrated a close association between bacterial adsorption and the presence of Fe-Mn oxyhydroxides in a range of surface water and aquifer environments and/or geological materials (e.g. Ferris et al., 1989, Grantham and Dove, 1996, Lundsdorf et al., 1997, Scholl and Harvey, 1992, Schultze-Lam et al., 1995). It has also been suggested that the presence of a biofilm might be expected to influence the subsequent deposition of metal oxides and as a consequence affect transition metal distribution (e.g. Davis and Leckie, 1978, Lo et al., 1996).

A preliminary microbiological examination of Teflon strips placed in the Swan River suggests a diverse bacterial flora is present with the Fe-Mn oxyhydroxides. Staining of the Teflon strip with DAPI (2, 4-diamidino-2-phenylindole), a dye which specifically binds to DNA so that the bacteria fluoresce when examined using epifluorescence microscopy, revealed large numbers of filamentous-, rod- and coccus-shaped bacteria which were intimately associated with the diagenetic Fe-Mn oxyhydroxides. Most bacteria ranged in size from 0.1-5 µm with the filamentous bacteria were up to 100 µm in length.

4.2. Changes in redox front morphology

A number of distinct changes occur in the morphology of the redox front as recorded on a monthly basis by the accretion of diagenetic Fe-Mn oxyhydroxides on the Teflon strips (Figure 2). Major morphological changes in the accretion of the diagenetic Fe-Mn oxyhydroxides correspond in broad terms to the propagation and removal of the salt wedge and changes in riverine flow, groundwater flow and dissolved oxygen status. Patterns of accretion of the diagenetic oxyhydroxides were broadly similar at each sample site. Major changes in redox front morphology are discussed below.

4.2.1 Riverine flow period: days 258/93 - 315/93 and days 181/94 - 237/94

During the riverine flow period which has low salinities (ca. 4 ppt) and high dissolved oxygen concentrations (ca. 6-8 mg/L, Figures 3, 4), substantial, dense accumulations of diagenetic Fe-Mn oxyhydroxides form on the Teflon strips at both sampling sites (Figure 2). The depth of accumulation (ca. 20 mm) of the diagenetic Fe-Mn oxyhydroxides is generally shallow in contrast to the other periods. Substantial accumulation of diagenetic Fe-Mn oxyhydroxides on the Teflon strips during periods of riverine flow occurs due to two main factors:
Figure 2. Seasonal changes in the deposition (morphology) of Fe-Mn oxyhydroxides on Teflon strips placed in the bottom sediments of the Swan River Estuary.

(i) the sharp redox gradient between the anoxic bottom sediments and the overlying water column which is at or near saturation in terms of dissolved oxygen concentration which would lead to effective and rapid oxidation of Fe$^{2+}$ which is at moderate concentrations in bottom waters (ca. 0.2-0.4 mg/L) during this period (Figures 3, 4)

(ii) the higher regional hydraulic groundwater head during winter (Campbell, 1996, Davidson, 1995). This provides a significant flux of reduced (anoxic) porewaters (containing Fe$^{2+}$) from deeper in the bottom sediments to the river channel which will be oxidised at the redox front.

4.2.2 Propagating wedge period: days 350/93 - 069/94

Physico-chemical conditions in both the water column and bottom sediments change substantially due to the propagation of the salt wedge into the upper Swan River Estuary. Salinities increase from low (ca. 3-4 ppt) to intermediate levels (ca. 15 ppt, Figures 3, 4). Coupled with the increase in salinity are large changes in the levels of dissolved oxygen which may be at or near saturation in the upper water column (ca. 6-8 mg/L, Figures 3, 4) due to the occurrence of major phytoplankton blooms. Concomitant decreases in dissolved oxygen occur intermittently in the lower water column due to the development of salinity stratification (Douglas et al., 1996, 1997). Moderate to low dissolved oxygen concentrations in the lower water column may also be punctuated by periods of hypoxia/anoxia due to the collapse of phytoplankton blooms (Douglas et al., 1996). The concentration of dissolved Fe is particularly low at the RCI site coinciding with the propagation of the salt wedge. These low concentrations may reflect scavenging of the dissolved Fe during the coagulation of
particulate matter preferentially trapped within this deep site during the mixing of riverine flow and the more saline salt wedge.

Substantial density-driven displacement of porewaters occurs during the propagation of the salt wedge into the upper Swan River Estuary. Investigations into surface river water-groundwater interaction in the upper Swan River Estuary suggest that the propagating salt wedge may penetrate to at least 60 cm over approximately two months into the bottom sediments at the RCI and TO/P sites respectively (Turner et al., 1996). It is possible that the dynamic nature of river water-groundwater interaction via diurnal cycles leads to the pattern of Fe-Mn oxyhydroxide accumulation observed during the propagation of the salt wedge (Figure 2). This period is characterised by the presence of multiple redox fronts which may overprint each other to a maximum depth of approximately 50 mm.

The multiple redox fronts observed during the Propagating wedge period may also be related to seasonal deposition of suspended sediment due to coagulation. Maximum sediment deposition rates (calculated on a monthly basis from sediment trap deposition rates monitored concurrently with the Teflon strip experiment) of between 26 mm/yr (TO/P) and 42 mm/yr (RCI) occur during the initial propagation of the salt wedge and coagulation of suspended material (Douglas et al., 1997). These maximum sediment deposition rates are similar to the total thickness of the multiple Fe-Mn oxyhydroxide layers recorded by the Teflon strips. It has been suggested that the redox front in underlying sediments may migrate upwards in response to the presence of a coagulated (floc) layer (Sweerts et al., 1986). Hence, it is possible that this process, perhaps in combination with the variable depth of penetration of saline water into the bottom sediment (and hence, variable redox front depth), may result in the observed redox front patterns of multiple bands recorded on the Teflon strips.

4.2.3 High salinity period: days 097/94 - 153/94

Two types of accumulation of diagenetic Fe-Mn oxyhydroxides were observed during the High salinity period. Early in this period, salinities are intermediate to high (ca. 15-25 ppt), dissolved oxygen concentrations in bottom waters are generally lower and may punctuated by short-term (1-7 day) periods of hypoxia (<2 mg/L) and at least two episodes of anoxia, particularly at the deeper, less well flushed RCI site (Figures 3, 4). This physico-chemical regime is likely to be a major factor in the diffuse accumulations of diagenetic Fe-Mn oxyhydroxides on the Teflon strips (Figure 2). The diffuse accumulations of Fe-Mn oxyhydroxides observed during this period reflect either the weak physico-chemical gradient between the anoxic deeper sediment and the overlying water column and/or partial dissolution and of previous accretions of diagenetic Fe-Mn oxyhydroxides. The depth of accumulation of diagenetic Fe-Mn oxyhydroxides (ca. 50 mm) is similar to that of the Propagating wedge period.
Figure 3. Dissolved oxygen, salinity, dissolved Fe and pH in the bottom waters from the Ron Courtney Island (RCI) sample site in the upper Swan River Estuary.
Figure 4. Dissolved oxygen, salinity, dissolved Fe and pH in the bottom waters from the Tonkin Overpass (TO/P) sample site in the upper Swan River Estuary.
The periodically higher concentrations of dissolved Fe in bottom waters at both sites (*ca.* 0.2-0.4 mg/L, Figures 3, 4) reflect the often substantially lower dissolved oxygen concentrations and intermittently lower pH during this period. A distinct lateral discontinuity of Fe-Mn oxyhydroxide accretion is frequently recorded across the Teflon strip. This suggests that there is not a continuous redox front present and that conduits connect the reduced bottom sediments and the overlying water column. These gaps in the redox front may be due to bioturbation (see later). Alternatively, a proportion of the available Fe may be utilised in the formation of diagenetic (framboidal) sulphides which are a common constituent of the sediments of the upper Swan River Estuary (Douglas *unpubl. data*). The presence of multiple generations of frambooidal sulphides is also noteworthy as they may contain high concentrations of trace metals (see later) which may be potentially be remobilised by oxidation or may be a sink for trace metals below the redox front or during periods of anoxia.

Later during the High salinity period only very diffuse, discontinuous accumulations of diagenetic Fe-Mn oxyhydroxides up to 50 mm in depth occur on the Teflon strips at both sites (Figure 2). Occasional conduits deeper into the sediment are suggestive of bioturbation. The absence of substantial Fe-Mn oxyhydroxide accumulation may reflect the sustained moderate to low oxygen conditions in the overlying water column accompanied by high salinity (*ca.* >25 ppt, Figures 3, 4) creating physico-chemical conditions analogous to those earlier in the High salinity period. As outlined above, active diagenetic sulphide formation may also reduce Fe (and trace element) availability. Low groundwater flows during this period (Campbell, 1996, Davidson, 1995) may also be important in limiting the resupply of dissolved Fe to the sediment-water interface.

### 4.3. Variation in Fe-Mn oxyhydroxide (redox front) geochemistry and comparison to sediment trap material and bottom sediments

Trace element analysis of Teflon strip samples from both the TO/P and RCI sample sites reveal large and often erratic monthly changes in the trace element geochemistry (normalised to the amount of Fe deposited on the strip) of the diagenetic Fe-Mn-oxyhydroxides (Figures 5, 6). It appears that although the two sample sites in this study may have substantially different bathymetry, flushing and physico-chemical characteristics, these characteristics do not substantially influence the majority of trace element/Fe ratios in the diagenetic Fe-Mn oxyhydroxides. This similarity in trace element concentrations may also reflect the broadly similar major and trace element chemistry and mineralogy in both the bottom sediments and seasonally deposited sediments collected in sediment traps at both sites (Table 1 and Douglas *unpubl. data*).
Figure 5. Monthly trace element/Fe ratios of Fe-Mn oxyhydroxides collected on Teflon strips at the Ron Courtney Island (RCI) sample site in the upper Swan River Estuary.
Figure 6. Monthly trace element/Fe ratios of Fe-Mn oxyhydroxides collected on Teflon

the Tonkin Overpass (TO/P) sample site in the upper Swan River Estuary.
Table 1. Statistical summary (mean - \( \mu \), standard deviation – \( \sigma \)) of Teflon strip, sediment trap and bottom sediment trace element/Fe ratios (\( \mu g \) element/g Fe) at the Ron Courtney Island (RCI) and Tonkin Overpass (TO/P) sites.

<table>
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<th>RCI</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
<th>Ni</th>
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<th>V</th>
<th>La</th>
<th>Ce</th>
<th>Th</th>
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<td>Entire Year</td>
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na = not analysed
Common trends are apparent for the majority of the trace element geochemistry as recorded in the diagenetic Fe-Mn oxyhydroxides. These are discussed below and compared to trace element/Fe ratios in sediment trap material and bottom sediments.

During both the Riverine flow period: days 258/93 - 315/93 and Propagating wedge period: days 350/93 - 069/94, monthly trace element/Fe ratios are highly variable at both the sample sites (Figures 5, 6). Mean trace element/Fe ratios from these two periods are similar and often indistinguishable within one standard deviation ($1\sigma$, Table 1, Figure 7).

In the High salinity period: days 097/94 - 153/94, monthly and mean trace element/Fe ratios are lower than other periods with often minimum recorded trace element/Fe ratios, particularly for Cu and Zn at both sample sites (Figures 5, 6, 7, Table 1). The low trace element retention by the Fe-Mn oxyhydroxides during this High salinity period is also important relative to other periods as only small amounts of Fe-Mn oxyhydroxides are actually deposited at the redox front during this period (Figure 2). Thus, the actual retention of trace elements in absolute terms in the redox front is even less compared to other periods than that documented in Table 1 as so little Fe is deposited on the Teflon strip. Thus, the High salinity period represents a time when there is apparently little trace element retention in the bottom sediments in a reducible form. It may indicate that trace elements are being retained in other forms (e.g. as diagenetic sulphides), or are being transported across the sediment-water interface into the overlying water column.

At the onset of increased riverine flow when saline water is flushed downstream (Riverine flow period: 181/94 - 237/94), trace element/Fe ratios within the diagenetic Fe-Mn oxyhydroxides increase to levels similar to that early in the previous Riverine flow period. At the TO/P site the return of riverine flow conditions coincides with the maximum trace element/Fe ratios for Cu, Zn, Ni and V recorded in this study.

The monthly monitoring of diagenetic Fe-Mn oxyhydroxides provides a basis to evaluate the role of the redox front in the cycling of trace elements in bottom sediments and to compare the relative enrichment of trace elements compared to Fe in newly deposited sediment trap material and bottom sediments. In this comparison, however, it must be noted that a substantial proportion of trace elements in the sediment trap material and bottom sediments may be bound to phases other than Fe-Mn oxyhydroxides (e.g. humic substances and/or clay minerals). Nonetheless, a comparison of the relative speciation of trace elements as function of Fe concentration in diagenetic Fe-Mn oxyhydroxides, sediment trap material and bottom sediments provides an indication of the possible role of diagenetic Fe-Mn oxyhydroxides in regulating trace element concentrations in bottom sediments.
Figure 7. Mean and standard deviation on element/Fe ratios (µg element/g Fe) for Teflon strips, sediment traps and bottom sediments at the Ron Courtney Island (RCI) and Tonkin Overpass (TO/P) sites.
At both the RCI and TO/P sample sites yearly average trace element/Fe ratios for the
diagenetic Fe-Mn oxyhydroxides have similar mean concentrations and are frequently
indistinguishable within 1σ of the mean from both sediment trap material and bottom
sediments (Table 1, Figure 7). Partitioning of trace element data from the diagenetic Fe-Mn
oxyhydroxides into three major groups (Riverine flow period: days 258/93 - 315/93 and days
181/94 - 237/94, Propagating wedge period: days 350/93 - 069/94 and High salinity period:
days 097/94 - 153/94, Figures 3, 4), however, highlights a few cases of relative
enrichment/depletion of trace elements in the diagenetic Fe-Mn oxyhydroxides relative to
sediment trap and bottom sediments (Table 1, Figure 7).

Trace element/Fe ratios are generally higher in the sediment trap material and bottom
sediments (as defined by 1σ) for the elements Cu, Pb, Zn, Ni, V, La and Ce relative to the
high salinity period. Interestingly, there are comparatively low mean Mn/Fe ratios
particularly in the bottom sediment material and to a lesser extent sediment trap material
compared to the Teflon strips. In general, both the sediment trap material and bottom
sediments have high Ce/Fe and high La/Fe ratios which (except for the Propagating wedge
period and the Entire year average La/Fe ratio at the TO/P sample site) are distinguishable
(1σ) from the diagenetic Fe-Mn oxyhydroxides (Table 1, Figure 7). Although many studies
have demonstrated rare earth elements such as La and in particular Ce will be strongly
partitioned into diagenetic Fe-Mn oxyhydroxides in both aquatic and terrestrial environments
(e.g. Fleet, 1984, Lottermoser, 1990) the relatively higher La and Ce concentrations in the
bottom sediments and sediment trap material are consistent with the presence of heavy
minerals (e.g. monazite) which have been identified in mineral separates of sediments in the
upper Swan River Estuary (Douglas unpubl. data).

There are a number of physical and biogeochemical factors which may in isolation or in
combination affect the rate of accumulation and ultimate concentration of trace elements
within the diagenetic Fe-Mn oxyhydroxides. The supply of trace elements to the upper
layers of the bottom sediment and redox front may be modified significantly in the upper
Swan River Estuary as a result of:

(a) Seasonal propagation of the salt wedge. The propagating salt wedge, particularly during
the High salinity period (days 097/94 - 153/94, Figures 5, 6), represents an impoverished
suspended sediment and dissolved trace element source compared to riverine flow. This
seasonal propagation of the salt wedge into the upper Swan River Estuary is concurrent with
the reduction and eventual cessation of flow of many of tributaries to the upper Swan River
system which are likely to have been important in the resupply of trace elements in both
suspended and dissolved form.
(b) **Coagulation of suspended particulate material.** Concurrent with the initial propagation of the salt wedge and mixing with riverine flow a turbidity maximum is generated by coagulation followed by a significantly reduced flux of particulate material to the bottom sediment. A monthly record of the gross flux (excluding resuspension) of suspended material indicates that the highest sediment fluxes occur during the initial propagation of the salt wedge at both the RCI and TO/P sites (days 322/93 - 006/94, Douglas et al., 1996).

As outlined previously, it has been suggested that the redox front in underlying sediments can migrate upwards in response to the presence of a coagulated (floc) layer (Sweerts et al., 1986), as a consequence of the often high oxygen demand of settling material (e.g. Kerner and Gramm, 1995). The coagulated layer (collected in the sediment traps) has concentrations of trace elements broadly similar (except Mn which is substantially higher) to that of the underlying bottom sediment (Table 1, Figure 7) and frequently higher trace element/Fe ratios than the diagenetic Fe-Mn oxyhydroxides. Hence, the floc layer is potentially an important source of trace elements to the concurrently forming diagenetic Fe-Mn oxyhydroxides in the period during and after the propagation of the salt wedge. The presence of a floc layer may also be particularly important due to high particle surface area and hence, the potential for rapid recycling of labile trace elements. The relatively high organic matter of the sediment trap material (Douglas unpubl. data) may also be important as it has been demonstrated that substantial release of trace metals can occur from recently deposited organic matter (e.g. Morphett and Hamilton-Taylor, 1988, Sigg et al., 1987), even under aerobic conditions (Gerringa, 1990, Petersen et al., 1995).

(c) **Modified groundwater flux.** Hydrological monitoring at both the RCI and TO/P sites has indicated a seasonal change in both the magnitude and direction of groundwater flow. A reduction of the regional hydraulic head and the penetration of the salt wedge into the bottom sediment is associated with the propagation of the salt wedge into the upper Swan River Estuary. During the initial propagation of the salt wedge there is significant displacement (ca. 50 cm) of the relatively fresh encumbent porewaters by the more dense overlying salt wedge. It is possible that this displaced porewater could supply a significant flux of trace elements which may be scavenged by the contemporaneously forming diagenetic Fe-Mn oxyhydroxides during their passage into the overlying water column.

(d) **Scavenging of trace elements by other processes.** One potentially important pathway in reducing trace element supply to actively forming diagenetic Fe-Mn oxyhydroxides at the redox front is the formation of diagenetic Fe-sulphides. Analysis of sediment cores from the RCI sample site suggest sulphate reduction is occurring within a few centimetres of the sediment-water interface (Douglas unpubl. data). Electron microprobe analyses of 37
framboidal pyrite aggregates suggests that multiple generations of framboids are present within the bottom sediments. There appears to be at least four distinct framboid populations in terms of trace element (Cu, Zn) geochemistry. One population has low concentrations of Cu and Zn below detection limits (n=9), another elevated Cu (510±180) and Zn (630±520) concentrations (n=14) and the remaining two populations either elevated Cu (760±750) concentrations (n=6) or Zn (1070±630) concentrations (n=7). Other studies also suggest that coprecipitation with Fe-sulphides was a major removal pathway for Cu and Zn under anoxic conditions (Hamilton-Taylor et al., 1996, Song and Muller, 1995, Cooper and Morse, 1998).

(e) Limitation of solid solution. Although the mineralogy of the diagenetic Fe-Mn oxyhydroxides could not be identified by X-ray diffraction (Douglas, unpubl. data), it is probable that phases such as goethite are present, perhaps in a microcrystalline form. Many mineralogical phases have a limited solid solution with other elements. Comparison of the total concentration of some of the metals contained within the diagenetic Fe-Mn oxyhydroxides in this study with observed levels of maximum substitution of goethites (Cornell and Schwertmann, 1996) indicate that the majority of metals there are present at comparatively low levels of substitution, frequently less than 1%. A notable exception are the maximum levels of Al (0.31 mol mol⁻¹ Fe) and Mn (0.15 mol mol⁻¹ Fe) which are similar to maximum levels of Al (0.33 mol mol⁻¹ Fe) and Mn (0.15 mol mol⁻¹ Fe) substitution in synthetically prepared goethites. In addition, preferential scavenging of some elements may occur.

(f) Bioturbation. Bioturbation will induce a range of effects on trace metal concentration and speciation in bottom sediments via solute exchange and changes in redox status. Biota may significantly modify the structure of bottom sediments, particularly in terms of nutrient exchange and oxygen dynamics at the sediment/water interface (e.g. Forster et al., 1995, Holdren and Armstrong, 1980, Yamada and Kayama, 1987). Conduits into the bottom sediment which are preserved as by the diagenetic Fe-Mn oxyhydroxides (Figure 2) and the colonisation of the polyethylene backing plate on the Teflon strip by polychaete worms suggest that bioturbation may irrigate the upper layers of the bottom sediment and regulate trace element supply.

A number of studies on the abundance and species diversity of benthic biota present in the upper Swan River Estuary have demonstrated significant differences depending on the presence or absence of the salt wedge (e.g. Chalmer et al., 1976, Papas and Davis, in prep., Rose, 1994). Statistical analysis of population data suggests that at a number of locations, both deep and shallow, increasing salinity (and probably changes in dissolved oxygen levels) were responsible for significant temporal modifications (Papas and Davis, in prep.).
(g) Variation in bottom/porewater pH, salinity and dissolved organic matter. During Propagating wedge period (days 083/94 - 153/94), the pH of bottom waters is frequently at its lowest level (ca. 7.6 - 8.0: RCI, 7.8 - 8.0: TO/P, Figures 3, 4). Studies of porewater pH during comparable periods at both the RCI and TO/P sites also suggest that the mean pH is slightly lower (ca. 7.0 - 7.6) during this period (Campbell, 1996). The predominantly downward flux of saline water into, and interaction with, the upper layers of the bottom sediments may have affected the porewater chemistry during this period. Small variations in pH in the range 7.0 - 8.0 have been demonstrated in a number of studies to influence the adsorption of metals on oxide and/or oxyhydroxide substrates (e.g. Balistieri and Murray, 1982, Spark et al., 1995a) as it is often in this pH region that the greatest rate and/or adsorption maxima may occur for a variety of trace metals.

Numerous laboratory studies have demonstrated that increasing chloride concentrations such as that occurring during the propagation of the salt wedge may induce a shift the onset of trace metal adsorption on model Fe-oxyhydroxide substrates to a higher pH (e.g. Millward and Moore, 1982). Other laboratory studies have also demonstrated that the presence of adsorbed organic matter may significantly influence the adsorption of trace metals onto model Fe-oxyhydroxide substrates (e.g. Ali and Dzombak, 1996, Spark et al., 1995b, Tipping et al., 1983).
5. Conclusions

A study of diagenetic Fe-Mn oxyhydroxides at two sites in the Swan River Estuary collected using in-situ Teflon strips has demonstrated significant changes in the morphology of diagenetic Fe-Mn oxyhydroxides and large seasonal variations in their trace element geochemistry. There was little difference between a deep and shallow site in either the morphology or trace element geochemistry of the Fe-Mn oxyhydroxides. It is likely that seasonal variation in trace element geochemistry occurs as a result of either a change in the supply of trace elements from either the bottom sediments and/or water column or changes in the physico-chemical status of bottom and/or porewaters which influence trace element adsorption by the diagenetic Fe-Mn oxyhydroxides.

Monitoring of bottom sediment geochemistry has demonstrated that significant concentrations of trace elements may accumulate at the redox front during the contemporaneous accumulation of diagenetic Fe-Mn oxyhydroxides. If sufficient amounts of these diagenetic Fe-Mn oxyhydroxides are preserved in the upper layer(s) of the bottom sediment it is possible that diagenetic (secondary) enrichment profiles may be produced which do not accurately reflect the historical input of anthropogenic trace element sources. Alternatively, partial or complete dissolution of the diagenetic Fe-Mn oxyhydroxides in response to (seasonal) changes in the redox status of the bottom sediment may lead to a significant underestimate of trace element concentrations in historical bottom sediment profiles. This study highlights that considerable care must be taken when interpreting geochemical profiles in bottom sediments due to the possible occurrence of rapid (month to seasonal) diagenetic processes.
6. Acknowledgements

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