Managing for Metal Mobility in the Gippsland Lakes (II)

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EXECUTIVE SUMMARY

Sediment cores from across the Gippsland Lakes were extracted from areas that were identified in a previous study (Reeves and Trewarn, 2016) to have elevated metal concentrations. These cores were subject to a range of incubation experiments designed to simulate expected changes under changed climate and hydrological conditions. Metal concentrations in the sediments and (where possible) porewater and water column were tested before and after the experiments to determine metal fluxes.

The experiments together revealed that largely the metal concentrations are stable, with predicted climate and hydrological change, but attention should be focussed on:

- Drying conditions at Heart and Dowd Morass
- Anoxia at Lake King North
- Changes in oxidation state at Hollands Landing

It is recommended that these sites are tested under changed environmental conditions, such as extended drought periods (morasses) and flooding or algal bloom events (Lake King). It is also recommended that the Zn and Cu levels of the water column be tested in a follow up study, as these were elevated above trigger at several sites sampled. Speciation of As and Cr should also be tested, particularly at Hollands Landing, where these metals potentially exceeded trigger levels and changes in oxidation state are likely.

1. PROJECT OVERVIEW

1.1. Program/project scope

The issue of heavy metal contaminants being present within the Gippsland Lakes sediments was first identified over 35 years ago (Bek and Bruton, 1979; Glover, 1980). Additional work has identified evidence of metal contaminants, particularly mercury, entering the biota of the lakes, such as Black Bream (Churchill et al., 2004; Fabris et al., 1999; Glover et al., 1980; Haynes et al., 1995) and the newly described *Tursiops australis* dolphin (Monk et al., 2014). The early records give levels up to 40-times higher than the high guideline (Harris, 2001). Elevated levels of selenium have also been detected in fish (Glover et al., 1980). However, the form of mercury, concentrations, accumulation pathways, distributions and associated ecological risks are not well understood. In addition, the confounding influences that impact on the mobilisation and bioavailability of particularly metals from a sedimentary source have not been studied. Therefore current and future risks cannot yet be properly evaluated.

Our research has shown mercury above the trigger threshold for environmental health at the mouth of the Latrobe River and elevated levels in arsenic, mercury, lead and cadmium in sediment from the mouth of the Mitchell River and McLennan Strait (Reeves and Trewarn, 2016). It also found potential areas of methylation in the deep lakes and brackish wetlands, which may be a mechanism to mobilise mercury within the sediment. A subsequent study, focussing on bioaccumulation in mussels in the Lakes, found levels of cadmium, zinc and copper exceeding human health guidelines (Willems et al., 2018).

This project aimed to conduct investigation in regions within the Gippsland Lakes where elevated concentrations of metals have previously been detected within the sediments and mobilisation is most likely, under a range of scenarios from predicted climate change. This may then contribute to building metal pathways into the biogeochemical models, such as for nutrient flux and climate change, already developed for risk assessment purposes in the Gippsland Lakes. In addition, the output of this project will help guide management decisions for the Lakes regarding not only metals in isolation, but also the mechanisms that effect mobilisation of metals, such as changes in oxidation state, salinity, nutrient flux and pH. This will lead to the most efficient coordination and prioritisation of management efforts to mitigate against future metal mobilisation.

1.2. Objectives

This project aims to determine the mechanisms and pathways for metal mobilisation within the Gippsland Lakes. This is necessary to identify key areas and mechanisms that may contribute to the metal load of the sediment and water of the Lakes, which potentially impact environmental and human health, so mitigation measures can be followed. The project –

- Determined the presence and concentrations of metal contaminants in the sediment, pore-water and water in three key regions of the Gippsland Lakes;
- Assessed metal mobility by undertaking *in situ* and laboratory experiments to manipulate the conditions in the sediments of these regions, controlling for redox, pH and salinity;
- Defined key areas of risk for metal mobility in the Gippsland Lakes, which may be used to build on the existing biogeochemical model.

1.3. Location/physical settings

The Gippsland Lakes are a network of lakes, marshes and lagoons covering an area of about 354 km^2. The largest of the lakes are Lake Wellington, Lake King and Lake Victoria. The lakes are fed by major rivers - the Latrobe, Avon, Mitchell, Nicholson and Tambo Rivers - which drain a 20,600 km^2 catchment. Of these, the Latrobe and Mitchell Rivers together drain almost one-half of the total catchment. The Gippsland Lakes system is connected to Bass Strait by a permanent narrow opening maintained by suction dredging at Lakes Entrance (Fabris et al., 1999).

The Gippsland Lakes have been described as "mega habitats" (Fig. 1.1) comprising of –

- Three main lakes with permanent deep water bodies of Lakes King and Victoria, and shallower Lake Wellington and Jones Bay.
- Extensive fringing wetlands throughout the Lake systems, including freshwater wetlands (such as Sale Common), brackish water and variable saline wetlands (such as Heart Morass, Clydebank Morass and Dowd Morass) and hypersaline wetlands (Lake Reeve and Victoria Lagoon).

- The estuarine reaches of the inflowing rivers also form an important part of the lakes system by providing habitat for fish and eel breeding and feeding.

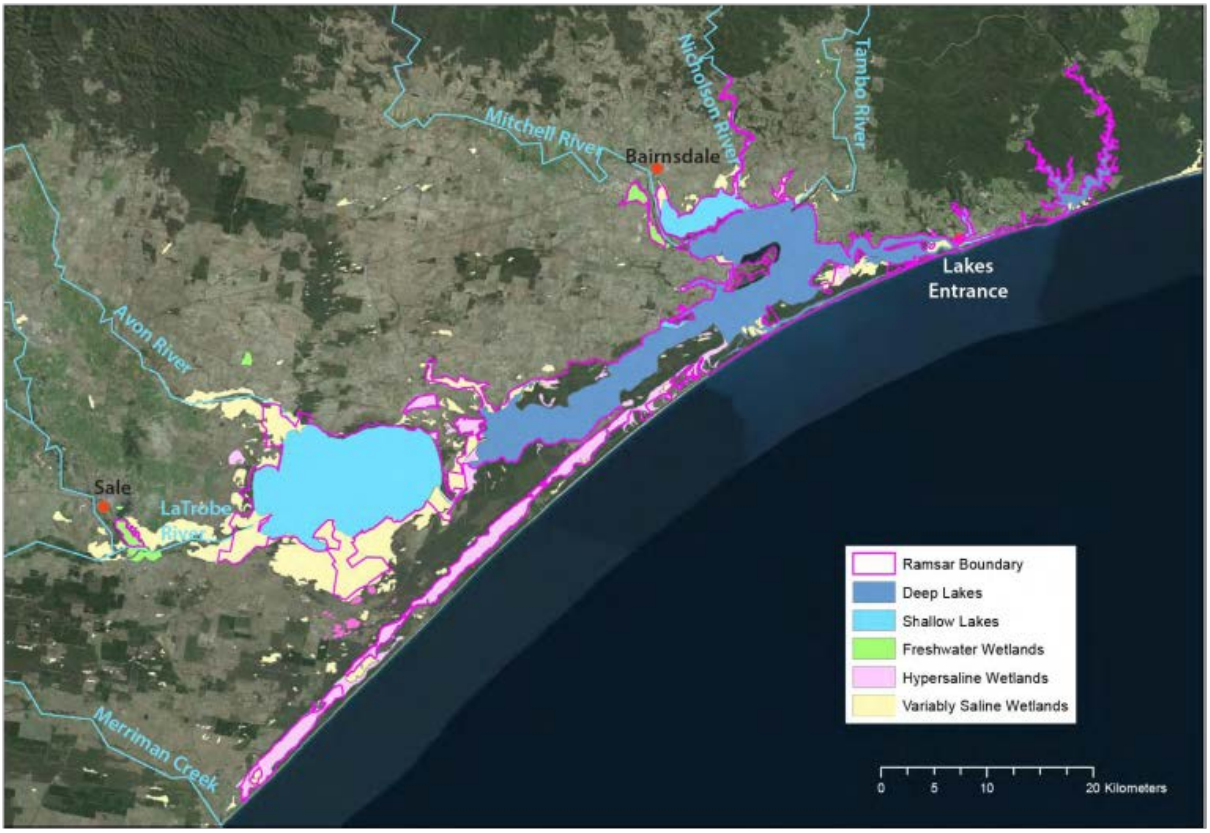

Fig. 1.1: Gippsland Lakes catchment (EGCMA, 2015).

The major streams that flow into the Gippsland Lakes originate in some of the highest terrain in south-eastern Australia, including areas that experience several months of snow cover. The catchment boundary between the headwaters of the Tambo River and Thomson River forms part of the Great Dividing in Victoria. Mount Hotham (1862 m) at the headwaters of the Dargo River is a major tributary of the Mitchell River (Boon et al., 2014).

Lake Wellington in the west is a large, shallow basin with an average depth of ~2.6 m, and typically has a salinity <15 g/l. Lakes King and Victoria in the east have an average depth of ~5 m, reaching 11 m in the deepest areas. Maximum river flows and floods typically occur in the Austral winter–spring, which reduce surface salinities to ~5–15 g/l, which then increase to > 25 g/l over summer in Lakes King and Victoria. Lakes King and Victoria are typically salinity stratified, with bottom water salinities of ~30 –

35 g/l and during intense stratification following high river flow, the bottom waters of the Lakes King and Victoria may become anoxic (Cook et al., 2015).

Since the construction and maintenance of the permanent entrance, the system has operated as an estuary with salinity fluctuating in response to freshwater inflows. During periods of drought, when freshwater inflows are low, salinity rises across the system. Conversely during flood periods, such as occurred in 1978, salinity across all surface waters dropped to near fresh (Fryer and Easton, 1980). As with many estuaries, there is stratification or layering of the water column with denser more saline water underneath a freshwater layer, particularly in the deeper lakes (Fig. 2). The entrance was responsible for the spatial pattern in salinity and freshwater inflows principally responsible for temporal variation in salinity (Tilleard et al., 2009).

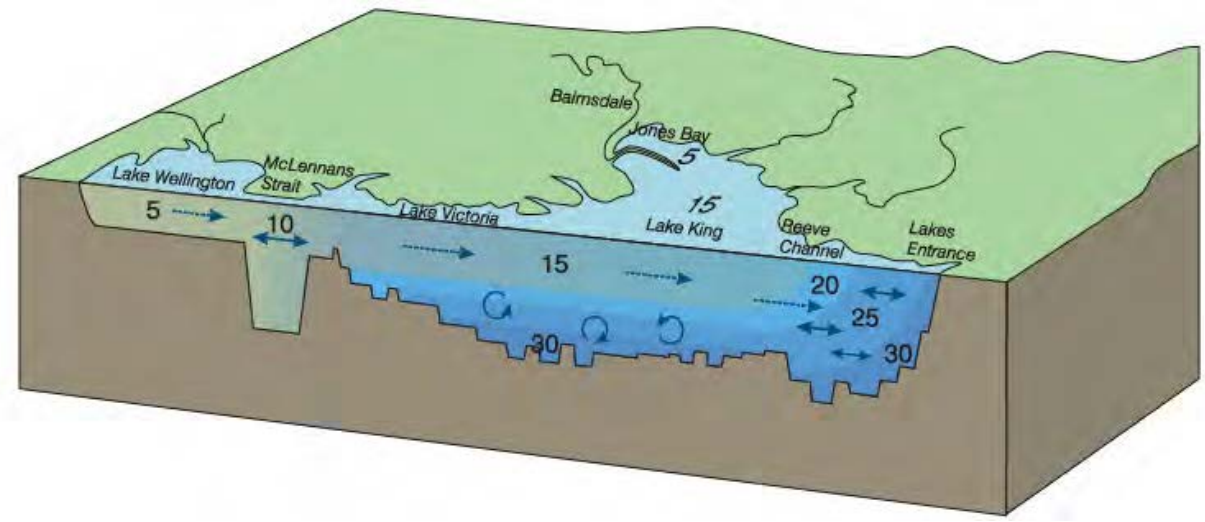

Fig. 1.2: Conceptual model of salinity and stratification in the Gippsland Lakes (Webster et al., 2001).

1.4. Site Significance

The Gippsland Lakes are listed as wetlands of National significance and International significance under the Ramsar Convention on the basis of the diversity of important wetland/habitat types and geomorphic landforms (BMTWBM, 2011). The system supports threatened species and large numbers of waterbirds. Fauna utilise the lakes in critical life stages such as breeding or during adverse conditions such as drought, as well as providing significant habitat and food for larger fish and crustaceans (Hale and Morgan, 2010).

In addition to the significant ecological values, the Gippsland Lakes and catchments also hold a significant economic value. Currently the Gippsland region and the Lakes support extensive agriculture and grazing, tourism from boating and recreational fishing contributed approximately $273 million in 2010, as well as housing Victoria's largest fishing fleet worth $200 million (EGCMA, 2015).

Many of Victoria's resource industries lie within the catchment of the Gippsland Lakes, including forestry, paper mills, horticulture and dairying. In addition, the Latrobe Valley's coal-fired power stations and associated open cut mines are approximately 60km west of Lake Wellington, and connected via the Morwell and Latrobe Rivers. The region is also home to one of Victoria's two main offshore oil and gas fields with proposed exploration and expansion closer to shore.

The Gippsland Lakes have been stated as ‘experiencing a constant process of change’ (Hale and Morgan, 2010). Variations in sea level, climate, freshwater flows, natural disturbances and most predominantly human activities cause substantial change over time (EPA, 2015; Hale and Morgan, 2010). Some change is incremental, such as saline incursions upstream from the permanent lakes' entrance constructed in 1889 (EPA, 2015) and other change is more episodic, such as substantial algal blooms from high nutrient runoff (EPA, 2013; Holland et al., 2013). The condition of the lakes is not static and variation over periods of years and decades needs to be understood as part of a constantly changing environment.

Over the past 150 years, there has been significant anthropogenic activity within the Gippsland Lakes’ catchments. Many activities have caused catchment disturbance (e.g. agriculture), increased sedimentation rates (e.g. forestry) or decreased sedimentation (e.g. reservoir construction). In addition, some are known to be associated with the release of heavy metal contaminants. Activities associated with contaminant mobilization that have occurred within the Gippsland Lakes catchments include; gold and resource mining (Hg, Pb and As), agriculture (nutrients, Cd, Cr and As), urbanisation and storm water runoff (Pb). The legacy of such contaminants may be preserved within the sediments of the lakes themselves as seen in similar cases such as Port Jackson (Birch and Taylor, 1999) and Lake Macquarie (Schneider et al., 2014) and on a smaller scale in the Lower Barwon catchment (Reeves et al., 2016).

Methods to be undertaken in this study have been developed during a proof of concept study on the impacts on the lower Barwon catchment (Reeves et al., 2016); a system with similarly associated historical influences.

There is ever-growing concern regarding the possibility and precedence for the presence of heavy metals the Gippsland Lakes system, particularly mercury (Langshaw, 2014; McGhee, 2015).

2. LITERATURE REVIEW

Although heavy metals are naturally occurring elements that are found throughout the earth's crust, most environmental contamination and human exposure to heavy metals results from anthropogenic activities such as mining and smelting operations, industrial production and domestic and agricultural use of concentrated metals and metal-containing compounds (Glover et al., 1980; Tchounwou et al., 2012). Environmental contamination can also occur through metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of heavy metals, sediment re-suspension and metal evaporation from water resources to soil and ground water (Tchounwou et al., 2012). Industrial sources include metal processing in refineries, coal burning in power plants, petroleum combustion and plastics, textiles, microelectronics, wood preservation and paper processing plants (Glover et al., 1980; Wuana and Okieimen, 2011).

The study of metals in estuarine environments has developed a comprehensive international body of work, looking at various aspects of contaminant sources and cycles. These have included the role of dissolved organic matter and dissolved inorganic sulphur (Hammerschmidt and Fitzgerald, 2004; Merritt and Amirbahman, 2009; Miller et al., 2007; Sunderland et al., 2006), nitrogen cycling (Driscoll et al., 2012), acid sulphate soils (Nordmyr et al., 2008) and salinity (Dauvin, 2008).

In Australia, only 2.5% of estuaries have been surveyed for sedimentary heavy metals, however some of the most contaminated maritime areas in the world have been located in this country (Birch, 2000). The most impacted regions are adjacent to single-purpose industrial complexes, e.g. smelters, refineries and chlor-alkali plants. Although Port Jackson in New South Wales (NSW) is by far the most contaminated mixed urbanised/industrialized estuary in Australia (Birch and Taylor, 1999; Irvine and Birch, 1998), Birch (Birch, 2000) also reports on metal contamination in other NSW's waterways include Lake Macquarie (Barwick and Maher, 2003; Peters et al., 1999;

Schneider et al., 2014) and Lake Illawarra (Schneider et al., 2015a). In NSW, metal and metalloid contamination of the sediment water column and biota in Lake Macquarie is well documented (Barwick and Maher, 2003; Kirby et al., 2001a; Kirby et al., 2001b; Roach, 2005; Schneider et al., 2014). As demonstrated by Schneider et al. (2014), coal mining activities and power generation in the Lake Macquarie region have resulted in significant inputs of metal and metalloids to the waterbody. Other industries, such as a lead and zinc smelter, may also have contributed in metal input in the Lake Macquarie catchments. Many of the advances in distribution, speciation and bioaccumulation of contaminants (Se, Cd, Cu, Zn, Pb) has taken place within Lake Macquarie, NSW (Schneider et al., 2016; Schneider et al., 2014). In Lake Macquarie, NSW, the major sources of heavy metals are coal-fired power stations, and the metal contamination of the sediment, water column, and biota is well documented (Schneider et al., 2016). This has included experimental work on the role of pH, salinity, dissolved oxygen and sediment disturbance on metal release (Atkinson et al., 2007) and modeling food web structure (Schneider et al., 2014; Schneider et al., 2015b).

Metal pollution research of Victorian's waterways has been less documented, to date, and mostly focused on inland waters. Most of the research on Victorian waterways has focused on the role of contaminants on waterway health and the sources of contamination (Allinson et al., 2015; Baker et al., 2016; Bycroft et al., 1982; Churchill et al., 2004; EPA, 2016; Fabris, 2002; Haynes et al., 1995; Kellar et al., 2014; Kibria et al., 2012; Pettigrove and Hoffmann, 2003; Sharley et al., 2016). Based on the available information, natural sources of mercury in the Gippsland Lakes catchment are unlikely. Historical mercury contamination occurred from the treatment of gold ores with mercury during the late 1890s (Glover et al., 1980). Activities within the catchment vary from heavy industrial (such as the mining and use of brown coal for Victoria's electricity supply; paper manufacturing) to agricultural (such as vegetables and ornamental plants, sheep grazing and cattle grazing), and commercial and recreational fishing (Fabris et al., 1999). Given the diversity of industries and practice in the Gippsland Lakes' catchments, the sources of contamination are likely to be variable throughout the system.

2.1. Metal biogeochemistry in changing environment

The Gippsland Lakes Ramsar Site Management Plan (EGCMA, 2015) and EPA report (EPA, 2013) have identified several changes to the Lakes' environment that may exacerbate the impact/mobility of heavy metals within the system. These include coastal acid sulphate soils, periodic anoxia, and increased salinity due to decreased freshwater inflow or increased marine incursion and more extreme fire and flood events, which increase the sedimentation rate and nutrient flux to the catchment.

Heavy metals within the environment can remain stable and immobile within certain environmental settings if left undisturbed; however their mobility and toxicity can be greatly influenced by a number of changes in the surrounding environment parameters. The primary factors that are known to influence heavy metal mobility include, but are not limited to, pH, redox, salinity, organic material/carbon and geochemical bound fraction (Merian et al., 2004). These primary factors can alter as a result of larger changes in the environment as noted in previous sections and in turn affect the metals' mobility and speciation.

2.1.1. pH

pH is considered possibly the single most important variable that influences the behavior of metals in the environment (Simpson et al., 2005). Typically, decreasing pH in sediment causes competition between hydrogen ions and the dissolved metals and ligands becomes more significant (Peng et al., 2009), decreasing the adsorption abilities and bioavailability of the metals. This in turn increases the mobility of heavy metals (Peng et al., 2009). In weathered sediment, due to the organic matter degradation and acid volatile sulphide oxidation, the pH of sediment usually decreases from neutral to acid, typically as a result of oxidation of coastal acid sulphate soils (CASS) (Price, 2010). This pH shift results in some metals being released into the water column (Peng et al., 2009; Price, 2010). In sediment, there exists a pH threshold, controlling heavy metal mobility releasing when certain pH range in reached (Peng et al., 2009). Depending on the metal, this pH threshold is different, therefore, under a similar a pH, the potential for mobilisation between heavy metals can differ. The point to which the pH can mobilise specific metals may also be influenced by the geochemical fractions in which the metal is associated (Simpson et al., 2005).

2.1.2. Redox potential

In organic, carbon-rich sediments, trapped interstitial fluids can commonly form a strongly reducing (anoxic) environment. Low redox potential in this environment can promote sulphate reduction and sulphide mineral deposition (Leventhal and John, 1995; Morse, 1994). During diagenesis, much of the non-silicate-bound fraction of potentially toxic metals such as arsenic, cadmium, copper, mercury, lead, and zinc, can be co- precipitated with pyrite, from insoluble sulphides, and become unavailable to biota (Morse, 1994). Seasonal variations in flow rates or storms surges that induce an influx of oxygenated sea water can result in rapid reaction of anoxic sediment and thereby release significant proportions of these metals (Leventhal and John, 1995). Pyritization and/or de-pyritization of trace metals can be an important process in controlling bioavailability of many trace metals, especially in a marine and coastal environment (Morse, 1994; Presley et al., 1998) such as ones around the Gippsland Lakes catchment.

2.1.3. Salinity

The mobility of heavy metal contaminants can also be influenced by changes in salinity. This is mainly related to the metal bound geochemical fractions and the possible bound colloids.

One of the main chemical influences associated with salinity changes is the ionic concentrations of chloride ions (Simpson et al., 2013). This association both affects the metals ‘speciation’ but also the sediment characteristics. Both of which can significantly influence the mobility and the toxicity of many heavy metals. The change in salinity, especially from fresh to saline waters, can induce the precipitation of iron and manganese oxyhydrides from both soluble ions and colloids, thus carrying other metals such as heavy metal/loids e.g. arsenic (Simpson et al., 2013).

Short term effects of saline inundation into estuarine and fresh water sediments, in particular ones with known high acid generation potential, can actually cause an initial decrease in sediment pH and thus allowing the mobilisation of the sequestered metals as highlighted in previous studies on coastal acid sulphate soils (Wong et al., 2010; Wong et al., 2013).

2.2. Metal mobility in the natural environment

Based on the previous studies conducted by Glover et al. (1980), there is some precedence for a number of heavy metals to be present in quantity within the Gippsland Lakes catchment. A select few of the most significant metals are outlined below.

2.2.1. Arsenic

Arsenic (As) is found in the environment as a result of natural weathering processes, volcanic activity and anthropogenic inputs (Garelick and Jones, 2008). It is usually associated with sulphide minerals, the most common of which arsenopyrite (FeAsS) are and As-rich pyrite (Merian et al., 2004).

Several forms of As occur in natural waters, depending on the redox potential and pH; however As(III) and As(V) are the most common (Merian et al., 2004). Once in the aquatic environment, As may be adsorbed to metal oxides in sediments, in particular iron, aluminium (Merian et al., 2004). Clays also adsorb As. Similar to soils, under acidic, anaerobic conditions; arsenic released from sediments tends to increase as iron is reduced and As is re-dissolved. As(III) is the more toxic form, it is removed by sulphides and As(V) by clays that can adsorb both redox states (Merian et al., 2004). When acid sulphate soils are exposed to aerobic conditions, the oxidation of As-rich pyrite can release significant amounts of As into the environment (Merian et al., 2004).

2.2.2. Chromium

In the natural environment, chromium (Cr) occurs as either trivalent Cr(III) or hexavalent Cr(VI) (Merian et al., 2004). The two species differ greatly in terms of their physical and chemical properties, as well as their bioavailability and toxicity to aquatic biota. Cr(III) is considered to be an essential trace element for most living organisms. In contrast, Cr(VI) is highly toxic (Merian et al., 2004). The ratio and presence of Cr(III) and Cr(VI) is controlled by pH, oxygen concentration and the presence of reducing agents, oxidation mediators and complexing agents (Merian et al., 2004). In anoxic to suboxic conditions, Cr(III) should be the only form present (Merian et al., 2004). In oxic sediments, a portion of Cr(III) can be oxidised to Cr(VI) by MnO_2 and, to a lesser extent, dissolved oxygen (ANZECC/ARMCANZ, 2000).

2.2.3. Mercury

In aquatic systems mercury exists mainly as complexes of mercury(II) and as organomercurial compounds (Merian et al., 2004). Mercury toxicity is hardness (i.e. $CaCO_3$ content) dependent, where uptake rate increases with decreasing water hardness and pH. Mercury bioavailability, bioaccumulation and toxicity to biota depend on its chemical forms. Transformation (e.g., methylation) of mercury chemical forms is associated with the microbial activity in aquatic systems (Celo et al., 2006; Merritt and Amirbahman, 2009; Whalin et al., 2007). Methylation of inorganic mercury in the aquatic environment is considered to be largely the result of biological processes, primarily involving sulfate-reducing bacteria; however, a growing body of evidence suggests that abiotic process (chemical reactions) represent another significant pathway for mercury methylation in the aquatic environment (Celo et al., 2006). Inorganic forms of mercury may be converted by bacteria into organomercury complexes that are more toxic and tend to bioaccumulate (Merian et al., 2004).

2.2.4. Lead

Lead (Pb) is a non-essential metal. Pb can bioaccumulate in aquatic organisms if present at sufficient concentrations. Pb toxicity is hardness dependant; Pb uptake and toxicity in freshwater organisms' decreases with increasing water hardness and alkalinity (ANZECC/ARMCANZ, 2000; Merian et al., 2004).

The predominant insoluble Pb compounds are lead phosphates, lead carbonates (form when the pH >6), and lead hydroxides (Merian et al., 2004). Lead sulphide is the most stable solid form and forms under reducing conditions. Under anaerobic conditions, a volatile organolead (tetramethyl lead) can be formed due to microbial alkylation (Merian et al., 2004).

2.2.5. Cadmium

Cadmium (Cd) in sediments is derived from both natural and anthropogenic sources. The major factors governing cadmium speciation, adsorption and distribution in sediments include pH and soluble organic matter content (Merian et al., 2004). In oxidizing conditions sediment release Cd as soluble and mobile Cd(II). Cd has a medium to high mobility in acidic soils and sediments, and absorbs rather weakly on

organic matter, clays, and oxides unless the pH is >6. In alkali condition (pH >7) Cd(II) can co-precipitate with $CaCO_3$, or precipitate as $CdCO_3$; Cd phosphates may also limit solubility. Therefore, the mobility and bioavailability of Cd in neutral to alkaline sediments is low (Merian et al., 2004).

2.3. Overview of sediment regulatory guidelines

In Australia, current primary sediment specific guidelines fall under the Australian Interim Sediment Quality Guidelines (ISQG) adopted in 2000 for Australia and New Zealand (Table 2.1). The guidelines were primarily derived from the effects range-low and effects range-median values from Long et al. (1995) and were based on a single large biological effects dataset of North American sediment data. The ISQG also included some metal guidelines adopted for Hong Kong (Chapman et al., 1999).

Table 2.1: Total Concentration (TC) ISQG risk classification

Condition	Risk	Recommended action
TC< ISQG-LOW	Effects negligible	No further investigation -Low priority investigation
TC>ISQG-LOW<ISQG-HIGH	Effects possible	Low – medium further investigation
TC> ISQG-High	Effects expected	High priority for further investigation

Within the sediment guidelines for Australia, there are two benchmark levels for contaminated classification. These benchmarks are classified based on the potential risk at particular concentrations. The two bench marks are ISQG Low that relates to the probably effects concentrations below which biological effects would rarely occur and ISQG High that relates to the probable effects concentrations below these values which biological effects would possibly occur. Concentration above these values represent a probable-effects range within which effects would be expected to frequently occur (ANZECC/ARMCANZ, 2000) see Tables 2.2 and 2.3.

Whilst these thresholds do provide a good benchmark for assessment, they should not be used in isolation. Rather, they should be used as a trigger to determine if further investigation must be conducted.

Table 2.2: ISQG Low and High concentration threshold (ANZECC/ARMCANZ, 2000)

Element	ISQG-LOW	ISQG-HIGH
Arsenic (As)	20	70
Cadmium (Cd)	1.5	10
Chromium (Cr)	80	370
Copper (Cu)	65	270
Lead (Pb)	50	220
Mercury (Hg)	0.15	1
Nickel (Ni)	21	52
Zinc (Zn)	200	410

Table 2.3: Metal contaminant trigger levels for freshwater and sea-water (ANZECC/ARMCANZ, 2000)

Element	Freshwater (µg/l)	Seawater (µg/l)
Arsenic (As)	24 As(III)	-
	13 As (V)	-
Cadmium (Cd)	0.2	0.7
Chromium (Cr)	- Cr (III)	27 Cr (III)
	1 Cr (VI)	4.4 Cr (VI)
Copper (Cu)	1.4	1.3
Lead (Pb)	3.4	4.4
Manganese	1900	-
Mercury (Hg)	0.06	0.1
Nickel (Ni)	11	7
Zinc (Zn)	8	15

3. METHODS

3.1. Core Incubations metal mobilisation

3.1.1. General methods

3.1.1.1. Site description

Samples were collected from four sites along the Gippsland Lakes (Table 3.1, Figure 3.1), focussing on areas where elevated levels of contaminants had been previously identified (Reeves and Trewarn, 2016).

Table 3.1: GPS locations of the sampling sites.

Site name	Location	Date of collection
Heart Morass	38°08'32.92"S 147°07'45.33"E	11/07/2017
Dowd Morass	38°09'32.34"S 147°10'39.45"E	11/07/2017
Hollands Landing	38°03'09.40"S 147°27'43.18"E	18/07/2017
Lake King North	37°52'31.2"S 147°46'25.3"E	03/07/2017

- **Heart Morass** is a large wetland system at the junction of the Thomson and Latrobe rivers. Heart Morass is considered a freshwater wetland, although salinity can increased to oligohaline (1.4-5‰) in the water column. The pH of the water is commonly significantly low (~4; pers. comm. Adrian Clements) and even lower in the underlying sediment (~2-4), due to acid sulphate soils (Unland et al., 2012) WGCMA. The water depth in the sampling region was < 30cm. During dry periods, areas of the wetland can dry out – including complete drying in 2006. The exposed sediments can also dry and oxidise, changing the pH of the sediments and therefore are potential sites for metal mobilisation upon re-wetting. There has been significant revegetation efforts in the Heart Morass over the last 10 years.
- **Dowd Morass** is a large wetland adjacent to Heart Morass, to the south of the Latrobe River, with more frequent connection to Lake Wellington. Salinity is generally higher (brackish) than Heart Morass, particularly during inflow from Lake Wellington, and pH circumneutral, although extensive iron staining are indicative of prior acid release events. The water column was ~0.5m deep at the sampling site

and there was a thick layer of iron-floc on the surface of the sediment. The site was also chosen to understand metal flux due to oxidation and acidification. This site has more remnant vegetation than Heart Morass and did not experience the same extensive drying during the Millennial Drought.

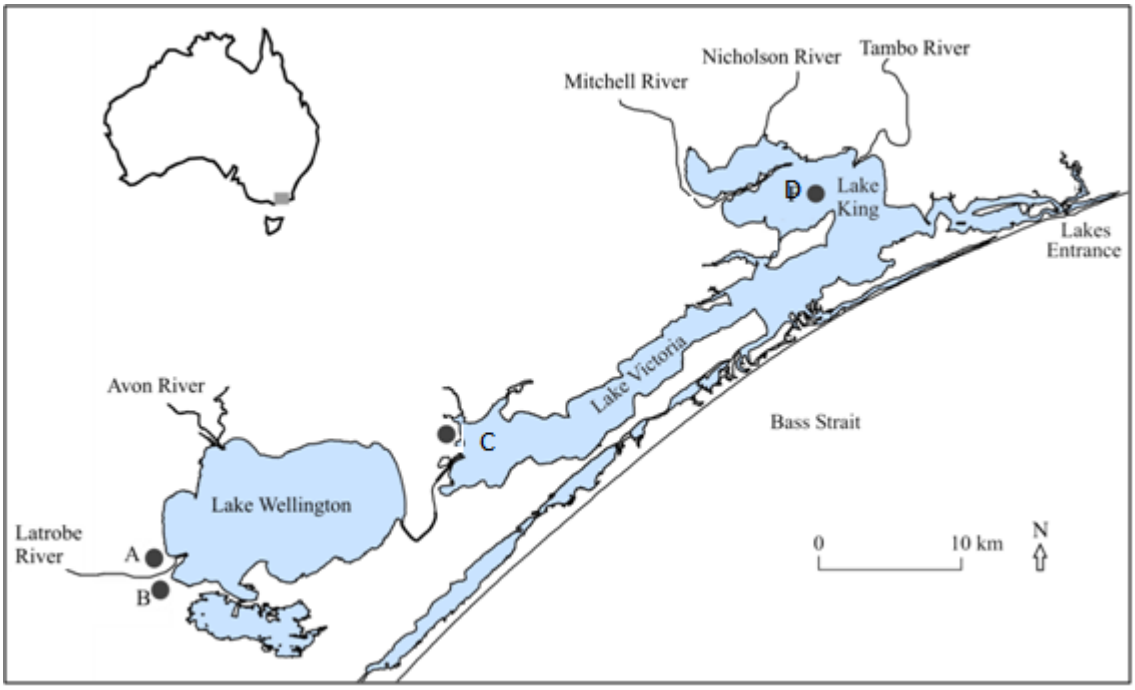

Fig. 3.1: Map of the Gippsland Lakes and major river inputs. Blue shading represents the main water bodies within the lakes. A – Heart Morass, B - Dowd Morass, C – Hollands Landing, D – Lake King North

- **Hollands Landing** is a salt marsh that is commonly hypersaline owing to significant evaporation. The water column is shallow (< 20cm) and it is dominated by anoxic sulfidic sediments owing to high organic matter decomposition. This area is ephemeral and has seen significant swamp paperbark die-back.
- **Lake King North** is a region of the lakes that experiences stratification of the water column induced by freshwater inflow. There are three main rivers which contribute to the Lake; the Mitchell River, the Nicholson River and the Tambo River. It averages 7 – 8 m depth and is commonly anoxic or hypoxic in the bottom waters owing to the salinity stratified water column. Therefore, the site was selected to determine whether these fluctuations in oxygen concentration alter metal mobilisation in the region. These fluctuations have been implicated in recent algal bloom events (e.g. Cook et al., 2015).

3.1.1.2. Sample collection

Intact sediment cores were collected using a piston corer (at depth) or by hand in 27.5 x 6.6cm acid (HCl) washed polyethylene cylinders and stoppered with a rubber bung. Cores collected were kept in a dark cool environment before they were transferred to the laboratory. Cores to be sliced for in situ concentrations of metals were kept in the refrigerator overnight before sub-sampling.

3.1.1.3. Laboratory setup for core incubation

Sediment cores were transferred to a temperature controlled water bath kept at the in situ temperature measured at the time of collection (Figure 3.2). Cores were allowed to equilibrate overnight. The cores were stirred gently to prevent the development of a diffuse boundary layer at the sediment surface. Oxygen concentration in the cores was manipulated with either air or using a hypoxic gas mix (20% air saturate containing 400 mg/kg CO_2) and anoxic cores were sealed.

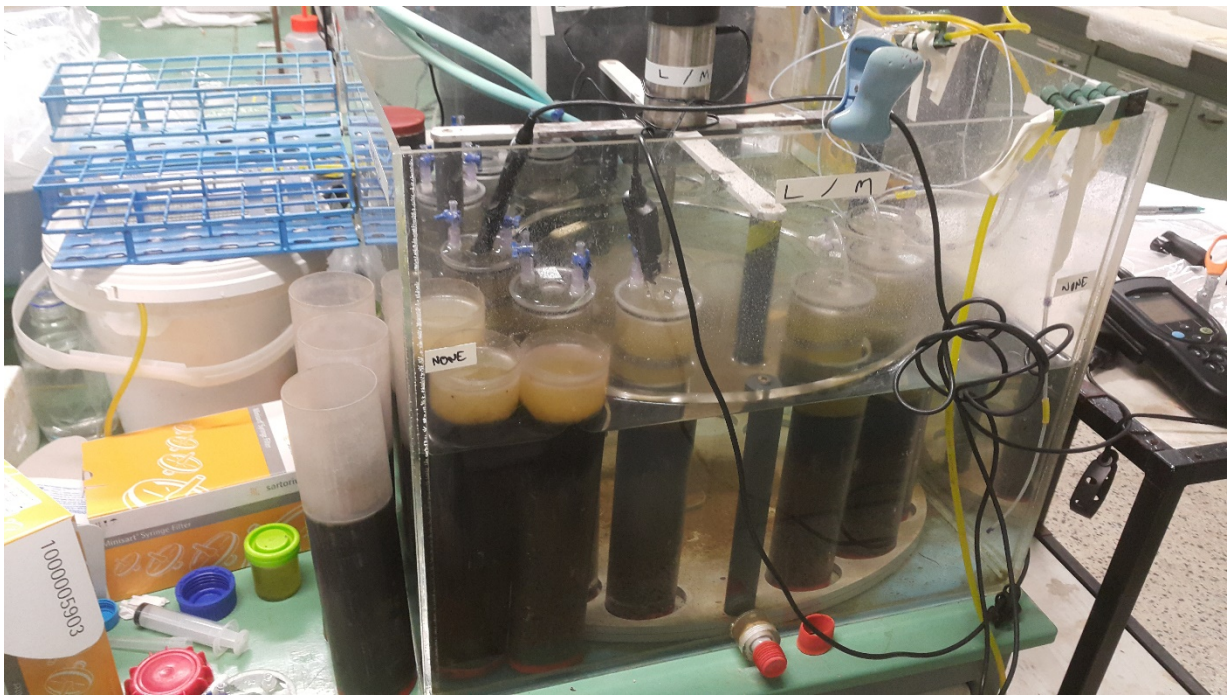

Fig. 3.2: Cores set up for incubation experiment.

At the start of the incubation and for the proceeding sampling times the oxygen concentration (accounting for salinity correction) and pH were measured using a calibrated Hach (40-d) probe. Then 30mL water sample was collected ~10mL was filtered (0.2µm Minisart Sartorius) and frozen immediately for metal speciation and another 10mL filtered sample was collected and preserved with 1mL concentrated nitric acid for total metals and refrigerated until analysis. The 30mL of water removed was replaced with site water and the incubation continued.

At the end of the incubation a final water column sample was collected along with DO and pH. The sediment core was sliced at intervals of 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 7.5, 10.0, 12.5, 15.0cm. The sediment slice was immediately placed into a 50mL centrifuge tube with a rubber septum and purged with N_2 gas for ~5 minutes to minimise oxidation. The samples were then centrifuged at 4000rpm for 10mins to collect the porewater. The porewater was filtered (0.2µm Minisart Sartorius) and a subsample for metal speciation was frozen until analysis. Another 5mL of filtered sample was preserved with 0.5mL concentrated nitric acid. In cases where there was not enough porewater, a smaller subsample was taken and the acid volume adjusted accordingly. The remaining sediment was immediately frozen in liquid nitrogen until it was crushed and dried using a freeze dryer.

In a subset of each treatment the moisture content of each sediment slice was determined after drying a known amount of wet sediment in the oven at 70°C for at least 1 week. Moisture content was calculated from the difference between the dry and wet mass.

3.1.2. Site Method

3.1.2.1. Heart and Dowd Morasses

Sample collection: 10 cores samples were collected per site, 8 for incubation, 2 *in situ* slicing.

Lab experiments: Sediment cores were collected and set up as described in sections 3.1.1.2 and 3.1.1.3. Water samples were collected (method 1.3) periodically throughout the incubation to determine the sediment-water flux of metals in the treatments. There were two treatments per site; cores kept under '*in situ'* conditions (temperature controlled and aerated) and cores that were dried in the oven and re-wet.

Water column samples were collected on day 1, the water column was then removed from the drying treatment and the cores kept at room temperature. For 2 weeks before being placed in the oven at 40°C to increase the drying process. Water samples were taken in the meantime in the remaining cores with a water column.

After drying (28/08/2017) the water column was replaced in three cores per site. The two remaining cores for each site were sliced to determine the background concentration of metals in the sediment (no pore-water was collected).

Water samples were collected in all cores (*in situ* and re-wet) for an additional 4 week before the cores were sliced and pore-water collected. The re-wet cores were kept for a month after re-wetting to observe to the change in the pH over time.

3.1.2.2. Hollands Landing

Sample collection: 14 sediment cores samples were collected, 12 for incubation and 2 for in situ slicing.

Lab experiments: Sediment cores were collected and set up as described in sections 3.1.1.2 and 3.1.1.3. Water samples were collected periodically throughout the incubation to determine the sediment-water flux of metals in the treatments. There were three cores per treatment; *in situ* (anoxic), oxic (aerated), drying and re-wetting (anoxic), altered salinity (anoxic).

For the first 3 days all cores were kept under 'in situ' conditions (temperature controlled and anoxic). On day 4 (24th July) the treatments were changed, 3 cores kept *in situ*, 3 cores oxygenated, 3 cores placed in oven at 40°C, the water column changed in 3 cores to a salinity of 7.4‰ to mimic flushing in a rain event. At this time 100 mL of the water column was exchanged with 100 mL of water at site salinity. In addition to the oxygen and pH measured in the water column, when the meter was available conductivity was also measured using a Hach (40-d) probe.

All treatments were maintained throughout the incubation. With the exception of the salinity treatment; on day 10 in the salinity treatment 50 mL of water was replaced with water of site salinity to increase the salinity to 22‰. Day 15 the salinity was further increased to 35 ‰ by replacing 100mL of the water column with water of site salinity. The whole water column in the salinity treatment was replaced with site water (salinity 70‰) on day 37.

Cores for the drying and re-wetting experiment were kept in the oven from Day 4 to day 40. The cores were re-wet with site water and maintained under anoxic conditions. One dry core was sliced to determine the metal concentration in the sediment before re-wetting. The incubation was ended day 47. All cores were sliced and the pH of the sediment measured using a food grade pH probe. Water and sediment samples were treated as described in general methods.

3.1.2.3. Lake King North

Sample collection: 20 sediment cores were collected, 18 for incubation experiments and 2 for in situ slicing.

Lab experiments: Sediment cores were collected and set up as described in sections 3.1.1.2 and 3.1.1.3. Water samples were collected (section 3.1.1.3) periodically throughout the incubation to determine the sediment-water flux of metals under changing oxygen conditions in three oxygen treatments anoxic (sealed core), hypoxic (bubbled with 20 % air saturated gas mix) and oxic (bubbled with air).

For the first two days (5-6 July 2017) after collection all cores were kept at in situ temperature and aerated. Six cores were kept under these conditions for the duration of the incubation to act as controls (oxic treatment). The oxygen concentration was altered on Day 3 (7th July AM) to reflect the two treatments; anoxic and hypoxic in the remaining 12 cores. Two cores from each treatment were sliced ~ 4 – 6 hours after the oxygen concentration was changed to determine if there was any immediate release of metals upon changing oxygen conditions. The remaining cores were kept at the oxygen concentration in the three treatments for 7 days. On day 10 of the incubation (14th July AM) 2 cores from each treatment were sliced to determine whether the budget of metals in the sediment had changed over the 7 day period. Day 10 the oxygen concentration was switched back to oxic by aerating the water column in the remaining cores. The remaining cores were sliced on day 15 (19th July 2017) to determine whether there was a change in metal mobilisation after re-oxygenated of the sediment.

3.2. Water Quality Analysis

Water quality parameters were measured in the field using a calibrated Hydrolab (DSX5) or Horiba U-50 multimeter that measured temperature, salinity, dissolved oxygen and pH. At the Lake King North site where the depth was ~ 7m, the water quality parameters were measured at the surface and bottom. Water samples for the analysis of in situ metal concentrations were also collected using a 0.2µm filter (Sartorius Minisart filter) and frozen until analysis for total dissolved metals. An unfiltered water sample was also collected to determine total metal concentration in the water column.

3.3. Chemical Analysis

3.3.1. Soil/sediment

3.3.1.1. Digestion

Collected samples were taken into plastic zipper bags and stored in freezer at -80°C. The frozen samples were then freeze dried and homogenize by grounding using a mortar. The homogenized samples were taken into plastic zipper bags under room temperature until digestion for chemical analysis.

Sediment samples were digested using a modified US-EPA 3051 method (EPA, 2007). This entails 0.5 g of dried homogenised (<50 µm particle size) sample was digested with 6.6 ml HNO_3 and 3.3 ml HCl. Controlled heated digestion was carried out using a Milestone ethos-up microwave digester unit fitted with a SK-15 high-pressure digestion vessels. Samples were then allowed to cool before removal from the microwave and degassing of the vessels (approximately 15 min).

Digested samples were then transferred to 50 ml centrifuge tubes, and final volume made up to 25 ml and allowed to settle before dilution for analysis on ICP-MS.

3.3.1.2. Analysis of samples by ICP-MS

Analysis of digested samples was undertaken on an Agilent 7900 ICP-MS. Calibration of the elements was carried out using a 5-7 point calibration. Stability and interference control was established using an in-line multielement internal standard. For machine stability, Tb159 was primarily used as this was found to be in negligible quantities in

the analysed samples. Recalibration of the ICP-MS was performed when standard internal drift went outside 90-110%.

3.3.1.3. Data refinement

ICP-MS data was primarily refined based on recovery of Certified Reference Matrials (CRMs; No 667 for total metals and ERM-CC580 for Hg). Sample concentrations were compensated and corrected based on the associated CRMs' recovery rates. Corrections were only carried out on elements that had a recovery outside 10% of the certified CRM concentrations. However, the final batch of samples that had a low Hg recovery were compensated for using the batches own CRM as using the average recovery would have undercorrected the concentrations.

3.3.1.4. Quality Control (QC) and Quality Assurance (QA)

All tubes and centrifuge tubes were washed in 5% nitric acid and rinsed thoroughly with ultrapure water. All core equipment was washed in 10% HCl and rinsed with ultrapure water before use.

In-batch controls included spiked samples and dilution replicates in every 5 samples processed. CRM and digest blanks were included in every rotor batch processed to determine any deviation in digestion.

3.3.2. Water analysis for heavy metals

Porewater samples were collected by centrifuge from all of the sediment samples. In addition, water from the water column of each of the incubated cores was also collected. These water samples were analysed commercially at EAL, Southern Cross University using an in-house method: W32, adapted from the standard methods (APHA 3125). Heavy metal analysis was done using a Perkin Elmer NexION 300D ICPMS. Note that in all samples, Hg, Pb and Zn were below detection limit and therefore not presented in the graphs herein.

4. RESULTS AND DISCUSSIONS

4.1. Water Quality

Water quality of the Gippsland Lakes was tested *in-situ* at sites: Heart Morass (HRT), Dowd Morass (DOW), Hollands Landing (HOL) and Lake King North (LKN). Water quality data are presented in Table 4.1.

Table 4.1: Water quality data from sampling sites of the Gippsland Lakes

Sampling Sites	Temperature (ºC)	pH	Salinity (mg/L)	DO (mg/L)
Heart Morass	9.21	6.69	1.4	9.39
Dowd Morass	11.61	6.34	5.6	9.26
Hollands Landing	18.1	8.15	70+	0.48
Lake King North - surface	9.56	7.44	27.6	8.08
Lake King North - (7m)	12.92	7.13	32.3	2.02

Water temperatures at Lake King North were recorded as 9.56 °C and 12.92 °C in the surface and bottom water, respectively. Water temperature at Dowd Morass was higher (11.61 °C) than that in Heart Morass (9.21 °C). The highest water temperature was recorded in Hollands Landing (18.1 °C).

The pH at Lake King North was 7.13-7.44, while it was 6.34 and 6.69 at Dowd and Heart Morass, respectively. Alkaline conditions were recorded at Hollands Landing (8.15). Salinity of surface and bottom water at Lake King North differs substantially (27.6 and 32.3 mS/cm for surface and bottom, respectively). At Dowd and Heart Morass, salinity was very low (Table 4.1) indicating these sites predominantly freshwater; however, hypersaline conditions were present at Holland Landing, exceeding the range of the instrumentation (70+ mS/cm).

Dissolved oxygen (DO) was 9.26, 9.39, and 8.08 mg/L at Dowd and Heart Morass and Lake King North (surface), whereas Lake King North (-7m) and Hollands Landing were hypoxic (2.02 mg/l and 0.48 mg/L).

These field measurements were taken into consideration when designing the incubation experiments, particularly with regards to alteration in dissolved oxygen and salinity.

4.2. Heavy metals in sediments

A representative of one control (*in-situ*) and one treated core of each manipulation experiment, from each sampling site was sliced, freeze-dried, digested and analysed for total metals. Other replicate cores have been archived for future experiments.

4.2.1. Heart Morass

Heart Morass is a large wetland system at the junction of the Thomson and Latrobe Rivers. The wetland has seen increasing salinity in the water column, particularly in recent years, and sulfidic material prevalence in the soils. During dry periods, the wetland sediments can dry out changing the pH of the sediments and therefore are potential sites for metal mobilisation upon re-wetting. Laboratory experiments were conducted by drying and re-wetting the natural sediment, to simulate these conditions. The results of heavy metal concentrations in treated sediments were compared with that of natural (*in situ*) sediments to see if there was a mobility of metals from the sediment into the porewater.

Due to drying and re-wetting of the natural sediment in the laboratory, the changes of pH and DO in the sediment over the period of incubation time are shown in Figure 4.1. Surprisingly the pH of the overlying waters of the undried sample was lower than that of the dried and re-wet sample. The control sample dropped more than 2 pH points over a quick period of time to around 4.5, suggesting acid sulfate materials, and then stabilised. This would have implications for any biota living in such water. Note that the decreases in O_2 levels at the commencement of the experiment were due to a blockage in the line, which was quickly rectified.

Cr concentration in the natural sediment was below the ISQG lower values, while its concentration in the treated (dry and re-wet) sediment between the depth of 4-15 cm was above the ISQG lower values as set by ANZECC/ARMCANZ (2000) (Fig. 4.2). Ni concentrations in the natural sediment was between the ISQG lower and higher values, however, its concentrations in the treated sediment between the depth of 4-15 cm was above the ISQG higher values. The concentrations of other heavy metals (e.g. Cu, As, Zn, Cd, Hg, Pb) in treated and natural sediments were below the ISQG lower values (Fig. 4.2). However As, Hg and Pb were all elevated, in some cases exceeding the lower trigger values.

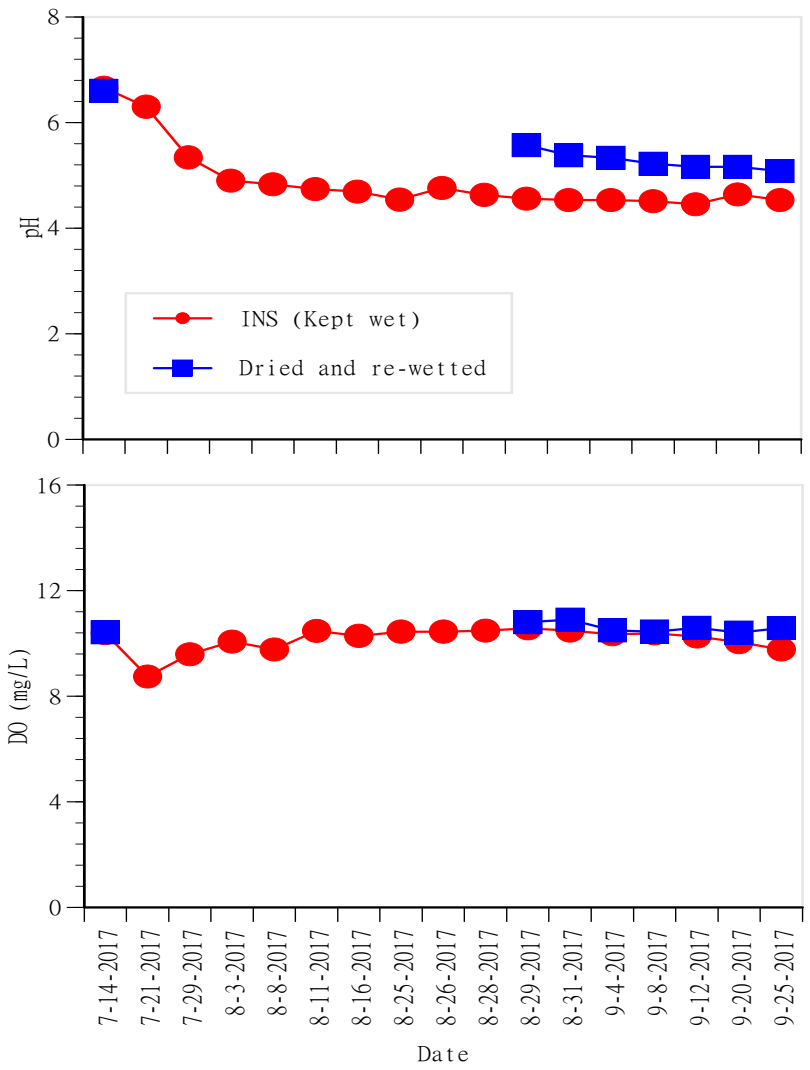

Fig. 4.1: Changes of pH and DO in the water column over the period of incubation time due to re-wetting (red = control sample, blue = dried and rewet).

Metal concentrations in sediments and porewater are presented in Figure 4.2 and Figure 4.3, respectively. The results of the incubation experiment, with involved drying and re-wetting of the cores, reveal that Cd, Cr, Mn, Ni, Pb and Zn all increased in the sediment, whereas As and Hg decreased. Unfortunately porewater concentrations of Hg, Cd and Pb were below detection and so fluxes cannot be verified. Also, not all samples recovered enough porewater in the treated samples to be analysed, hence some gaps in the data. However, porewater concentrations of Zn, Mn (Fig. 4.3) and Ni all increased significantly in the rewetting experiments. Ni and Zn levels both exceed trigger levels in the treated sediment samples and Ni, Zn and Cu exceeded trigger levels for porewater in both the treated and untreated samples. As and Cr also attained high concentrations in the lowermost samples of both the treated and untreated sediments and warrant speciation determination.

Analyses of the overlying water of the cores were also tested at the commencement and cessation of the treatments (Table 4.1). Note that again recovery for Hg, Pb and Cd was below detection. Almost all metals in both the treated and untreated samples showed a decrease in concentration – in some cases quite significant, with the exception of Mn, and Zn in the untreated sample. Contaminant trigger levels were exceeded for Zn and Ni in all samples and for Cu in the initial samples. The flux of metals during the experiment seems to be predominantly from the water column into both the sediment and porewater.

Table 4.2: Metal analyses for water column samples prior to and at the cessation of incubation experiment for Heart Morass. All concentrations in µg/L. Values in red exceed the contaminant trigger levels (ANZECC/ARMCANZ, 2000).

		As	Cr	Cu	Mn	Ni	Zn
In Situ	Initial	0.3	7.3	1.6	456.3	32.5	28.5
	Final	0.4	0.6	0.4	1137.5	15.2	76.9
Dry & re-wet	Initial	1.2	1.3	5.7	592.5	107.8	683.8
	Final	0.4	1.0	0.8	1031.5	23.3	103.9

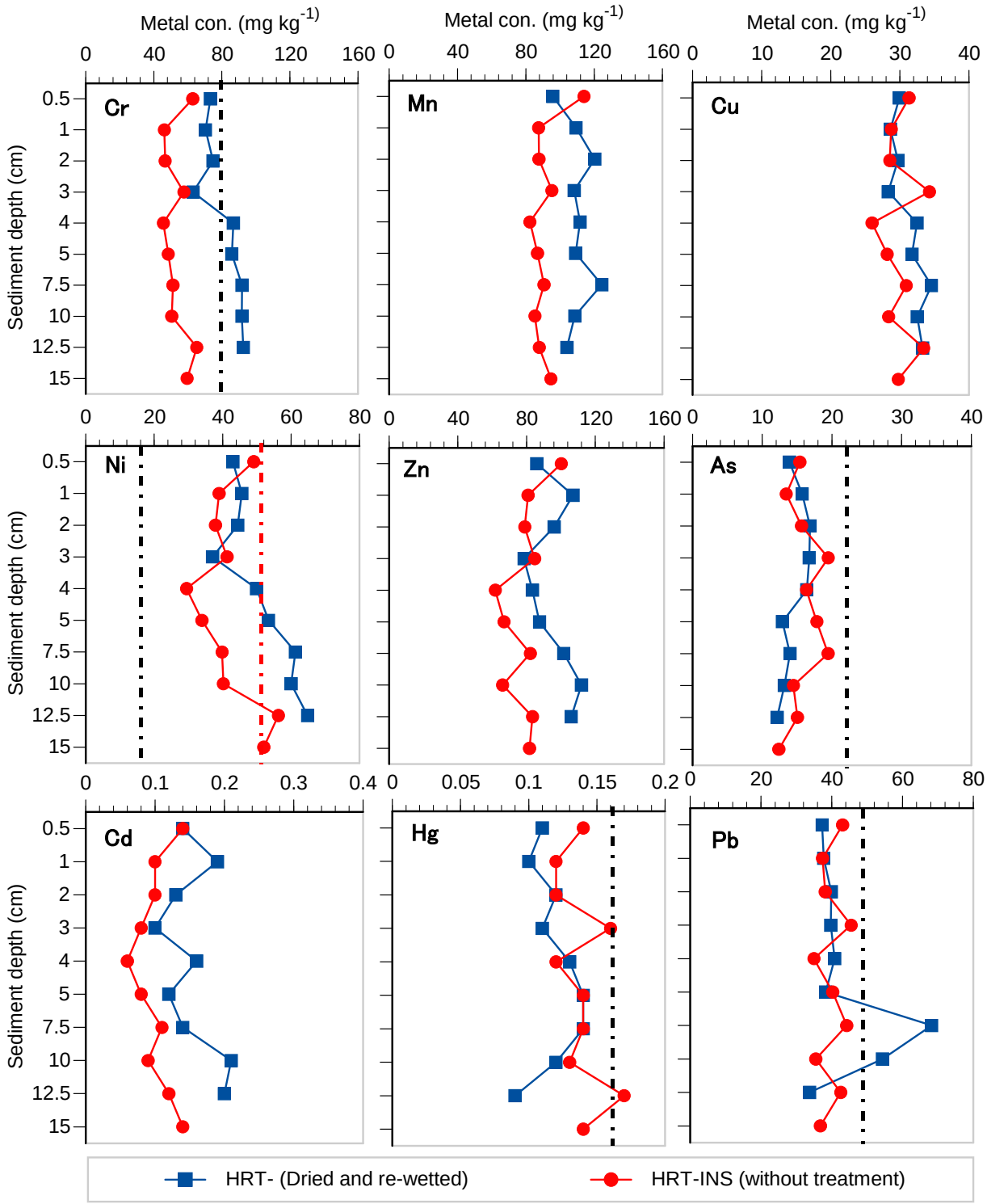

Fig. 4.2: Mobilization of heavy metals in sediments from Heart Morass (HRT) under dry (blue) and unaltered conditions (red). The dashed lines represent the ISQC low (black) and high (red) trigger levels.

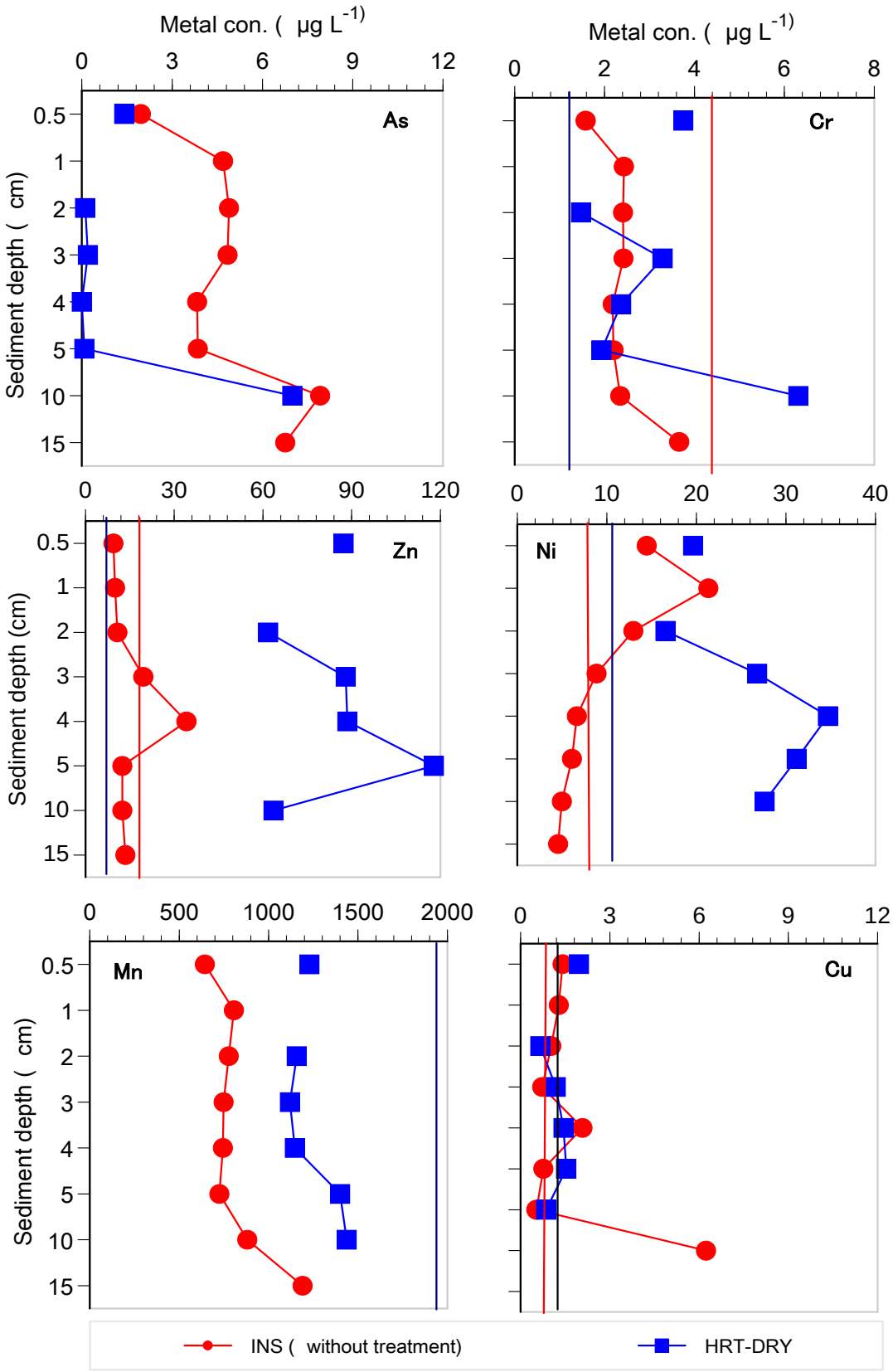

Fig. 4.3: Mobilization of As, Mn, Cr, Ni, Cu and Zn into porewater from sediments of Heart Morass (HRT) under dried and re-wet (blue) and natural (red) conditions. Trigger values; freshwater (blue line) and seawater (red line).

4.2.2. Dowd Morass

Dowd Morass (DOW) is a large shallow wetland, usually with low salinity and prevalence for acid sulfate soils. The water column was ~0.5m at the sampling site and there was a thick layer of iron-floc on the surface of the sediment. Ten cores samples were collected per site, 8 for incubation, 2 *in situ* slicing. There were two treatments per site; cores kept under '*in situ*' conditions (DOW-*in situ*) and cores that were dried in the oven and re-wet (DOW-WC), to simulate wetting and drying conditions of floods and drought and promote oxidation. Water quality changes of the overlying water column were sampled throughout the experiment for pH and dissolved oxygen (DO over the period of incubation time due to re-wetting are shown in Figure 4.4).

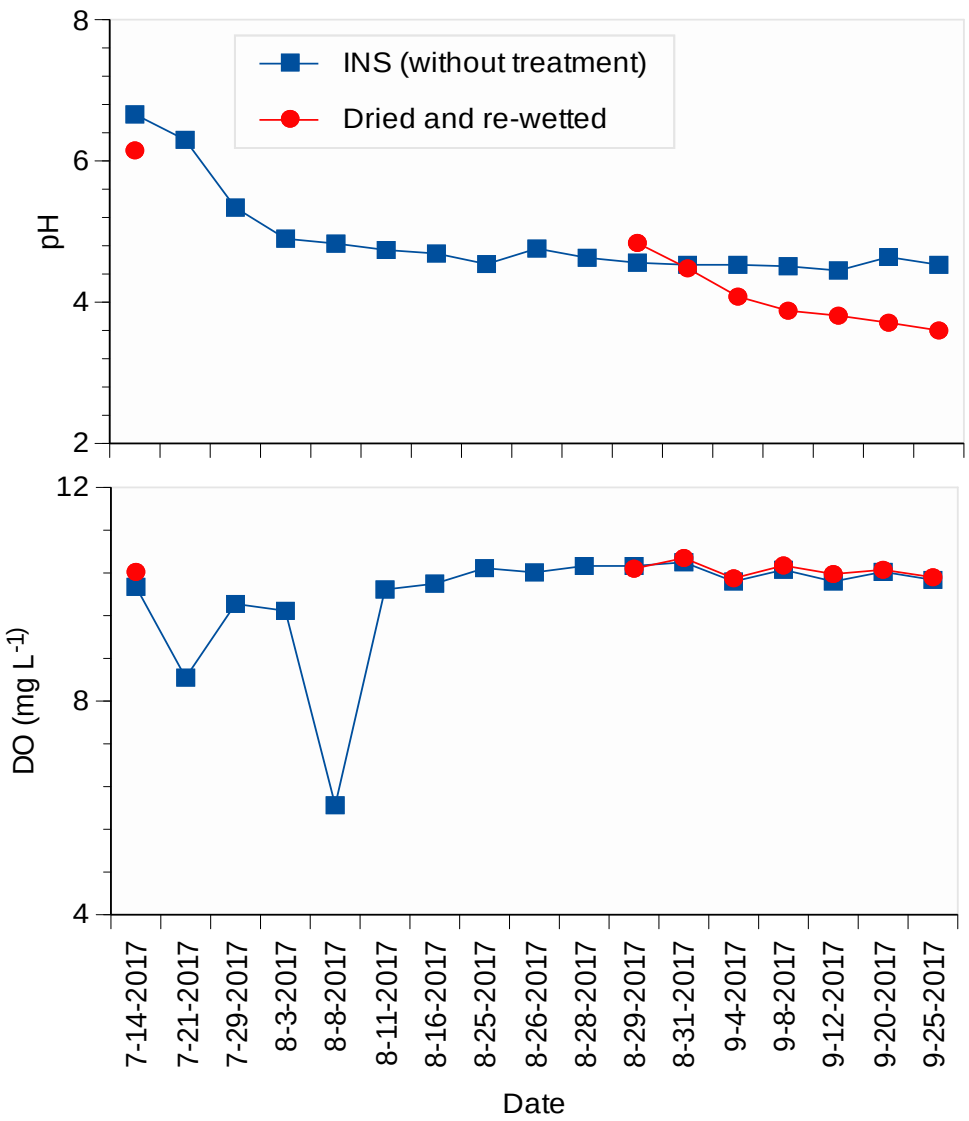

Fig. 4.4: Changes of pH and DO of the water column over the period of incubation time due to drying and re-wetting (red) and in the control (blue) cores.

Water samples were collected from both the DOW-*in-situ* (DOW-INS) and DOW-WC and metal concentrations were measured in sediment and pore-water to see metal flux into the water column from the sediments. Metal concentrations in sediments are shown in Figure 4.5 and in the porewater in Figure 4.6. The water column was also tested for metal concentrations at the commencement and cessation of the incubation experiments (Table 4.2).

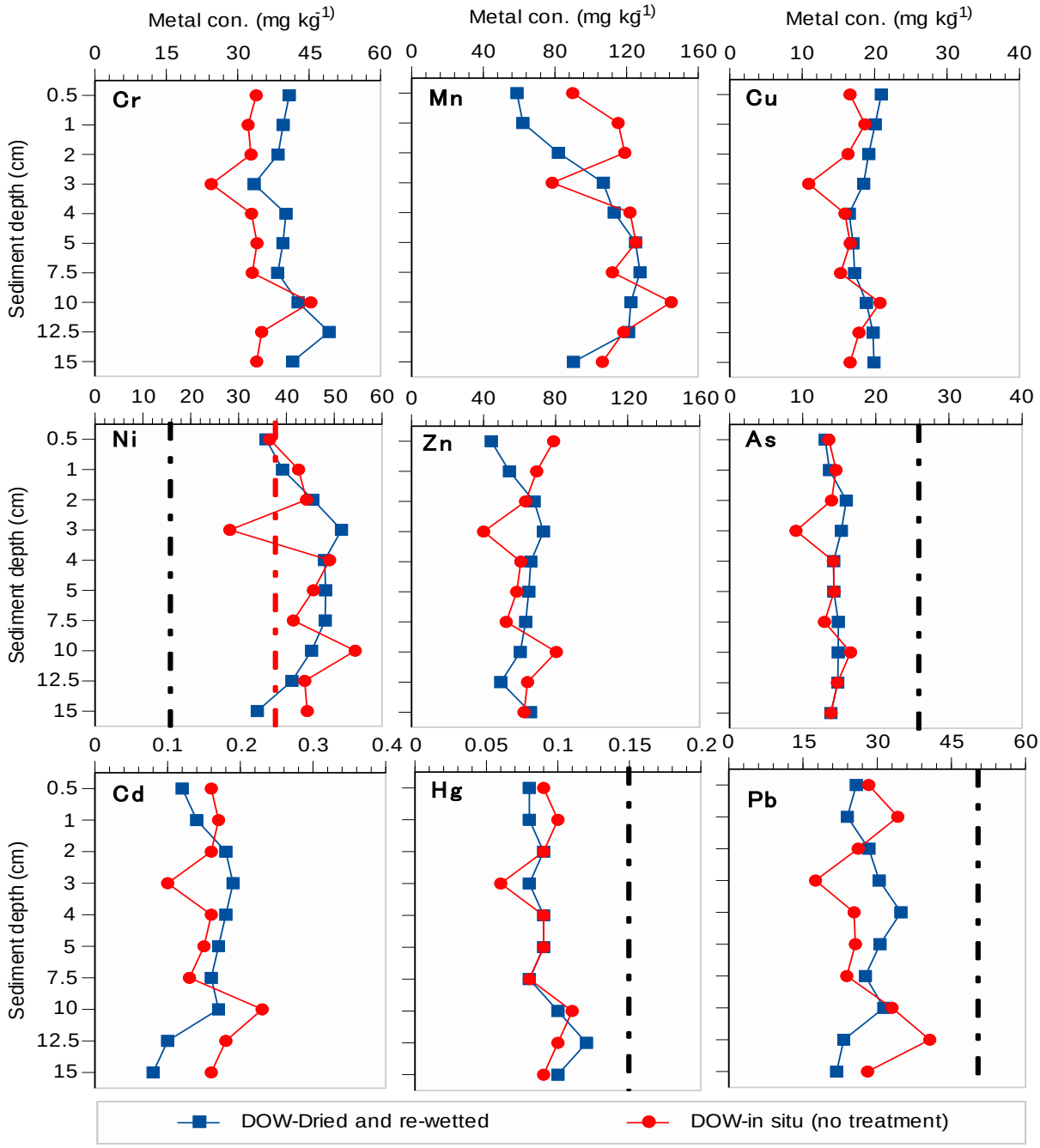

Fig. 4.5: Mobilization of heavy metals in sediments from Dowd Morass (DOW) under dried and re-wet (blue) and natural (red) conditions. The dashed lines represent the ISQC low (black) and high (red) trigger levels.

Results for the sediments showed that all metals in both the treated and untreated samples were below the ISQC guidelines, with the exception of Ni, which were within the ISQG Lower and upper values as set by ANZECC/ARMCANZ (2000). As, Hg and Pb had elevated levels approaching the low ISQC trigger. The drying and re-wetting experiments generally produce little metal flux, with the exception of slightly elevated concentrations of Cr, Cu and Hg and lower concentrations of Zn in the upper 5 cm of the core. Note that all metals recorded decreased concentrations at 3 cm, which may be due to the presence of some external material, relatively diluting the total metal concentration.

Analysis of the porewater showed low concentrations for most metals, but fairly consistent trends between treated and untreated samples. Both the treated and untreated porewater exceeded the trigger levels for Zn in the uppermost samples. Cr levels were elevated in the lower samples and may warrant testing for speciation. Cr and Cu were higher in the majority of the treated samples, whereas Zn was lower. Mn concentrations in treated sediment were lower than the un-treated sediment between 0.5-3.0 cm of the core (Fig. 4.6). The marginally higher levels of Mn in the porewater of treated sediment compares with the untreated sediment (DOW-INS) (Fig. 4.5) indicate that some of the Mn was likely to be released into the porewater from the sediment by treatment. Ni concentrations throughout the core were inconsistent for both the treated and un-treated sediment. It is not clear why Cr, Cu and Hg concentrations in treated sediment were higher than the un-treated sediment in the upper layers of the core.

The water column samples showed a significant increase flux of Ni, Zn and Cr in both the treated and untreated samples, with concentrations of each of these metals higher in each of the untreated samples. The concentrations of Ni, Zn and Cu exceeded trigger levels in all but the treated Cu sample. Concentrations of As and Cu increased in the *in situ* samples and decreased in the treatment samples. The decrease in pH of the water column may be responsible for the flux of Ni and Zn, particularly in the uppermost samples of the core.

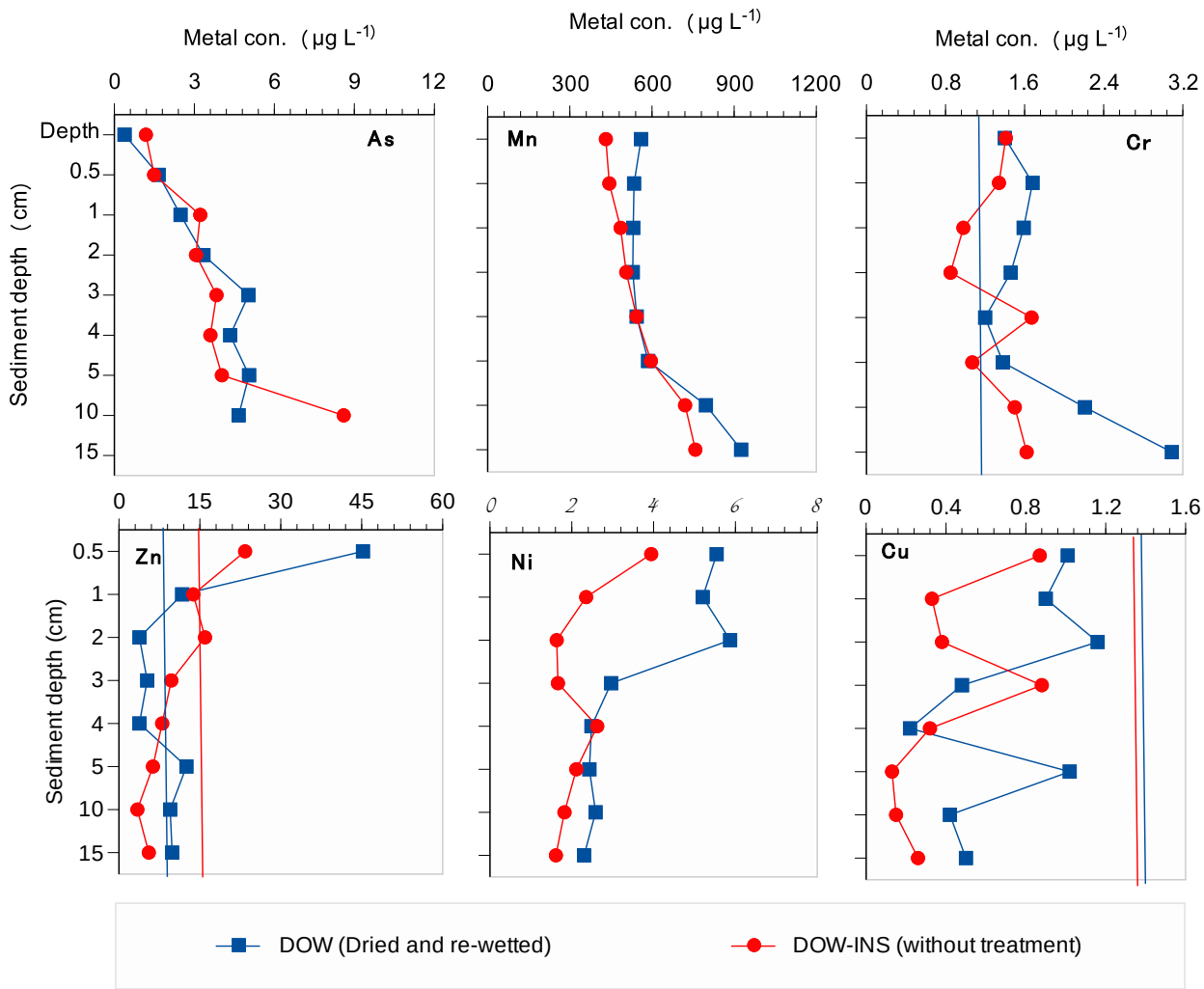

Fig. 4.6: Mobilization of As, Mn, Cr, Ni, Cu and Zn into porewater from treated (dried and re-wetted) and natural (without treatment) sediments of Dowd Morass (DOW). Trigger values; freshwater (blue line) and seawater (red line).

Table 4.3. Metal analyses for water column samples prior and at the cessation of incubation experiment for Dowd Morass. All concentrations in µg/l. Values in red exceed the contaminant trigger levels (ANZECC/ARMCANZ, 2000).

		As	Cr	Cu	Mn	Ni	Zn
In Situ	Initial	0.7	1.7	2.1	403.8	75.4	164.4
	Final	2.5	6.2	2.8	384.8	218.2	292.3
Dry & re-wet	Initial	0.9	0.8	2.3	353.9	15.1	14.2
	Final	0.1	1.3	0.9	580.4	25.0	70.3

4.2.3. *Lake King North*

4.2.3.1. Metal mobilization under anoxic condition

Lake King North is a region of the Gippsland Lakes that experiences stratification of the water column induced by freshwater inflow on the surface and saline tidal inflow at depth. It is located close to three main river entrances; the Mitchell River, the Nicholson River and the Tambo River. Its' average depth of water column is 7 – 8 m and is commonly anoxic or hypoxic in the bottom waters owing to the salinity stratified water column. However, mixing can occur, bringing oxygenated waters to the deeper zones. The site was selected to determine whether these fluctuations in oxygen concentrations (oxic, anoxic and hypoxic) alter metal mobilisation in the region. The oxygen content and pH of the overlying water column were tested throughout the course of the experiment (Fig. 4.7). pH was seen to maintained throughout the experiment, but oxygen levels were dropped to around 2 g/L and 0 g/L for the hypoxic and anoxic experiments respectively.

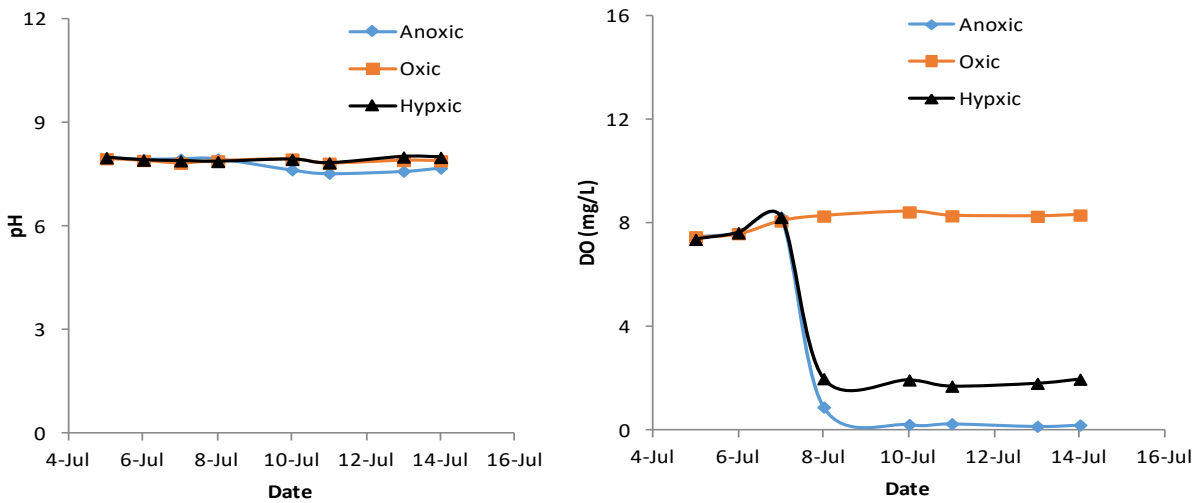

Fig. 4.7: Changes of pH and DO over the period of incubation, with changes in oxygen concentration (oxic – orange, hypoxic – black, anoxic – blue).

Metals concentrations of the sediment were analysed at the cessation of the experiment, on the dried samples and extracted porewater (Figs. 4.8). Concentration of each of the metals was again low, with the exception of Ni, which was in between the low and high ISQC trigger values. Elevated levels of Cr, As and to a lesser extent, Hg were recorded at some depths. Almost all of the metals showed lower concentrations in the sediment after the anoxic treatment, suggesting that the metals were released into the porewater and/or water column. The results indicate that if

oxygen levels in the sediment decrease due to stratification, such as by freshening of surface waters through flood, metals are likely to be released into the water column from the sediment. This result is in agreement with the report of DeLaune and Smith (1985) that anoxic conditions result in the release of the higher concentrations of metals into solution.

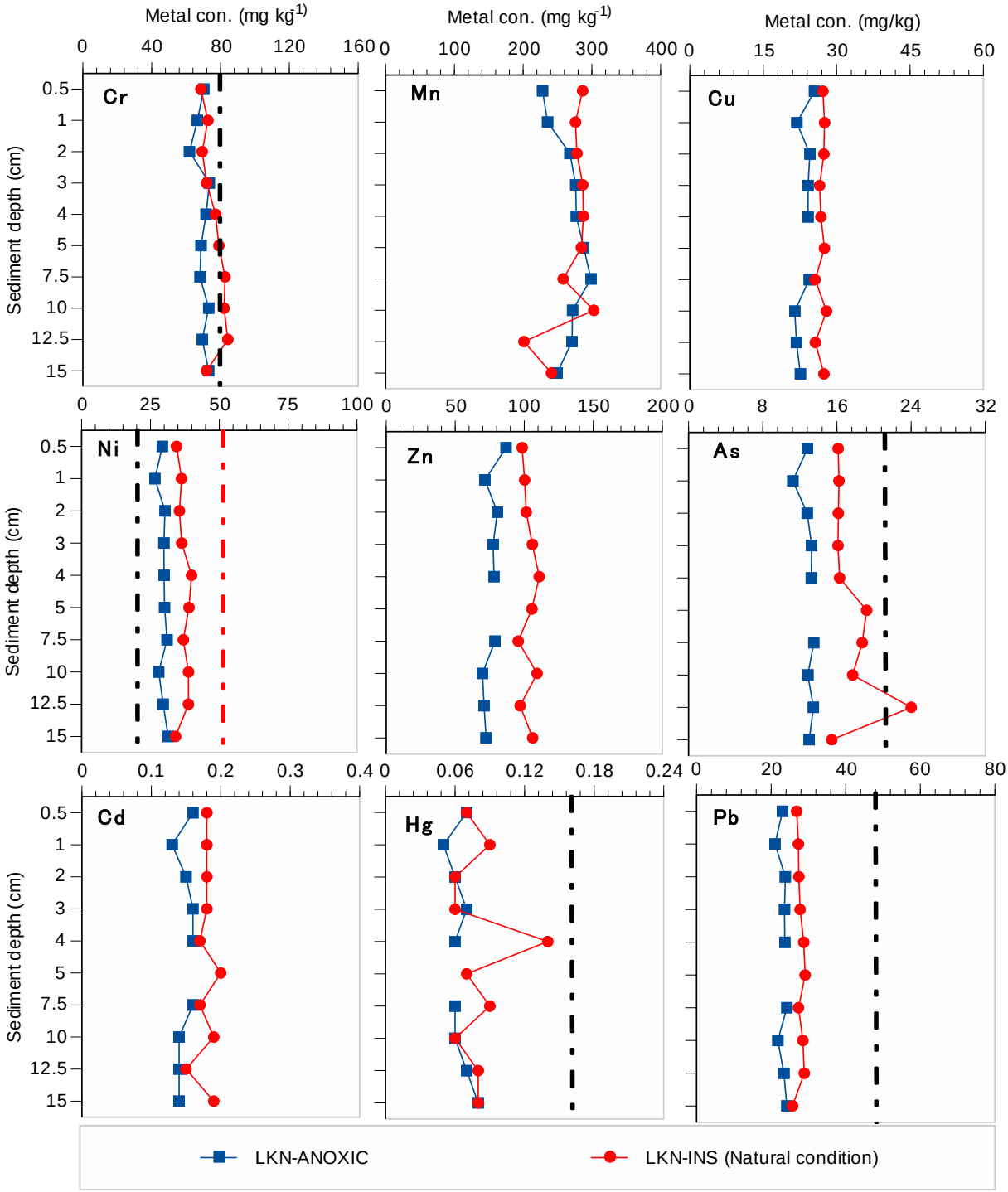

Fig. 4.8: Mobilization of heavy metals in sediments from Lake King North (LKN) under anoxic (blue) and natural conditions (red).

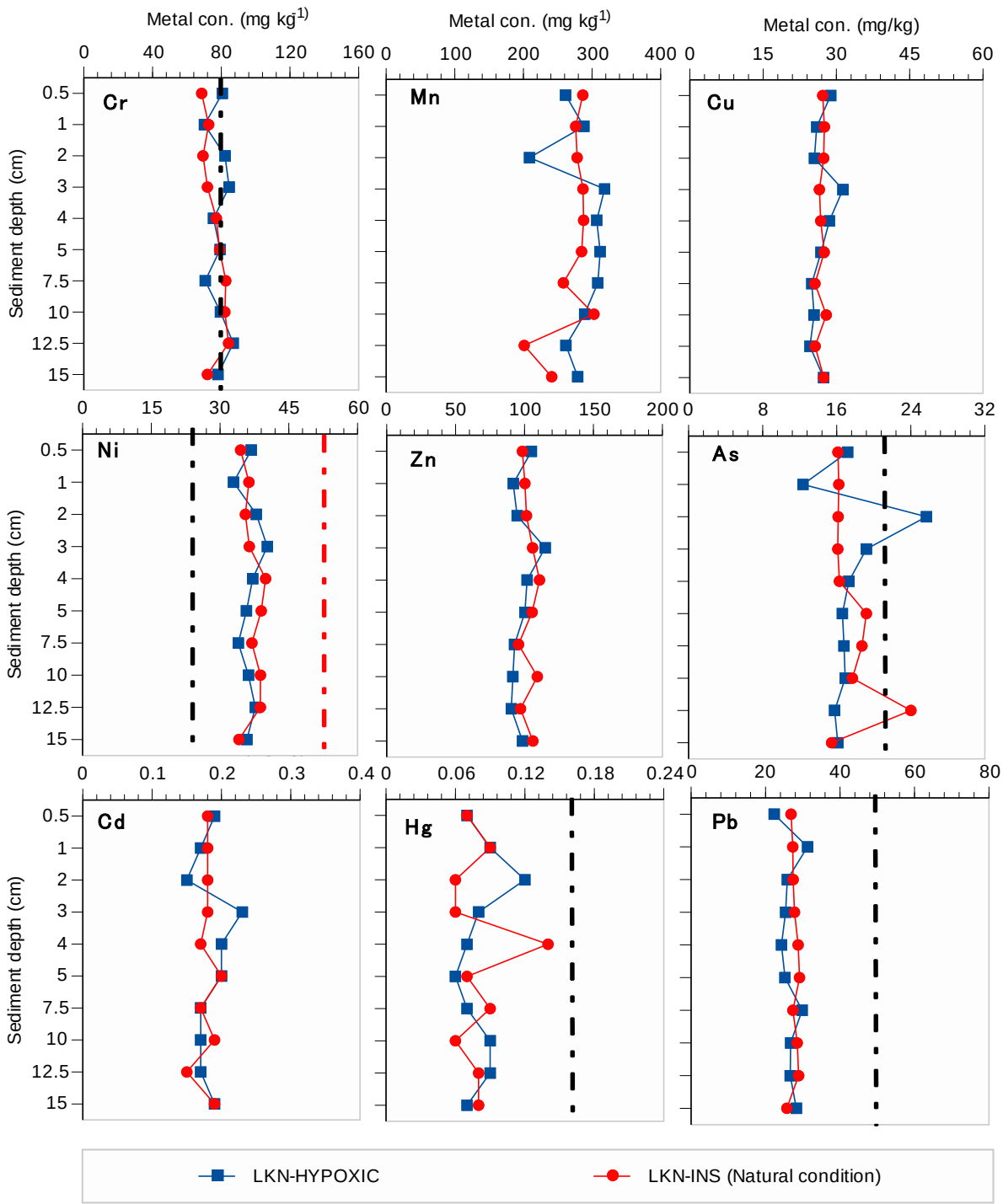

Fig. 4.9: Mobilization of heavy metals in sediments from Lake King North (LKN) under hypoxic (blue) and natural (red) conditions.

4.2.3.2. Metal mobilization under hypoxic condition

A further experiment was undertaken whereby the samples were incubated under low oxygen conditions. In general, no consistent or significant differences in metal concentrations between natural sediment (LKN-INS) and hypoxic sediments (LKN-

HYP) were observed in this study (Figs. 4.9). This implies that hypoxic conditions are unlikely to influence metal mobilization in the water in Lake King North.

One exception to this is the elevated levels of As in the upper sediments, in excess of the ISQC low trigger. As this is not coupled with a decrease in As in the porewater at this depth, it is suggested that further sampling be undertaken to confirm the response. Note that the anomalously high concentration of Hg in the untreated sample at 4 cm depth is not replicated in the hypoxic sample, suggesting that the untreated reading may be an outlier.

4.2.3.3. Metal mobilization under oxic condition

To understand the influence of changes in oxidation conditions on metal mobility in lake sediment, the sediments were bubbled with air to simulate oxic conditions with the breakdown of stratification. The results showed that, in general, there was little flux between the metals in the sediment and water. Each of the metals As, Cr, Cu, Ni and Zn showed slight decreases in the sediment, with more significant decreases in Cd, Pb and Hg, and only Mn increasing (Figs. 4.10).

The results indicate that oxidation treatment is likely to release Cd, Pb and Hg in the pore water from the sediment. A previous laboratory experiment under natural conditions (e.g. constant pH) showed that re-oxidation of the sediment can remobilise up to 2% of the particulate bound Cd from the sediments (Petersen et al., 1997).

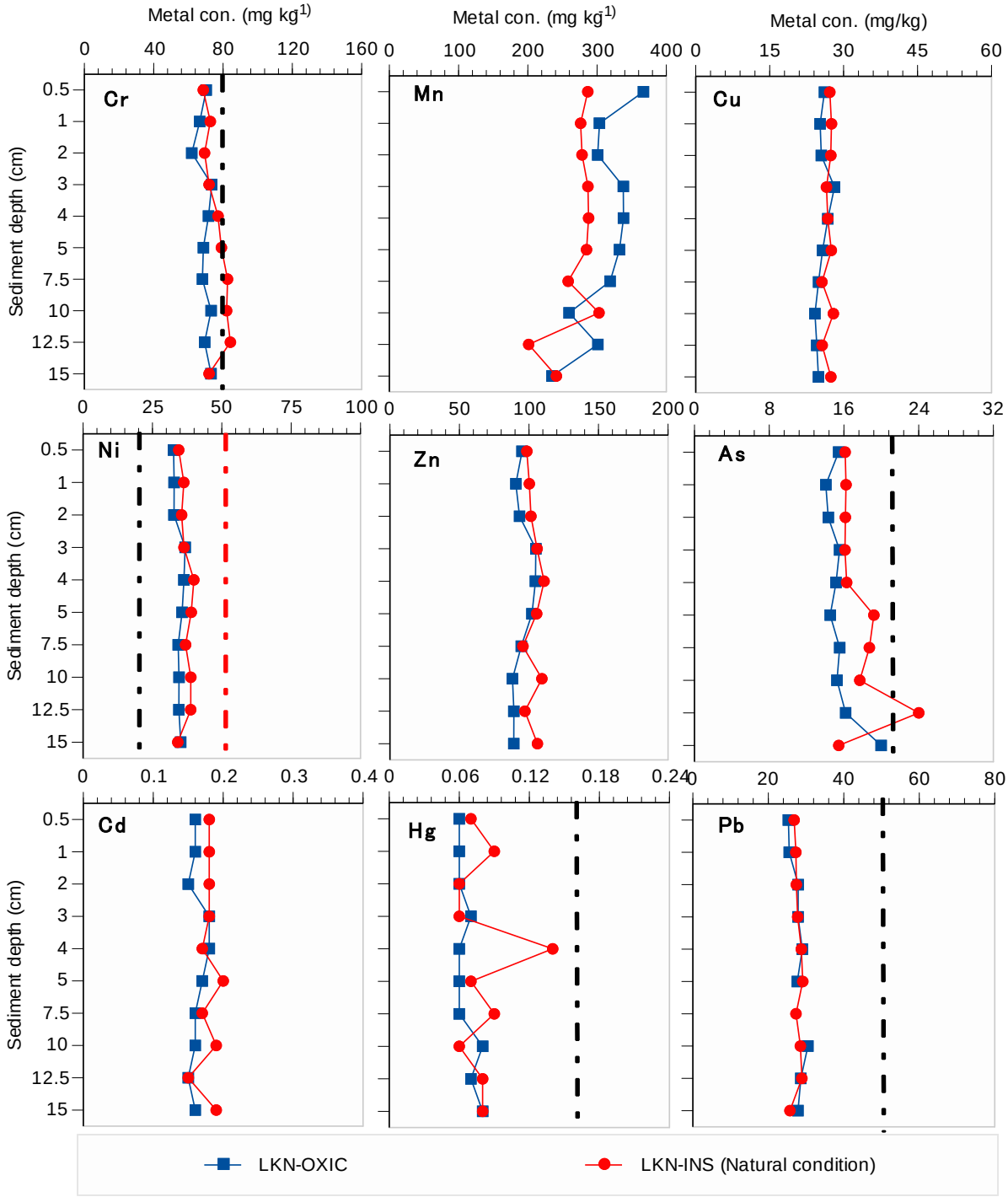

Fig. 4.10: Mobilization of heavy metals in sediments from Lake King North (LKN) under oxic (blue) and natural conditions (red).

4.2.3.4. Metal fluxes in porewater of Lake King North through incubation experiments

Fluxes of metals between the sediment and waters through the different incubation experiments for Lake King North are shown in Figures 4.11. Although there is

significant variation in some metals, most show the same general trend. The highest metal concentrations in the porewater are found in the anoxic treatments for As, Zn, Cr and Ni, whereas the oxic treatments produced the highest levels for Cu and Mn. Metals in the porewaters exceeded seawater trigger levels for Zn and Cu in the oxic and anoxic treatments for the upper 1 cm and in the lower 10 cm.

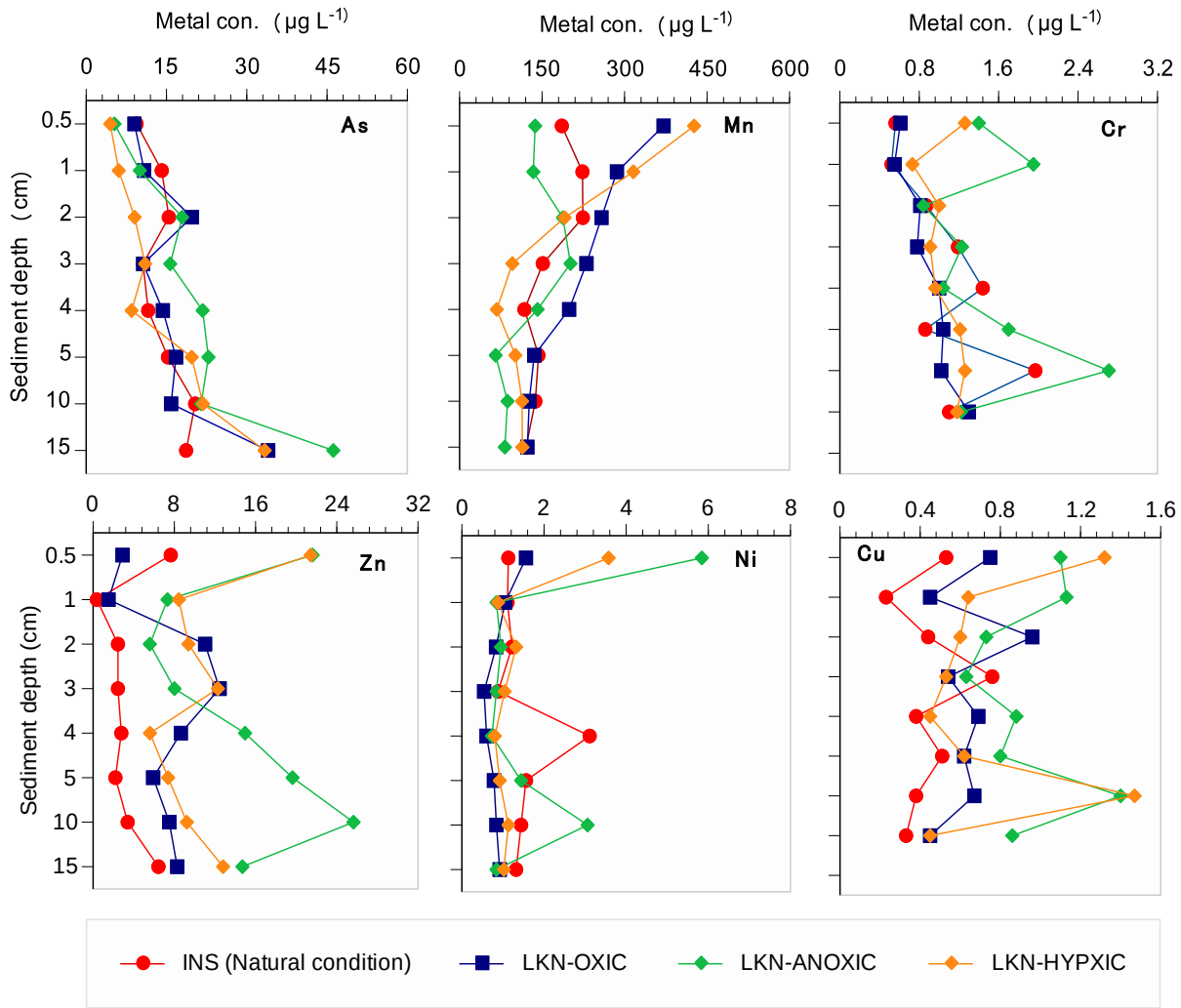

Fig. 4.11: Mobilization of As, Mn, Cr, Ni, Cu and Zn in porewater of the sediments from Lake King North under oxic (blue), anoxic (green), hypoxic (orange) and natural (red) conditions. Trigger values; freshwater (blue line) and seawater (red line).

Water column samples were tested at the commencement and cessation of each of the experiments. Most of the metals showed a decreased in the overlying water, with the exceptions of As in the hypoxic experiment, Ni in the oxic experiment and Zn in all treatments. Both Cu and Zn exceeded trigger concentrations in many samples, particularly for treated samples for Zn and untreated for Cu. The metal fluxes for the

Lake King North experiments seem greatest in the samples with the anoxic treatment, which resulted in metal liberation from the sediments to the pore water. Only Zn showed a consistent flux to the overlying water column.

Table 4.4. Metal analyses for water column samples prior and at the cessation of incubation experiments for Lake King North. All concentrations in µg/l. Values in red exceed the contaminant trigger levels (ANZECC/ARMCANZ, 2000).

		As	Cr	Cu	Mn	Ni	Zn
Anoxic	Initial	3.2	0.7	6.2	5.3	2.0	12.0
	Final	1.9	1.1	2.1	0.6	1.6	18.5
Hypoxic	Initial	0.9	1.0	9.0	4.8	2.7	14.9
	Final	1.4	0.7	1.1	5.2	2.8	17.0
Oxic	Initial	2.0	0.5	5.2	5.4	0.7	6.4
	Final	1.1	0.6	1.2	0.7	1.8	8.6

4.2.4. *Hollands Landing*

Hollands Landing is a salt swamp region of the Gippsland Lakes, adjacent to the McLennan Strait that is commonly hypersaline due to significant evaporation. The water column is shallow (< 20cm) and it is dominated by anoxic sulphidic sediments, particularly monosulfidic black ooze, due to high organic matter decomposition.

The effects of changed redox conditions and salinity, due to flooding and drying, on metal mobility, on Hollands Landing were investigated. The sediment samples were incubated after manipulating the oxygen saturation (anoxic, oxic), simulating drying and wetting conditions and altering the salinity of the overlying water, and the results were compared with the natural sediments (referred to *in-situ*; INS).

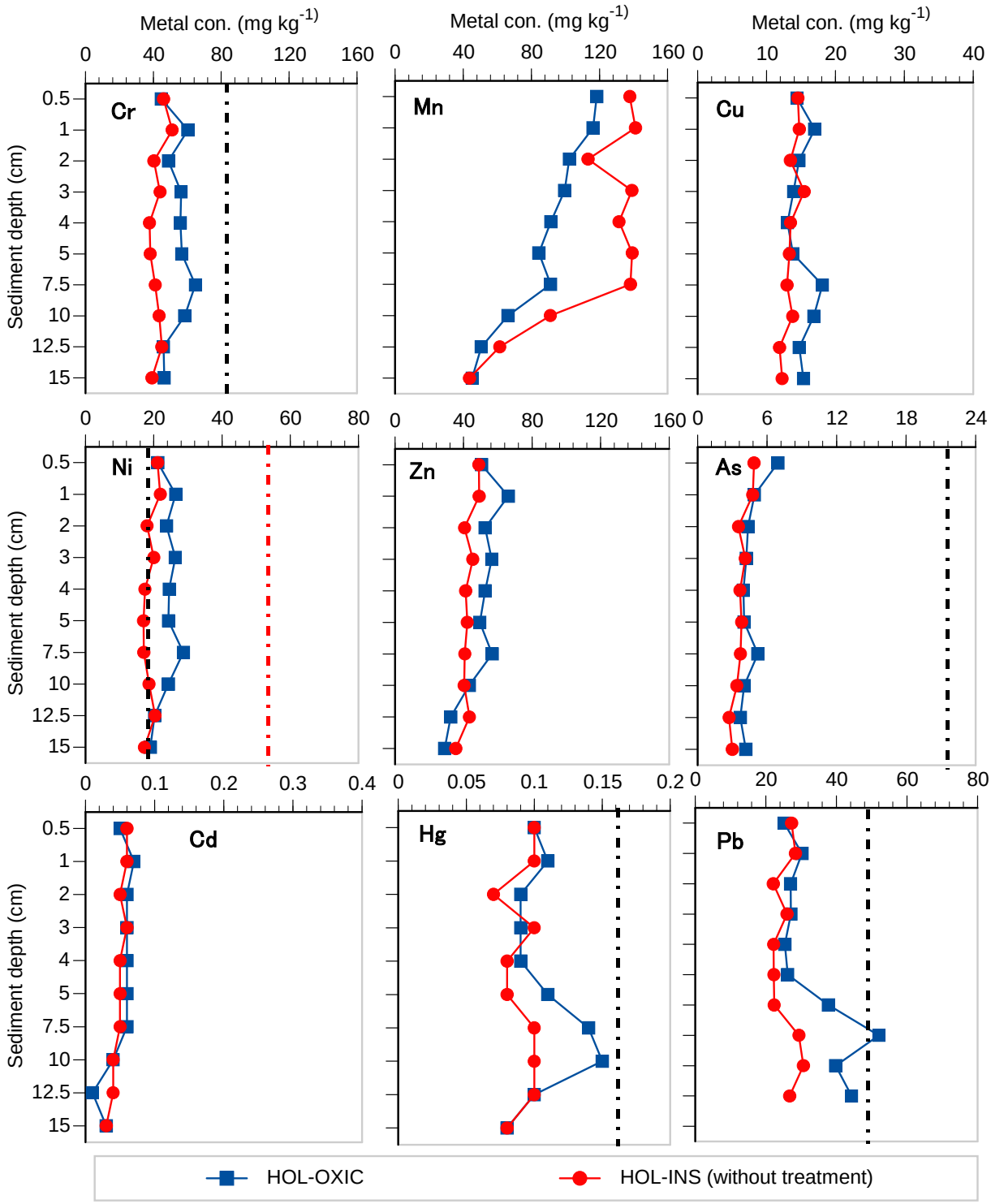

Fig. 4.12: Mobilization of heavy metals in sediments from Hollands Landing (HOL) under oxic (blue) and natural (red) conditions.

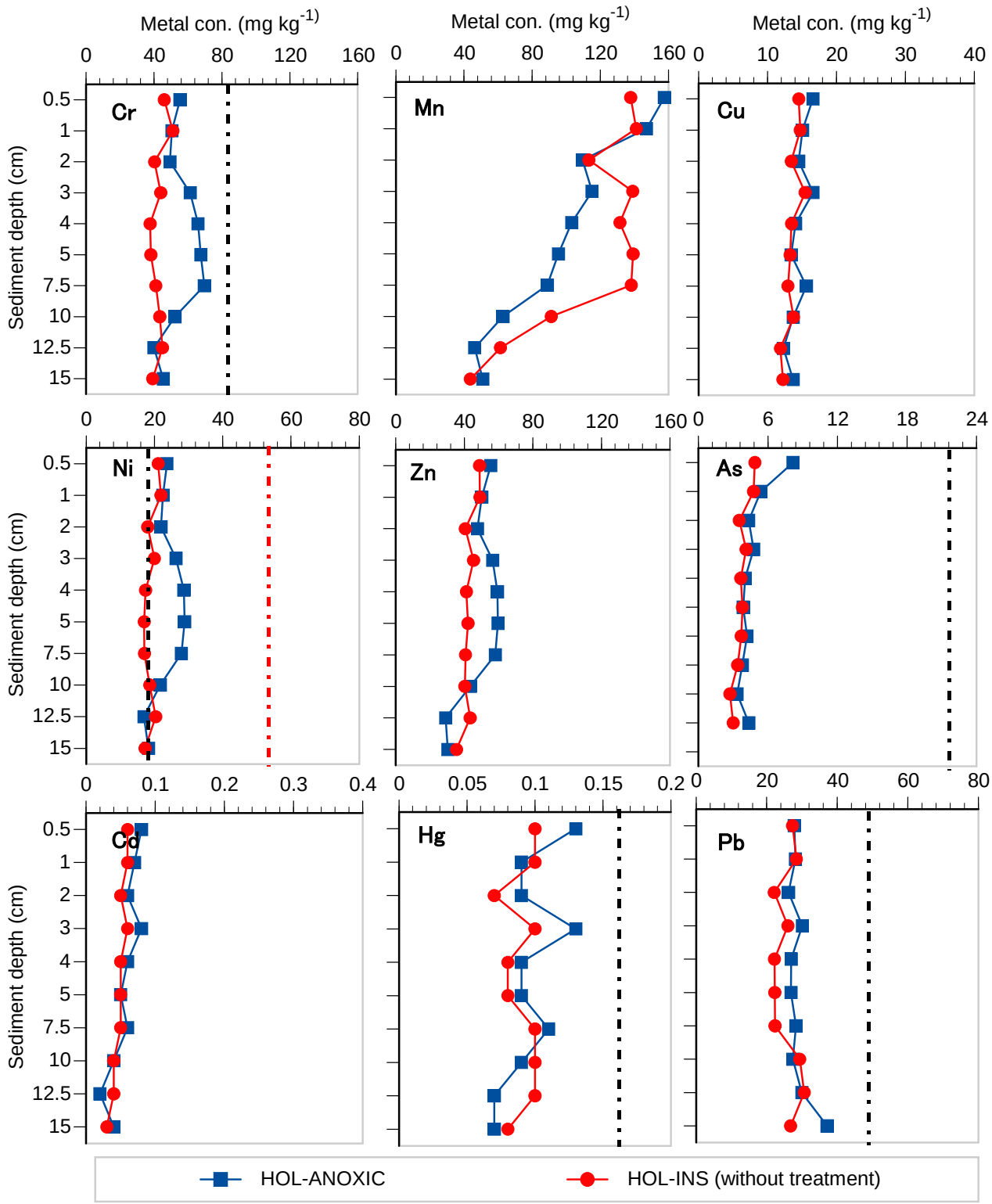

Fig. 4.13: Mobilization of heavy metals in sediments from Hollands Landing (HOL) under anoxic (blue) and natural (red) conditions.

4.2.4.1. Metal mobilization under oxic and anoxic conditions

For both the oxic and anoxic treatments, concentrations of most metals in the sediments was relatively low while the concentration of Ni was in between the ISQG lower and higher values as set by ANZECC/ARMCANZ (2000) (Fig. 4.12, 4.13). Concentrations of Cr, Pb and Hg were elevated, particularly below 7.5 cm in the oxic experiments. In most cases the treated samples had higher concentrations of metals, with the exception of Mn, which again was lower. Concentrations of both Pb and Hg deviated significantly from the control samples and approached the ISQG low trigger levels in the lower samples. A study by Miao et al. (2006) reported that the increase in sediment acidity upon oxidation resulted in the release of Pb into solution.

The porewater concentrations showed a mixed response, with Cr, Cu and Zn levels being significantly higher in the treated porewater samples and As, Mn and Ni being lower (Fig. 4.14). Trigger levels for freshwater were exceeded in all samples for Cu, particularly in the oxygen manipulation experiments, and for As and Ni in the untreated porewaters below 4 cm. Cr levels were also elevated in the oxygen treatments at lower levels and may warrant speciation tests. Zn levels also exceeded trigger levels in the oxic treatments below 2 cm.

The water column samples (Table 4.4) show decreases in both oxic and anoxic treatments for As and Cr, but significant increases after both treatments for Zn and Cu. Levels of As and Cu were significantly high throughout, exceeding trigger levels.

Fluxes of metals are minor in the sediments, with the exception of Hg and Pb at depth in the anoxic samples. Fluxes in the pore and overlying water seem more prevalent, including Mn from the porewater to the sediment and Cu and Zn from the sediment to overlying water. The concentrations of As and Cu in the water column warrant further investigation.

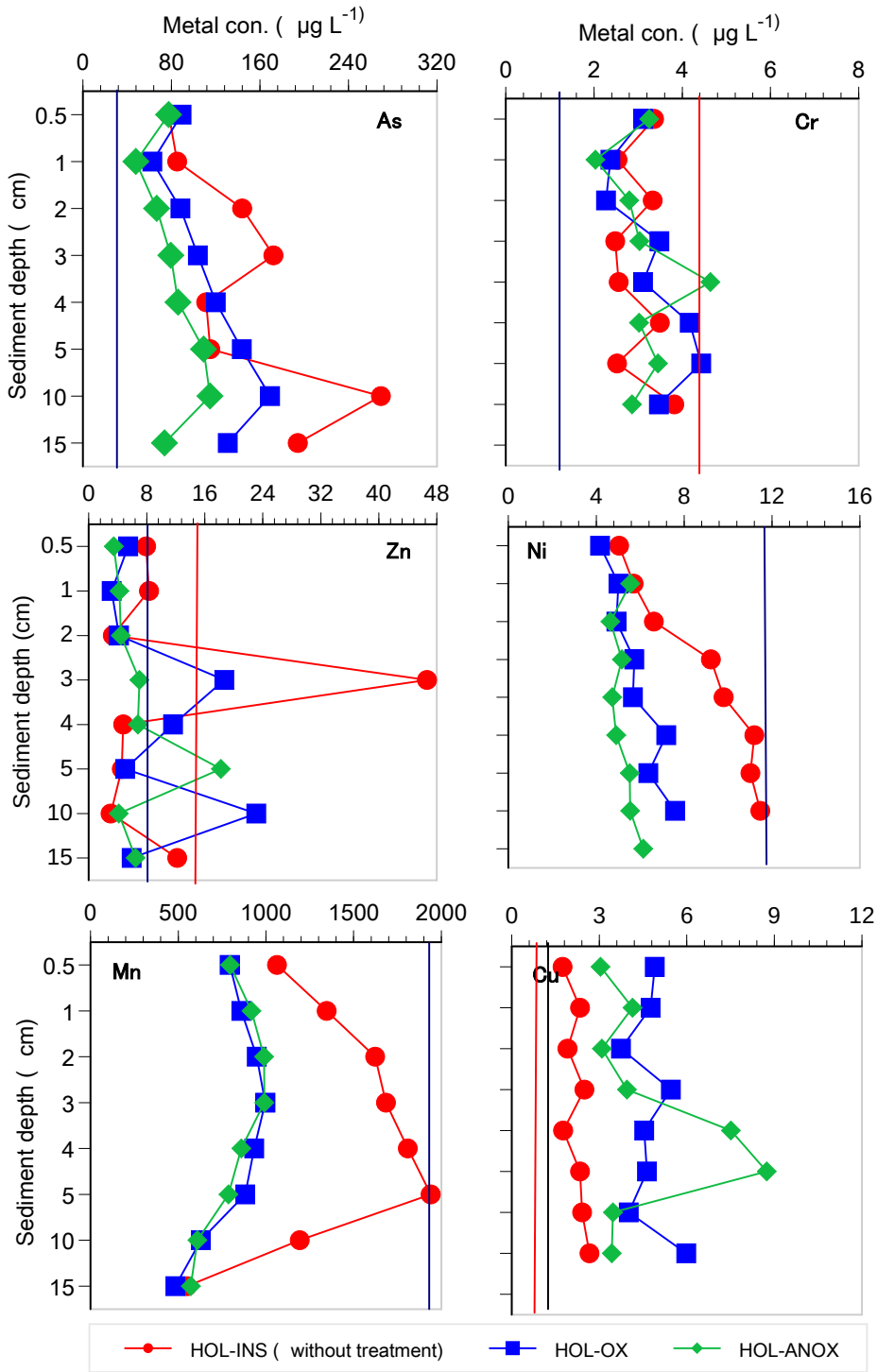

Fig. 4.14: Mobilization of As, Mn, Cr, Ni, Cu and Zn into porewater from sediments of Hollands Landing (HOL) under oxic (blue), anoxic (green) and natural (red) conditions. Trigger values; freshwater (blue line) and seawater (red line).

Table 4.5. Metal analyses for water column samples prior and at the cessation of the oxygen manipulation experiments for Hollands Landing. All concentrations in

µg/L. Values in red exceed the contaminant trigger levels (ANZECC/ARMCANZ, 2000).

		As	Cr	Cu	Mn	Ni	Zn
Anoxic	Initial	36.8	1.9	1.7	842.1	2.9	3.9
	Final	27.9	1.4	4.0	767.8	2.6	10.2
Oxic	Initial	39.0	3.2	3.4	859.8	2.2	5.2
	Final	23.5	1.6	4.9	761.8	1.9	8.9

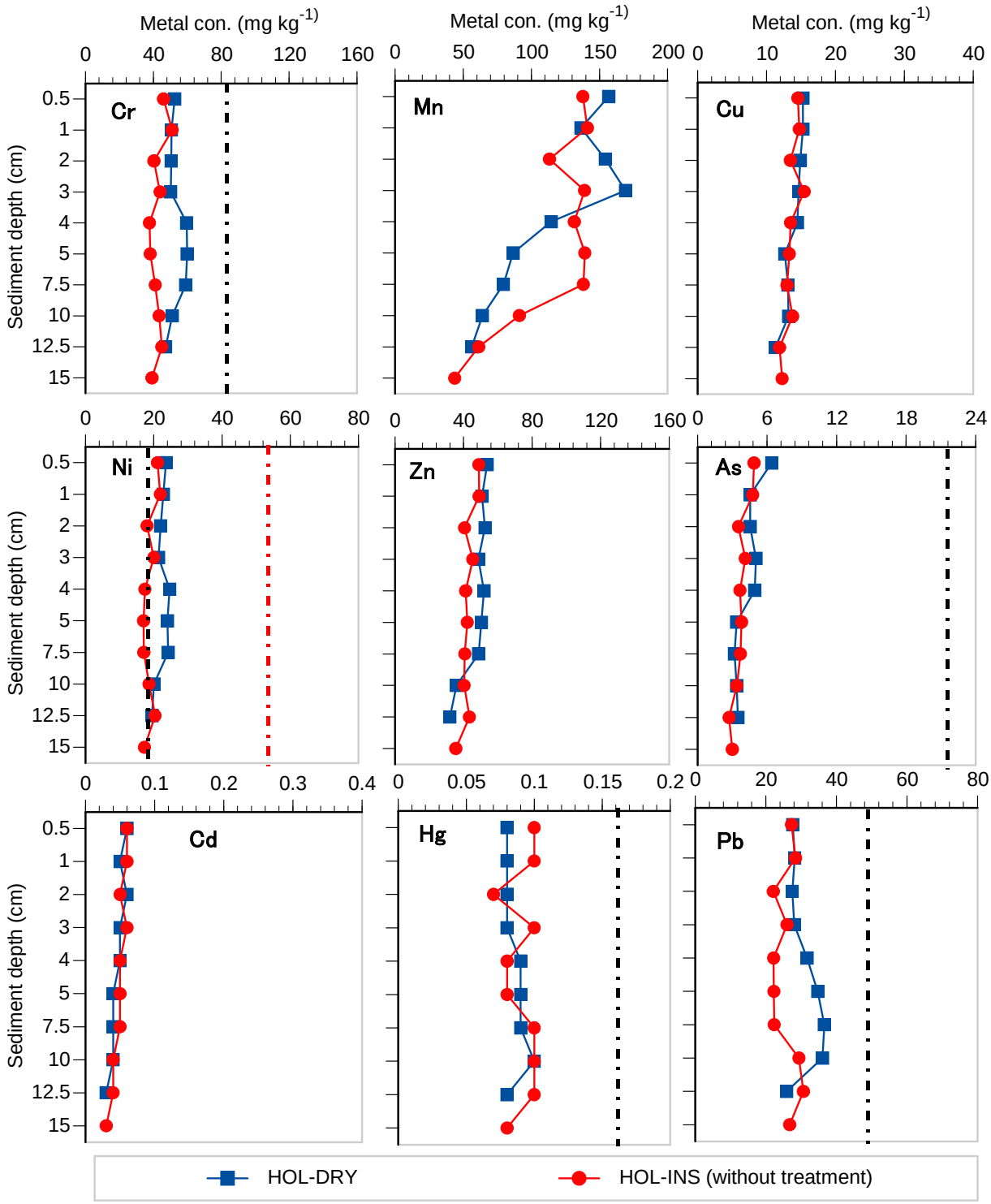

Fig. 4.15: Mobilization of heavy metals in sediments from Hollands Landing (HOL) under dry (blue) and natural (red) conditions.

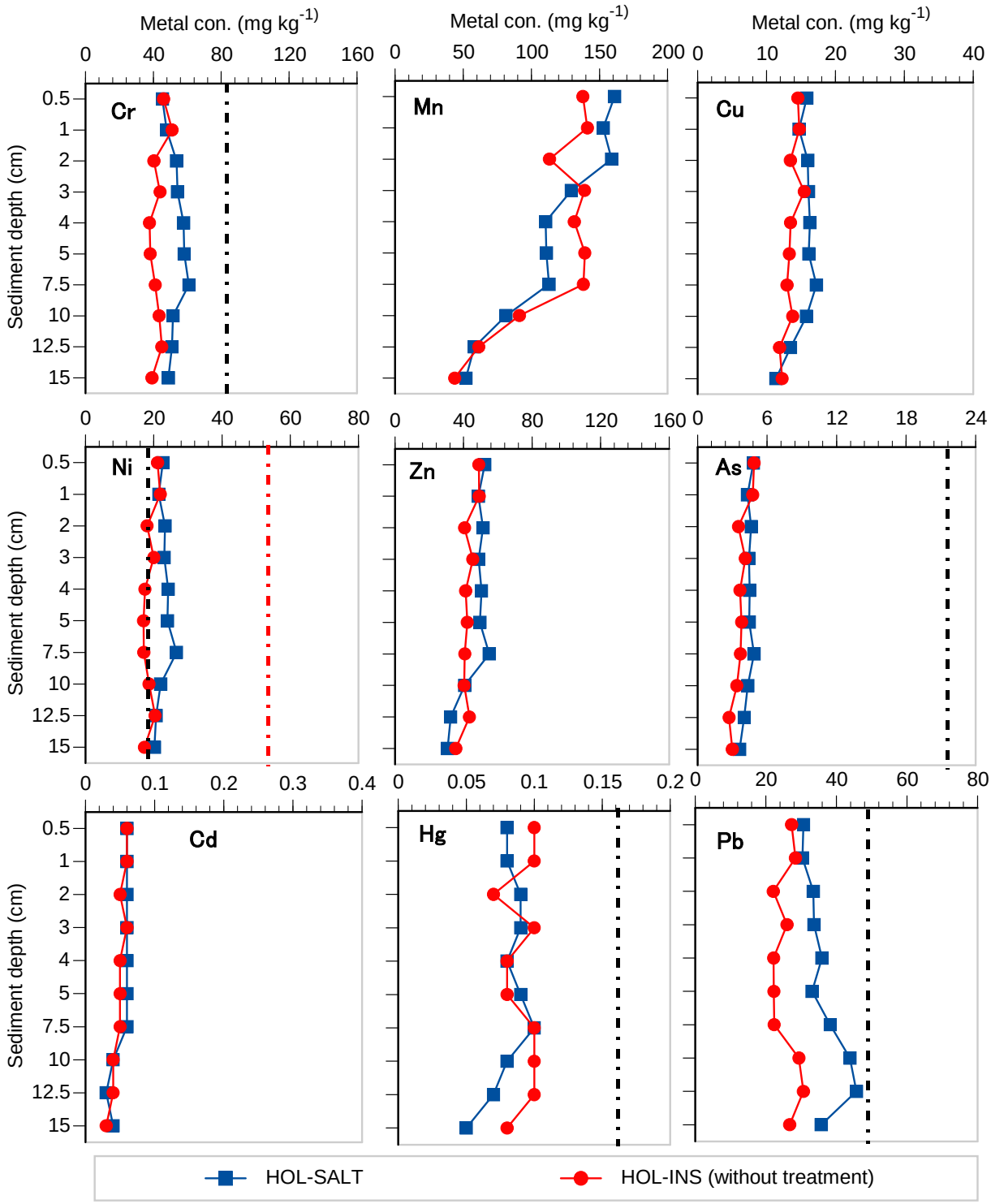

Fig. 4.16: Mobilization of heavy metals in sediments from Hollands Landing (HOL) under salty (blue) and natural (red) conditions.

4.2.4.2. Metal mobilization under dry and re-wet conditions with low salinity and high salinity water

The sediment cores from Hollands Landing were dried and rewet with low salinity and high salinity water. This was to simulate rain events following dry conditions, in both

winter and summer, which remobilise salt from the surface seidments. The concentrations of Cr, Mn, Cu As, Zn, Cd, Hg and Pb in the treated and *in situ* sediments were below the ISQG lower values as set by ANZECC/ARMCANZ (2000) (Figs. 4.15-4.156. However, Ni concentrations in the treated and natural sediments were between the ISQG lower and higher values. Incubation test showed that metal concentrations in the natural (*in situ*) and treated sediments did not differ substantially either from the reference conditions or under either treatment. Higher levels of Cr, Zn and Pb and lower levels of Mn were recorded after treatment, with the highest shift being an increase in Pb under saline water conditions, approaching the trigger values. Neither porewater, nor water column samples, were analysed from the wetting and drying experiments.

5. CONCLUSION

The sediments analysed throughout this investigation showed relatively low levels of metal contaminants, with the exception of Ni. High Ni concentrations are typical of many Victorian sediments (e.g. Reeves et al., 2015). Some of the target areas revealed elevated levels of known contaminants, such as Cr, Hg, As and Pb at Heart Morass, As, Hg and Pb at Dowd Morass, Cr, As and Hg at Lake King North and Cr, Hg and Pb at Hollands Landing.

However, the main purpose of this work was to investigate metal fluxes under a range of controlled incubation experiments, which simulated likely impacts under changed climatic conditions. The Heart Morass experiment, which used drying and rewetting of the sediment, produced acidic conditions. Concentrations of many metals (Cr, Mn, Cu, Ni, Zn, Cd) increased in the sediments and porewater and decreased in the water column as a result of the experiment. This suggests a flux from the overlying water to the sediment after drying and rewetting, perhaps due to complexation onto the dried clay particles. Levels of Ni, Zn and Cu were significantly elevated in the water column and porewater and warrant further investigation.

Dowd Morass also produced acidic conditions in the overlying waters over the duration of the experiment. Metal flux in the sediments was less notable here than at Heart Morass, although Ni, Zn and Cu were liberated from the sediment to the porewater,

possibly as a result of the acidity, and again, exceeded trigger levels in the water column.

The Lake King North experiments focussed on altering the oxygen saturation of the water column to simulate conditions experienced through stratification and mixing, such as after a flood event. The most significant fluxes occurred under anoxic conditions from the sediment to the pore water, with most metals (As, Cd, Cr, Cu, Ni, Pb, Zn) showing mobility. This may be related to methylation processes, but further investigation is required to confirm the mechanism. Metal concentrations in the water column largely decreased, with the exception of Zn.

The Hollands Landing experiments considered both oxygen saturation and wetting and drying experiments, as well as changes in salinity. Each of these factors are currently experienced by the site. Metal fluxes were largely negligible, with the exception of increases in Hg and Pb at depth, close to trigger levels, in the oxic experiments and minor increases in Cr, Ni and Zn, and decreased Mn. Porewaters again exceeded trigger levels for Cu and Zn, and potentially As and Cr – depending on speciation. It is recommended that speciation be undertaken on these sediments to more clearly determine risk levels, but changes in oxidation of these sediments may cause significant fluxes of the more toxic metal species. Water column data from the oxygen manipulations revealed decreases in As, Cr and Ni, which correlate with the sediment increase. Unfortunately porewater and water column data was unavailable for the drying and rewetting experiments.

The experiments together revealed that largely the metal concentrations are stable, with predicted climate and hydrological change, but attention should be focussed on:

- Drying conditions at Heart and Dowd Morass
- Anoxia at Lake King North
- Changes in oxidation state at Hollands Landing

Although the likelihood for metal fluctuation currently is low, caution should be applied under changed environmental conditions, such as extended drought periods (morasses) or flooding events (Lake King).

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REFERENCES

Allinson G, Zhang P, Bui A, Allinson M, Rose G, Marshall S, et al. Pesticide and trace metal occurrence and aquatic benchmark exceedances in surface waters and sediments of urban wetlands and retention ponds in Melbourne, Australia. Environmental Science and Pollution Research 2015; 22: 10214-10226.

ANZECC/ARMCANZ. Australian and New Zealand guidelines for fresh and marine water quality. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand. ACT Canberra, Australia, 2000.

Atkinson CA, Jolley DF, Simpson SL. Effect of overlying water pH, dissolved oxygen, salinity and sediment disturbances on metal release and sequestration from metal contaminated marine sediments. Chemosphere 2007; 69: 1428-1437.

Baker JK, Long SM, Hassell KL, Pettigrove VJ, Gagnon MM. Health Status of Sand Flathead (*Platycephalus bassensis*), Inhabiting an Industrialised and Urbanised Embayment, Port Phillip Bay, Victoria as Measured by Biomarkers of Exposure and Effects. PLOS ONE 2016; 11: e0164257.

Barwick M, Maher W. Biotransference and biomagnification of selenium copper, cadmium, zinc, arsenic and lead in a temperate seagrass ecosystem from Lake Macquarie Estuary, NSW, Australia. Marine Environmental Research 2003; 56: 471-502.

Bek P, Bruton G. The Hydrochemistry ofthe Gippsland Lakes and Streams. Environmental Studies Series. Ministry of Conservation, Victoria, Publication No. 238, Victoria, Australia, 1979.

Birch G, Taylor S. Source of heavy metals in sediments of the Port Jackson estuary, Australia. Science of The Total Environment 1999; 227: 123-138.

Birch GF. Marine pollution in Australia, with special emphasis on central New South Wales estuaries and adjacent continental margin. International Journal of Environment and Pollution 2000; 13: 573-607.

BMTWBM. Ecological Character Description of the Gippsland Lakes Ramsar Site – Final Report. Department of Sustainability, Environment, Water, Population and Communities, Australian Government, Canberra, Australia, 2011, pp. 281.

Boon P, Cook P, Woodland R. The Gippsland Lakes: management challenges posed by long-term environmental change. Marine and Freshwater Research; 67: 721-737.

Boon P, Rosengren N, Frood D, Oates A, Reside J. Shoreline geomorphology and fringing vegetation of the Gippsland Lakes. Institute for Sustainability & Innovation, Victoria University, 2014, pp. 67.

Bycroft BM, Coller BAW, Deacon GB, Coleman DJ, Lake PS. Mercury contamination of the Lerderberg River, Victoria, Australia, from an abandoned gold field. Environmental Pollution Series A, Ecological and Biological 1982; 28: 135-147.

Celo V, Lean DRS, Scott SL. Abiotic methylation of mercury in the aquatic environment. Science of The Total Environment 2006; 368: 126-137.

Chapman PM, Allard PJ, Vigers GA. Development of sediment quality values for Hong Kong special administrative region: a possible model for other jurisdictions. Marine Pollution Bulletin 1999; 38: 161-169.

Churchill RC, Meathrel CE, Suter PJ. A retrospective assessment of gold mining in the Reedy Creek sub-catchment, northeast Victoria, Australia: residual mercury contamination 100 years later. Environmental Pollution 2004; 132: 355-363.

Cook PLM, Jennings M, Holland DP, Beardall J, Briles C, Zawadzki A, et al. Blooms of cyanobacteria in a temperate Australian lagoon system post and prior to European settlement. Biogeosciences Discussions 2015; 12 18829-18853.

Dauvin J-C. Effects of heavy metal contamination on the macrobenthic fauna in estuaries: The case of the Seine estuary. Marine Pollution Bulletin 2008; 57: 160-169.

DeLaune RD, Smith CJ. Release of Nutrients and Metals Following Oxidation of Freshwater and Saline Sediment. Journal of Environmental Quality 1985; 14: 164-168.

Driscoll CT, Chen CY, Hammerschmidt CR, Mason RP, Gilmour CC, Sunderland EM, et al. Nutrient supply and mercury dynamics in marine ecosystems: A conceptual model. Environmental Research 2012; 119: 118-131.

EGCMA. Gippsland Lakes Ramsar Site Management Plan. East Gippsland Catchment Management Authority, Bairnsdale. Victoria, 2015, pp. 224.

EPA. Microwave assisted acid digestion of sediments, sludges, soils, and oils. EPA, Victoria, 2007, pp. 30.

EPA. Gippsland Lakes condition report 1990–2011. Environment Protection Authority, Victoria, Carlton, Victoria, 2013, pp. 62.

EPA. Gippsland Lakes and catchment literature review. Environment Protection Authority Victoria, Carlton, Victoria, 2015, pp. 30.

EPA. Mercury and arsenic in Victorian waters: a legacy of historical gold mining. Environment Protection Authority Victoria (EPA), Victoria, Victoria, 2016, pp. 25.

Fabris G. Mercury Concentrations in Brown Trout (*Salmo trutta*) from Eastern Victorian Waterways. Marine and Freshwater Resources Institute Report No. 49. Fisheries Victoria, Victoria, 2002.

Fabris G, Theodoropoulos T, Sheehan A, Abbott B. Mercury and Organochlorines in Black Bream, Acanthopagrus butcheri, from the Gippsland Lakes, Victoria, Australia: Evidence for Temporal Increases in Mercury levels. Marine Pollution Bulletin 1999; 38: 970-976.

Fryer JJ, Easton AK. Hydrodynamics of the Gippsland Lakes. 7th

Australasian Conference on Hydraulics and Fluid Mechanics 1980: Preprints of Papers. Institution of Engineers, Australia, 1980, pp. 500.

Garelick H, Jones H. Arsenic pollution and remediation: an international perspective: Special foreword. Reviews of environmental contamination and toxicology 2008; 197: v-vi.

Glover J, Bacher G, Pearce T. Gippsland regional environmental study : heavy metals in biota and sediments of the Gippsland lakes. Heidelberg, Victoria: Arthur Rylah Institute for Environmental Research, 1980.

Glover JW. Gippsland regional environmental study : heavy metals in biota and sediments of the Gippsland lakes. Melbourne, Australia: Ministry for Conservation, Victoria, Environmental Studies Division, 1980.

Hale J, Morgan D. Ecological Character Description for the Lakes Argyle and Kununurra Ramsar Site. Department of Sustainability, Environment, Water, Population and Communities, Canberra, 2010, pp. 96.

Hammerschmidt CR, Fitzgerald WF. Geochemical Controls on the Production and Distribution of Methylmercury in Near-Shore Marine Sediments. Environmental Science & Technology 2004; 38: 1487-1495.

Harris GP. Biogeochemistry of nitrogen and phosphorus in Australian catchments, rivers and estuaries: effects of land use and flow regulation and comparisons with global patterns. Marine and Freshwater Research 2001; 52: 139-149.

Haynes D, Leeder J, Rayment P. Temporal and spatial variation in heavy metal concentrations in the bivalve Donax deltoides from the Ninety Mile Beach, Victoria, Australia. Marine Pollution Bulletin 1995; 30: 419-424.

Holland D, Woodland R, Cook P, Clarke R, Herrod A. Ecological impacts of a Nodularia bloom on nitrogen dynamics in food webs and seagrass beds. Monash University, Victoria, Clayton, Victoria, 2013, pp. 17.

Irvine I, Birch GF. Distribution of heavy metals in surficial sediments of Port Jackson, Sydney, New South Wales. Australian Journal of Earth Sciences 1998; 45: 297-304.

Kellar CR, Hassell KL, Long SM, Myers JH, Golding L, Rose G, et al. Ecological evidence links adverse biological effects to pesticide and metal contamination in an urban Australian watershed. Journal of Applied Ecology 2014: 426-439.

Kibria G, Lau TC, Wu R. Innovative ‘Artificial Mussels’ technology for assessing spatial and temporal distribution of metals in Goulburn–Murray catchments waterways, Victoria, Australia: Effects of climate variability (dry vs. wet years). Environment International 2012; 50: 38-46.

Kirby J, Maher W, Harasti D. Changes in Selenium, Copper, Cadmium, and Zinc Concentrations in Mullet (Mugil cephalus) from the Southern Basin of Lake Macquarie, Australia, in Response to Alteration of Coal-Fired Power Station Fly Ash Handling Procedures. Archives of Environmental Contamination and Toxicology 2001a; 41: 171-181.

Kirby J, Maher W, Krikowa F. Selenium, Cadmium, Copper, and Zinc Concentrations in Sediments and Mullet (Mugil cephalus) from the Southern Basin of Lake Macquarie, NSW, Australia. Archives of Environmental Contamination and Toxicology 2001b; 40: 246-256.

Langshaw J. Calls for lakes mercury tests. Gippsland Times. Gippsland Times, Gippsland, Victoria, 2014.

Leventhal JS, John DA. Bioavailability of Metals. In: Bray Ed, editor. Preliminary Compilation of descriptive Geoenvironmental Mineral Deposit Models. Department of the interior U.S. Geological survey, USGS, Denver, 1995, pp. 10-18.

Long ER, Macdonald DD, Smith SL, Calder FD. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. Environmental management 1995; 19: 81-97.

McGhee A. Doctors warn of potentially high levels of mercury in Gippsland Lakes fish, urge further testing. ABC News. ABC, Australia, 2015.

Merian E, Anke M, Ihnat M, Stoeppler M. Elements and their compounds in the environment: occurrence, analysis and biological relevance. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA, 2004.

Merritt KA, Amirbahman A. Mercury methylation dynamics in estuarine and coastal marine environments — A critical review. Earth-Science Reviews 2009; 96: 54-66.

Miao S, DeLaune RD, Jugsujinda A. Influence of sediment redox conditions on release/solubility of metals and nutrients in a Louisiana Mississippi River deltaic plain freshwater lake. Science of The Total Environment 2006; 371: 334-343.

Miller CL, Mason RP, Gilmour CC, Heyes A. Influence of dissolved organic matter on the complexation of mercury under sulfidic conditions. Environmental Toxicology and Chemistry 2007; 26: 624-633.

Monk A, Charlton-Robb K, Buddhadasa S, Thompson RM. Comparison of Mercury Contamination in Live and Dead Dolphins from a Newly Described Species, Tursiops australis. PLOS ONE 2014; 9: e104887.

Morse JW. Interactions of trace metals with authigenic sulfide minerals: implications for their bioavailability. Marine chemistry 1994; 46: 1-6.

NAGD. National Assessment Guidelines for Dredging. Department of the Environment, Water, Heritage and the Arts, Canberra, 2009, pp. 92.

Nordmyr L, Österholm P, Åström M. Estuarine behaviour of metal loads leached from coastal lowland acid sulphate soils. Marine Environmental Research 2008; 66: 378-393.

Peng J-f, Song Y-h, Yuan P, Cui X-y, Qiu G-l. The remediation of heavy metals contaminated sediment. Journal of hazardous materials 2009; 161: 633-640.

Peters GM, Maher WA, Jolley D, Carroll BI, Gomes VG, Jenkinson AV, et al. Selenium contamination, redistribution and remobilisation in sediments of Lake Macquarie, NSW. Organic Geochemistry 1999; 30: 1287-1300.

Petersen W, Willer E, Willamowski C. Remobilization of trace elements from polluted anoxic sediments after resuspension in oxic water. Water, Air, and Soil Pollution 1997; 99: 515-522.

Pettigrove V, Hoffmann A. Impact of urbanisation on heavy metal contamination in urban stream sediments: influence of catchment geology. Australian Journal of Ecotoxicology 2003; 9: 119-128.

Presley BJ, Wade TL, Santschi P, Baskaran M. Historical contamination of Mississippi River Delta, Tampa Bay and Galveston Bay sediments. NOAA Technical Memorandum NOS ORCA 1998; 127: 136.

Price R. Victorian best practice guidelines for assessing and managing coastal acid sulfate soils. Department of Sustainability and Environment, Victoria, 2010, pp. 52.

Reeves JM, Gell PA, Reichman SM, Trewarn AJ, Zawadzki A. Industrial past, urban future: using palaeo-studies to determine the industrial legacy of the Barwon estuary, Victoria, Australia. Marine and Freshwater Research 2016; 67: 837-849.

Reeves JM, Trewarn A. Assessment of Heavy Metals and Other Contaminants of the Gippsland Lakes. DELWP, Victoria, Australia, 2016.

Roach AC. Assessment of metals in sediments from Lake Macquarie, New South Wales, Australia, using normalisation models and sediment quality guidelines. Marine Environmental Research 2005; 59: 453-472.

Schneider L, Maher W, Floyd J, Potts J, Batley G, Gruber B. Transport and fate of metal contamination in estuaries: Using a model network to predict the contributions of physical and chemical factors. Chemosphere 2016; 153: 227-236.

Schneider L, Maher W, Potts J, Batley G, Taylor A, Krikowa F, et al. History of metal contamination in Lake Illawarra, NSW, Australia. Chemosphere 2015a; 119: 377-386.

Schneider L, Maher W, Potts J, Gruber B, Batley G, Taylor A, et al. Recent history of sediment metal contamination in Lake Macquarie, Australia, and an assessment of ash handling procedure effectiveness in mitigating metal contamination from coal-fired power stations. Science of The Total Environment 2014; 490: 659-670.

Schneider L, Maher WA, Potts J, Taylor A, Batley G, Krikowa F, et al. Modeling food web structure and selenium biomagnification in lake macquarie, New South Wales, Australia, using stable carbon and nitrogen isotopes. Environmental Toxicology 2015b; 9999: 1-10.

Sharley DJ, Sharp SM, Bourgues S, Pettigrove VJ. Detecting long-term temporal trends in sediment-bound trace metals from urbanised catchments. Environmental Pollution 2016; 219: 705-713.

Simpson SL, Batley GE, Chariton AA. Revision of the ANZECC/ARMCANZ sediment quality guidelines. CSIRO Land and Water Report 2013; 8: 128.

Simpson SL, Batley GE, Chariton AA, Stauber JL, King CK, Chapman JC, et al. Handbook for sediment quality assessment. NSW, Australia: Centre for Environmental Contaminants Research, 2005.

Sunderland EM, Gobas FAPC, Branfireun BA, Heyes A. Environmental controls on the speciation and distribution of mercury in coastal sediments. Marine Chemistry 2006; 102: 111-123.

Tchounwou PB, Yedjou CG, Patlolla AK, Sutton DJ. Heavy metal toxicity and the environment. In: Luch A, editor. Molecular, clinical and environmental toxicology. Springer, Berlin, Germany, 2012, pp. 133-164.

Tilleard JW, O'Connor N, Boon PI. Understanding the environmental water requirements of the Gippsland Lakes system. Moroka Pty Ltd, Victoria, Australia, 2009, pp. 83.

Unland NP, Taylor HL, Bolton, Cartwright I. Assessing the hydrogeological impact and distribution of acid sulfate soils, Geart Morass, West Gippsland. Applied Geochemistry 37: 2001-2009.

Webster IT, Parslow J, Grayson R, Molloy R, Andrewartha J, Sakov P, et al. Gippsland Lakes Environmental Study: Assessing Options for Improving Water Quality and Ecological Function. CSIRO, SA, Australia, 2001, pp. 97.

Whalin L, Kim E-H, Mason R. Factors influencing the oxidation, reduction, methylation and demethylation of mercury species in coastal waters. Marine Chemistry 2007; 107: 278-294.

Willems DJ, Reeves JM, Morrison PD, Trestrail C, Nugegoda D. Trace metal analysis in the east Gippsland Lakes estuary using Amphibalanus variegatus and Mytilus edulis. 2018.

Wong VNL, Johnston SG, Burton ED, Bush RT, Sullivan LA, Slavich PG. Seawater causes rapid trace metal mobilisation in coastal lowland acid sulfate soils: implications of sea level rise for water quality. Geoderma 2010; 160: 252-263.

Wong VNL, Johnston SG, Burton ED, Bush RT, Sullivan LA, Slavich PG. Seawater-induced mobilization of trace metals from mackinawite-rich estuarine sediments. Water research 2013; 47: 821-832.

Wuana RA, Okieimen FE. Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. ISRN Ecology 2011; 2011: 1-21.

APPENDIX

Table 1: Metal concentrations (mg/kg dry weight) in sediments from Lake King North of Gippsland Lakes

Sediment depth (Cm)	**Cr**				**Mn**				**Ni**			
	Oxic	Anoxic	Hypoxic	In situ	Oxic	Anoxic	Hypoxic	In situ	Oxic	Anoxic	Hypoxic	In situ
0.5	70.27	60.25	80.63	68.60	366.85	228.14	261.41	286.48	32.61	29.32	36.81	34.49
1	66.54	54.48	70.22	72.66	303.41	235.53	287.95	276.14	32.82	26.63	32.94	36.30
2	61.95	59.71	82.17	69.34	300.81	268.02	208.78	278.24	32.77	30.30	37.91	35.53
3	73.48	58.20	84.58	71.96	337.80	276.42	318.26	286.72	36.79	29.89	40.32	36.38
4	71.61	58.81	75.48	77.11	338.08	277.25	306.77	287.63	36.35	29.96	37.12	39.94
5	68.65	59.22	79.30	79.04	332.26	288.10	311.72	284.73	35.68	30.12	35.76	38.99
7.5	68.12	60.33	70.66	82.62	318.77	298.67	308.36	258.15	34.30	31.04	33.98	36.95
10	73.11	57.02	79.53	82.08	259.54	271.80	289.16	302.77	34.59	28.00	36.20	38.82
12.5	69.40	60.63	86.92	84.23	301.10	271.08	261.90	201.10	34.53	29.61	37.69	38.80
15	73.07	68.68	78.05	71.91	234.82	249.33	279.02	241.13	35.18	31.46	35.85	34.12
Sediment depth (Cm)	**Cu**				**Zn**				**As**			
	Oxic	Anoxic	Hypoxic	In situ	Oxic	Anoxic	Hypoxic	In situ	Oxic	Anoxic	Hypoxic	In situ
0.5	26.11	25.49	28.83	27.20	95.02	86.82	104.98	98.45	15.43	12.82	17.18	16.13
1	25.23	21.87	25.97	27.54	90.58	71.52	91.83	100.26	14.06	11.24	12.35	16.22
2	25.47	24.54	25.50	27.40	93.21	80.47	94.63	101.40	14.32	12.79	25.69	16.15
3	28.15	24.16	31.33	26.52	104.94	77.46	114.98	105.84	15.53	13.26	19.20	16.11
4	26.80	24.16	28.56	26.79	104.65	78.10	101.85	110.84	15.15	13.23	17.31	16.29
5	25.73	-	26.85	27.51	102.16	-	100.27	105.50	14.53	-	16.61	19.20
7.5	24.91	24.40	24.96	25.60	94.47	78.8	92.78	95.64	15.54	13.50	16.78	18.72
10	24.18	21.45	25.42	27.92	88.10	69.68	91.51	109.28	15.25	12.86	16.91	17.69
12.5	24.55	21.79	24.58	25.64	89.11	70.88	90.38	97.04	16.18	13.46	15.77	24.01
15	24.89	22.60	27.37	27.41	89.06	72.36	98.54	106.07	19.98	13.00	16.11	15.44
Sediment depth (Cm)	**Cd**				**Hg**				**Pb**			
	Oxic	Anoxic	Hypoxic	In situ	Oxic	Anoxic	Hypoxic	In situ	Oxic	Anoxic	Hypoxic	In situ
0.5	0.16	0.16	0.19	0.18	0.06	0.07	0.07	0.07	25.73	23.05	28.13	26.86
1	0.16	0.13	0.17	0.18	0.06	0.05	0.09	0.09	25.77	21.03	27.35	27.31
2	0.15	0.15	0.15	0.18	0.06	0.06	0.12	0.06	25.75	23.81	29.21	27.43
3	0.18	0.16	0.23	0.18	0.07	0.07	0.08	0.06	28.34	23.59	30.74	27.78
4	0.18	0.16	0.20	0.17	0.06	0.06	0.07	0.14	28.24	23.68	28.60	28.75
5	0.17		0.20	0.20	0.06	-	0.06	0.07	27.91		27.80	29.13
7.5	0.16	0.16	0.17	0.17	0.06	0.06	0.07	0.09	26.92	24.23	26.72	27.34
10	0.16	0.14	0.17	0.19	0.08	0.06	0.09	0.06	26.88	21.80	28.71	28.51
12.5	0.15	0.14	0.17	0.15	0.07	0.07	0.09	0.08	27.45	23.43	27.73	28.90
15	0.16	0.14	0.19	0.19	0.08	0.08	0.07	0.08	27.60	24.23	28.49	25.73

Table 2: Metal concentrations (mg/kg dry weight) in sediments from Dowd Morass of Gippsland Lakes

Sediment depth (Cm)	Cr			Mn			Ni			Cu (mg/kg dry weight)		
	Water column	Dried & rewet	In situ	Water column	Dried & rewet	In situ	Water column	Dried & rewet	In situ	Water column	Dried & rewet	In situ
0.5	43.26	40.82	33.89	58.85	185.39	89.94	35.73	37.20	36.51	20.93	15.21	16.60
1	37.60	39.55	32.18	62.10	144.32	115.33	39.21	46.06	42.54	20.07	14.60	18.66
2	36.69	38.47	32.80	81.99	136.66	119.02	45.56	48.07	44.22	19.18	15.45	16.32
3	34.96	33.43	24.43	107.01	114.22	78.49	51.51	37.45	28.18	18.47	15.76	10.89
4	31.96	40.14	32.90	113.11	146.61	121.92	47.98	39.62	49.02	16.48	17.70	15.90
5	33.61	39.50	34.05	125.05	157.58	125.24	48.20	49.30	45.65	17.02	16.70	16.63
7.5	32.62	38.41	33.06	127.57	153.63	112.10	48.11	42.61	41.45	17.24	15.46	15.29
10	36.17	42.69	45.36	122.43	127.59	144.98	45.26	55.41	54.39	18.86	17.29	20.74
12.5	37.38	49.21	35.03	121.12	118.92	118.43	41.15	50.26	43.83	19.78	16.89	17.84
15	36.68	41.53	33.98	90.34	131.57	106.55	33.90	46.74	44.36	19.90	14.64	16.62

Sediment depth (Cm)	Zn			As			Cd			Hg		
	Water column	Dried & rewet	In situ	Water column	Dried & rewet	In situ	Water column	Dried & rewet	In situ	Water column	Dried & rewet	In situ
0.5	44.25	62.76	78.87	13.08	13.02	13.57	0.12	0.20	0.16	0.10	0.08	0.09
1	54.35	63.62	69.47	13.67	13.53	14.56	0.14	0.18	0.17	0.12	0.08	0.10
2	68.03	70.81	63.31	15.96	12.88	13.94	0.18	0.22	0.16	0.09	0.09	0.09
3	73.22	65.21	39.99	15.28	11.26	9.08	0.19	0.20	0.10	0.10	0.08	0.06
4	66.20	74.69	60.66	14.23	12.62	14.20	0.18	0.24	0.16	0.09	0.09	0.09
5	65.05	82.21	58.42	14.25	12.29	14.30	0.17	0.27	0.15	0.09	0.09	0.09
7.5	63.36	73.49	52.57	14.87	12.46	12.97	0.16	0.24	0.13	0.09	0.08	0.08
10	60.34	89.86	80.36	14.86	14.34	16.55	0.17	0.32	0.23	0.10	0.10	0.11
12.5	49.55	95.60	64.40	14.80	12.72	14.74	0.10	0.18	0.18	0.10	0.12	0.10
15	66.01	77.20	62.45	13.85	15.55	13.87	0.08	0.16	0.16	0.09	0.10	0.09

Sediment depth (Cm)	Pb		
	Water column	Dried and re-wet	In situ
0.5	28.49	25.78	28.29
1	28.35	23.96	34.17
2	26.57	28.31	26.15
3	27.32	30.40	17.53
4	25.51	34.80	25.33
5	25.91	30.56	25.59
7.5	26.32	27.59	23.85
10	27.22	31.37	33.00
12.5	27.02	23.24	40.63
15	26.54	21.81	28.06

Table 3: Metal concentrations (mg/kg dry weight) in sediments from Heart Morass of Gippsland Lakes

Sediment depth (Cm)	Cr			Mn			Ni			Cu		
	Water column	Dried & rewet	In situ	Water column	Dried & rewet	In situ	Water column	Dried & rewet	In situ	Water column	Dried & rewet	In situ
0.5	108.93	73.29	62.90	111.61	95.82	114.05	61.68	43.00	49.09	31.28	29.91	31.32
1	81.15	70.38	46.22	92.12	109.42	87.47	46.57	45.61	38.97	30.70	28.63	28.75
2	116.81	74.77	46.68	100.21	120.38	87.68	62.41	44.43	37.89	32.62	29.73	28.54
3	76.91	63.09	57.73	109.63	108.33	95.28	48.82	37.06	41.29	30.8	28.32	34.28
4	64.46	86.76	45.63	108.09	111.77	82.42	46.14	49.90	29.46	28.70	32.48	25.97
5	51.00	85.84	48.51	110.72	109.13	86.81	54.87	53.41	33.94	25.86	31.76	28.17
7.5	60.10	91.90	51.26	99.22	124.52	90.63	40.72	61.26	39.83	26.54	34.56	30.93
10	76.06	91.79	50.56	106.38	108.66	85.33	42.29	60.01	40.21	30.79	32.51	28.37
12.5	85.30	92.63	65.28	95.75	104.06	87.89	61.85	64.83	56.28	32.96	33.29	33.45
15	91.82	-	59.59	76.19	-	94.72	71.23	-	52.02	36.49	-	29.76

Sediment depth (Cm)	Zn			As			Cd			Hg		
	Water column	Dried & rewet	In situ	Water column	Dried & rewet	In situ	Water column	Dried & rewet	In situ	Water column	Dried & rewet	In situ
0.5	138.48	85.94	100.23	13.77	13.91	15.40	0.18	0.14	0.14	0.14	0.11	0.14
1	125.86	107.06	80.89	13.41	15.73	13.45	0.15	0.19	0.10	0.14	0.10	0.12
2	133.99	96.06	78.95	14.47	16.85	15.64	0.18	0.13	0.10	0.15	0.12	0.12
3	136.94	78.53	84.73	12.31	16.74	19.48	0.19	0.10	0.08	0.13	0.11	0.16
4	118.63	83.39	61.80	18.41	16.39	16.35	0.16	0.16	0.06	0.13	0.13	0.12
5	126.93	87.54	66.92	21.34	12.89	17.84	0.24	0.12	0.08	0.14	0.14	0.14
7.5	108.98	101.67	82.21	16.20	13.99	19.45	0.18	0.14	0.11	0.13	0.14	0.14
10	92.07	111.98	66.05	16.91	13.17	14.48	0.09	0.21	0.09	0.16	0.12	0.13
12.5	110.18	106.02	83.47	12.41	12.15	15.06	0.15	0.20	0.12	0.14	0.09	0.17
15	123.67	-	81.74	12.31	-	12.39	0.20	-	0.14	0.05	-	0.14

Sediment depth (Cm)	Pb		
	Water column	Dried & rewet	In situ
0.5	40.76	37.30	43.07
1	39.96	37.72	37.41
2	43.79	39.88	38.16
3	39.21	39.73	45.50
4	38.79	40.83	34.98
5	36.02	38.27	40.29
7.5	40.67	68.26	44.24
10	43.01	54.34	35.49
12.5	28.04	33.75	42.56
15	26.37	-	36.81

Table 4: Metal concentrations (mg/kg dry weight) in sediments from Hollands Landing of Gippsland Lakes

Sediment depth (Cm)	Cr				Mn				Ni			
	Oxic	Dried & rewet	Salt	In situ	Oxic	Dried & rewet	Salt	In situ	Oxic	Dried & rewet	Salt	In situ
0.5	44.69	52.56	45.37	46.05	118.35	156.80	161.06	137.80	21.18	23.59	22.66	21.09
1	60.34	50.64	47.88	51.10	116.25	136.41	152.80	141.13	26.41	22.78	21.48	21.90
2	48.91	50.51	53.68	40.32	102.30	154.33	158.94	113.30	23.73	21.99	23.32	18.03
3	56.33	50.23	54.22	43.95	99.56	169.06	129.35	139.03	26.30	21.40	23.05	19.99
4	55.90	59.61	57.78	37.75	91.51	114.54	110.48	131.49	24.51	24.65	24.20	17.39
5	56.77	59.93	58.16	38.15	84.45	86.59	111.02	139.21	24.29	24.02	23.99	16.99
7.5	64.83	59.08	60.97	41.10	91.30	79.48	112.98	138.15	28.68	24.20	26.66	17.07
10	58.54	51.12	51.62	43.40	66.31	64.10	81.43	91.18	24.28	20.04	22.02	18.61
12.5	45.98	47.26	50.95	44.99	50.55	56.28	58.13	61.40	20.25	19.50	20.69	20.37
15	46.41	-	48.87	39.22	45.28	-	52.01	43.71	18.97	-	20.18	17.25
Sediment depth (Cm)	**Cu**				**Zn**				**As**			
	Oxic	Dried & rewet	Salt	In situ	Oxic	Dried & rewet	Salt	In situ	Oxic	Dried & rewet	Salt	In situ
0.5	14.41	15.27	15.83	14.53	50.50	53.70	52.37	48.88	6.93	6.40	4.82	4.87
1	16.99	15.28	14.71	14.75	66.16	50.76	48.67	49.09	4.91	4.55	4.31	4.76
2	14.70	14.89	15.98	13.45	52.58	52.53	51.34	40.55	4.35	4.55	4.63	3.53
3	13.92	14.65	16.08	15.46	56.44	48.72	48.83	45.38	4.21	5.04	4.43	4.12
4	13.02	14.47	16.29	13.48	52.55	51.88	50.45	41.21	3.95	4.94	4.49	3.66
5	13.82	12.65	16.12	13.30	49.44	50.39	49.52	42.15	4.02	3.38	4.46	3.80
7.5	18.09	13.09	17.23	12.97	56.70	48.83	55.01	40.70	5.21	3.18	4.87	3.70
10	16.86	13.18	15.78	13.78	43.30	35.87	40.66	40.32	4.03	3.38	4.34	3.39
12.5	14.74	11.29	13.47	11.88	32.47	32.04	32.42	43.40	3.69	3.48	4.03	2.72
15	15.35	-	11.34	12.25	28.93	-	30.66	35.42	4.17	-	3.63	3.00
Sediment depth (Cm)	**Cd**				**Hg**				**Pb**			
	Oxic	Dried & rewet	Salt	In situ	Oxic	Dried & rewet	Salt	In situ	Oxic	Dried & rewet	Salt	In situ
0.5	0.05	0.06	0.06	0.06	0.10	0.08	0.08	0.10	25.18	27.62	30.68	27.31
1	0.07	0.05	0.06	0.06	0.11	0.08	0.08	0.10	30.23	28.16	30.41	28.41
2	0.06	0.06	0.06	0.05	0.09	0.08	0.09	0.07	27.01	27.48	33.46	22.12
3	0.06	0.05	0.06	0.06	0.09	0.08	0.09	0.10	27.10	28.06	33.66	26.01
4	0.06	0.05	0.06	0.05	0.09	0.09	0.08	0.08	25.40	31.68	35.91	22.20
5	0.06	0.04	0.06	0.05	0.11	0.09	0.09	0.08	26.18	34.70	33.11	22.28
7.5	0.06	0.04	0.06	0.05	0.14	0.09	0.10	0.10	37.74	36.57	38.26	22.36
10	0.04	0.04	0.04	0.04	0.15	0.10	0.08	0.10	52.04	36.07	43.85	29.38
12.5	0.01	0.03	0.03	0.04	0.10	0.08	0.07	0.10	39.80	25.91	45.69	30.64
15	0.03	-	0.04	0.03	0.08	-	0.05	0.08	44.29	-	35.70	26.77