METAL DYNAMICS IN HAMILTON HARBOUR

METAL DYNAMICS IN HAMILTON HARBOUR

By

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Abstract

Metal contamination from anthropogenic activities is of great concern due to the associated detrimental effects on ecosystem health. An increase in metal concentrations in the dissolved phase creates greater ecosystem impacts. Thus, the relative extent of metal distribution between sediment and dissolved compartments, and an understanding of the factors that control this partitioning is key to assessing metal impacts. In this thesis, metal concentrations were determined for a suite of 12 metals (Cr, Mn, Co, Cu, Sn, Ag, As, Ni, Zn, Cd, Se and Fe) associated with three compartments, dissolved, surficial bed sediment and suspended particulate matter (SPM) in Hamilton Harbour, Ontario. Due to highly dynamic interactions of anthropogenic impacts that may work together to affect metal distributions as well as processes that occur over small or rapid scales, a high-resolution temporal and spatial scale was used to evaluate these metal distributions over a seasonal timeframe.

Concentrations of metals amongst sediment fractions indicated that sediment metal uptake was largely controlled by the concentration of the sediment associated amorphous and crystalline oxyhydroxide fractions accounting for up to 90% of total sediment bound metal, even though the oxyhydroxides only accounted for a maximum of 23% of the total sediment mass for both surficial bed sediment and SPM compartments. The formation and dissolution of amorphous oxyhydroxides is commonly a microbially mediated process. Thus, these results underscore the important role of oxyhydroxides and the microbial processes that contribute to their formation and dissolution in controlling metal dynamics, and likely metal impacts in Hamilton Harbour.

Metal partitioning was found to be both spatially and temporally variable for all compartments, temporally ranging 0.5 to 4 orders of magnitude for a given element; indicating highly dynamic metal exchanges between sediment and solution compartments and fluctuating distributions over the time and spatial scales examined.

The suite of variables that are considered to control metal distribution between dissolved and sediment compartments, and thus impact metal toxicity (i.e., temperature, pH, specific conductivity, oxidation-reduction potential, dissolved organic carbon concentration, SPM concentration (for SPM associated metals only), fraction concentrations i.e. g carbonate /g solid, g amorphous oxyhydroxide / g solid, etc., and dissolved metal concentrations) did not constrain the variability in observed metal distribution behaviour, indicating that other factors in this system, such as hydrodynamic disturbances associated with shipping traffic and channelized water currents, as well as specific point source metal discharges, may play a larger role in determining metal partitioning in Hamilton Harbour, compared to less anthropogenically, impacted systems. Furthermore, no one master variable defining metal partitioning between the dissolved and sediment compartments was found, rather relationships controlling metal distribution behavior were site, compartment, sediment fraction and element specific highlighting the challenges for the development of a Harbour-wide management plan for priority metal contaminants. The results presented in this thesis, show that it is necessary to consider metal, site and compartment specific conditions as well as fully addressing temporal variability in metal behaviour. In addition, the results of this thesis point to the need to address hydrodynamic disturbance and point source influences on metal behaviour in Hamilton Harbour and likely extend to other multi-impacted metal contaminated systems.

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Table of Contents

List of Figures

List of Tables

Chapter 1: Introduction

The impact of metal contamination from anthropogenic activities is of great concern due to the deleterious effects of high metal concentrations on ecosystem health. The bioavailability and toxicity of metals and hence, the effect that metals will have on organisms in the ecosystem is predicated by the concentration of metal in solution. In turn, the concentration of metal in solution is controlled by the distribution of metals between solid compartments (i.e. surficial bed sediment and suspended particulate matter (SPM)) and the dissolved compartment (Figure 1.1; Warren and Haack, 2001).

1.1 Compartment Characteristics

1.1.1 Dissolved Compartment

The metals in the dissolved compartment are the most mobile, bioavailable and toxic in the system therefore, greater metal concentrations in the dissolved compartment typically lead to increased negative impacts on the ecosystem (Ankley et al., 1996; Warren et al., 1998; Ma et al., 2002). Further, the increased mobility of dissolved forms allows metals to be easily transported among compartments and throughout the system.

1.1.2 Suspended Particulate Matter (SPM)

The SPM compartment is made of an active biological component (i.e. viruses and bacteria), non-viable biological material (i.e. detritus, extracellular polymeric substances and cellular debris), inorganic material (i.e. minerals such as clays, silicates, oxyhydroxides and carbonates) and intrapore spaces that allow the retention or circulation of water (Droppo, 2001). The SPM compartment provides a dynamic, reactive surface and transport vector for metals, as well as acting as an important link between bed sediments and dissolved metals in the water column via sedimentation, resuspension and sorption and flocculation processes (Turner and Millward, 2002 and references therein).

1.1.3 Surficial Bed Sediment Compartment

The surficial bed sediment layer (henceforth, referred to as the bed sediment compartment in this document) is important in the overall cycling of metals because this compartment is the locus of reactive mineral and biofilm formation, and decomposition processes, thereby concentrating metal movement and exchange processes across the sediment water interface, in a relatively thin (typically a few millimeters), dynamic zone at the sediment surface. This compartment is in constant contact with the overlying water column and hence the solution compartment and is the zone where deposition of SPM occurs. Bed sediments act as a long-term sink for metals in aqueous systems and are considered relatively stationary. However, short-term temporal shifts in geochemical conditions can cause metal release from bed sediments, e.g. summer decompositional maxima leading to shifting redox conditions and liberation of metals to the overlying water column (Morel and Herring, 1993). Further, systems that experience greater turbulence, such as harbours where shipping activity occurs, are subject to hydrodynamic disturbances, that can increase rates of resuspension of surficial bed sediment layers, which can lead to an increase in metal content in more labile forms and release of metals to the dissolved compartment (Calmano et al., 1993; Theis et al., 1988).

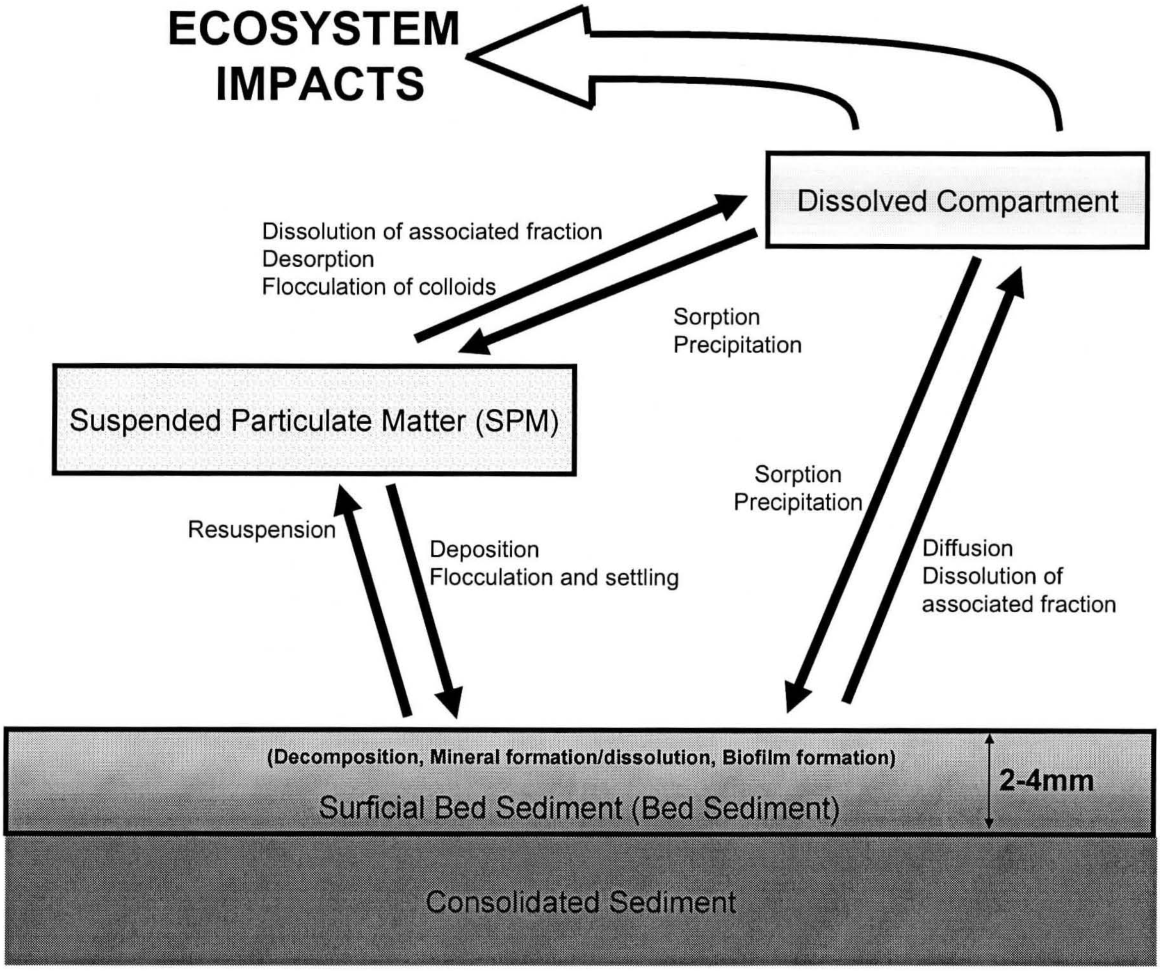

Figure 1.1: Schematic diagram of important compartments (boxes) determining metal distribution in aquatic systems. Metals can lead to ecosystem impacts through dynamic and reversible reactions (arrows) among the surficial bed sediment, SPM and dissolved compartments. Processes that lead to an increase in the metal distribution to the dissolved compartment increase the likelihood of deleterious impacts on ecosystem health.

1.2 Important Physico-Chemical and Geochemical Factors Controlling Metal Distribution

In aqueous systems, it is the reactions that occur among (1) dissolved, (2) surficial bed and (3) SPM compartments that determine metal distribution and hence metal impacts. Typically, processes that shift metals into sediment compartments decrease the potential negative impacts, while those that shift metal loads into the dissolved or solution phase increase the potential for harm (Luoma, 1983; Warren et al., 1998). In addition, these sediment – solution reactions are dynamic and reversible, their behavior being highly influenced by factors including physico-chemical conditions, such as pH, oxidation-reduction potential (redox), ionic strength, temperature and organic ligands (Serpaud et al., 1994; Sauvé et al., 2000; Masscheleyn et al., 1990), the presence and concentration of other, competing metals (Kaoser et al., 2004; Power et al., 2005), and the composition of the bed sediment and SPM compartments (i.e. type and quantity of reactive minerals and organic matter present; e.g. Peng et al, 2005, Taillefert et al., 2002).

1.2.1 pH: Master Variable

Oftentimes, pH is considered the master variable in aqueous systems because of the wide-ranging effects that it can have on metal behavior (Warren and Haack, 2001). pH affects solid surface sorption processes by shifting the charge, and hence the reactivity, of a myriad of surface functional groups that are important for metal adsorption (Stumm and Morgan, 1996). In addition, pH affects the precipitation/dissolution of mineral fractions that act as important sorbents for metals (Warren and Haack, 2001; Stumm and Morgan, 1996). Speciation of metals in solution is also determined by pH and has implications for the bioavailability, toxicity and ability of a metal to form surface complexes (Stumm and Morgan, 1996).

1.2.2 Oxidation-Reduction Potential (ORP)

Changes in redox have implications for both the speciation of redox-sensitive metals i.e. As, Cr, Mn and Se which can radically alter their behaviour (Kimbrough, 1999; Harrington et al., 1998; Moore, 1991; Masscheleyn et al., 1990; Warren and Haack, 2001), as well as the behaviour of redox-sensitive solid fractions i.e. oxyhydroxides (Hamilton-Taylor et al., 1996; Davison, 1993; Tessier et al., 1979) and organic matter (Wetzel, 1983; Tessier et al., 1979). The reactivity and hence, bioavailability of some metals may be directly linked to changes in redox state e.g. Cr(III) is relatively insoluble while Cr(VI) is typically dissolved and highly bioavailable.

Biological processes can have a substantial effect on redox status by mediating redox reactions that are otherwise kinetically slow e.g. the oxidation of Mn (Tebo et al., 1997). Further, bacterial associated decompositional processes in bed sediments lead to highly reducing sediments where only the top few millimeters may remain oxygenated depending on the overlying water column oxygen status (Wetzel, 1983). In particular, the concentrations of oxyhydroxide minerals (e.g. Fe and Mn) and organic matter, both highly reactive and ubiquitous metal sorbents in aqueous systems, are directly linked to the intensity of bacterial decompositional processes in bed sediments, thus, metals associated with these sediment fractions show dynamic behaviour reflecting changing bed sediment redox conditions driven by bacterial decomposition. The redox processes that are dominant in a particular location will depend largely on the biological activity and the linked physico-chemical conditions of the system, such as mixing processes, turbidity and temperature.

1.2.3 Ionic Strength

Ionic strength is a measure of the electrical interactions between ions in solution. An increase in ionic strength reflects greater ionic concentrations, and leads to a relative decrease in the activity of ions in solution (under freshwater conditions). Typically, increasing ionic strength will decrease ionic interactions with solid surfaces due to a compression of the electrical double layer surrounding the surface (Lützenkirchen, 1997; Puls et al., 1991) and commonly induces greater intra-metal competition where metals with similar chemistries compete with each other for a reduced number of surface reactive sites on particles. This phenomenon has been shown to increase the concentration of less competitive metals in solution as sorption of metals with higher affinities for the solid surface is favoured in this competitive environment (Bradbury and Bayens, 2005; Staunton, 2004; Christophi and Axe, 2000).

1.2.4 Temperature

Temperature affects reaction rates between metals and mineral surfaces with increasing temperature, typically increasing reaction rates. It is well documented as an important factor in determining metal sorption to solid surfaces (Dho and Lee, 2003; Sheckel and Sparks, 2001; Angrove et al., 1999 and 1998; Rodda et al., 1996; Warren and Zimmerman, 1994). Temperature also positively affects growth rates of bacteria and other organisms presenting ramifications for other biologically controlled or influenced processes in environmental systems, particularly those sensitive to changes in ORP and pH.

1.2.5 Dissolved Organic Carbon

Dissolved organic carbon (DOC) is composed of carbohydrates, proteins, peptides, amino acids, fats, waxes, resins, pigments, and other low-molecular weight organic substances as well as relatively resistant, dark coloured, and acidic compounds called humic and fluvic substances (Morel and Herring, 1993; Wetzel, 1983). Humic substances are the acidic fraction of DOC that is resistant to oxidation while fluvic substances are acid soluble and usually have a lower molecular weight (Morel and Herring, 1993). These substances are the product of organic material in varying states of decomposition. DOC is typically associated with sewage treatment plant effluent complexation reactions, form stronger associations than outer sphere complexes and are defined as reactions that form covalent bonds between ions in solution and surface species (Stumm, 1992).

Solid compartments, which include the bed sediment and SPM compartments are composed of mineral and organic components. Total sediment associated metals are often used as a reference indicator of metal contamination in a system, however, metals are bound differentially to potentially reactive fractions within the solid compartment (Tessier et al., 1979), and thus the concentration of metal associated with these potentially metal-reactive solid fractions within a heterogeneous sediment are of profound importance in defining metal behaviour. However, it is not currently physically possible to separate out these sediment components from a mixed, heterogeneous mixture and determine their associated metal loads. Thus, sequential extraction procedures were developed that utilize analytical methods designed to extract metals associated with a series of identified reactive sediment components through progressive dissolution of those phases in an operationally defined scheme. In a sequential extraction each fraction is dissolved, starting with the most labile fractions and progressing to the least labile, typically refractory mineral components. There are many variations on the sequential extraction procedure, the first and perhaps best known procedure was developed by Tessier et al. (1979) and many procedures developed since then have used his protocol as a starting framework, including the extraction procedure used in this research (Haack and Warren, 2003).

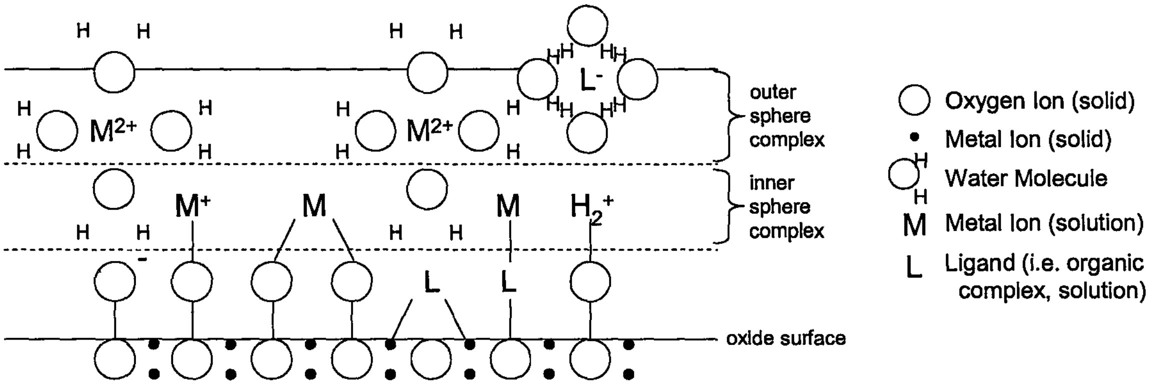

Figure 1.2: Inner and Outer sphere associated ions. Inner sphere ions are sorbed to the mineral surface (metal oxyhydroxide is used as an example) by covalent bonds, while relatively weaker, electrostatic interactions sorb outer sphere complexes, the definition of these reactions usually requires separation of at least one water molecule between solid surface and outer sphere ion (adapted from Stumm, 1992 and Warren and Haack, 2001).

The sequential extraction procedure used in this research includes an additional step to allow the differentiation between amorphous and crystalline oxyhydroxides (Haack, 2004). It is useful to differentiate between these two components due to their differences in reactivity with respect to metals (Nelson et al., 2002; Warren and Haack, 2001). In total, there are 6 operationally-defined steps in the extraction procedure. Each step is designed to extract metals associated with a specific reactive fraction that is commonly found in aqueous systems. The scheme is comprehensive in its sediment fraction inclusions to ensure that all potential reactive metal phases associated with the bulk sediment pool are analyzed. The sequential extraction fractions are: 1) exchangeable, 2) carbonate, 3) amorphous oxyhydroxide, 4) crystalline oxyhydroxide, 5) organic matter and 6) residual, which operationally define metals associated with these sediment phases (i.e. exchangeable refers to metals loosely sorbed at the sediment surface, and residual refers to refractory mineral phases where metals are typically held within mineral lattices).

1.2.7.1 Exchangeable

The exchangeable fraction refers to the metals that are bound by electrostatic interactions to a charged surface, usually referred to as outer sphere complexes; this definition requires that one (or more) water molecules occurs between the metal and the charged surface (Stumm and Morgan, 1996; Tessier, 1979; Warren and Haack, 2001; see Figure 1.2). These metals are exchanged between the solid surface and the solution with relative ease because the forces holding the metals in place are relatively weak. Metals that are held in close proximity to a surface (i.e. mineral) by this physical process may then become more easily available for interactions with other solid surfaces in the sediment system; therefore, should a sorption site become available, the exchangeable fraction is readily incorporated into an inner sphere complex (Brown et al., 1999a).

The exchangeable fraction is easily influenced by the ionic strength of the solution because it involves diffusion from the solution to the solid. As mentioned earlier, an increase in the ionic strength of the overlying solution causes a decrease in the activity, or effective concentration, of the ions in solution, furthermore, there is a decrease in thickness of the interfacial charge differential zone surrounding the surface where the exchangeable ions are adsorbed (Warren and Haack, 2001). Both of these conditions decrease the electrostatic force of the attraction of the ions to the surface. In general, there is a decrease in the number of outer sphere ions with an increase in ionic strength that can take place at the solid surface – solution interface between surface functional groups and metal ions in solution with an increase in ionic strength (Lores and Pennock, 1998; Puls et al., 1991; Hayes and Leckie, 1987).

1.2.7.2 Carbonates

Metals may be sorbed to carbonates surfaces via complexation reactions or metals may coprecipitate with carbonate minerals (Reeder et al., 1999). Studies indicate that the sorption mechanism involved for some metals to carbonates may be initiated by an adsorption reaction first on the surface of the carbonate mineral which is then followed by a nucleation and subsequent formation of a surface metal precipitate that can further sorb metals (Franklin and Morse, 1983; McBride, 1979; Davis et al., 1987; Zachara et al., 1988). Zachara et al. (1991), in a study of metal sorption on calcite, report that desorption processes are metal dependent with Zn, Co and Ni being more easily desorbed than Cd and Mn. Carbonates have also been reported as a substrate for adsorption and precipitation of organic matter (Morse, 1986, and references therein).

Because of their prime importance in alkalinity reactions in freshwater environments, carbonates are susceptible to dissolution with a decrease in pH and, consequently, a release of carbonate associated metals can occur with decreasing pH conditions (Tessier et al., 1979; Stumm and Morgan, 1996). In areas that are high in carbonate minerals, such as the Hamilton Harbour watershed, carbonates are typically of greater importance for metal uptake.

1.2.7.3 Amorphous and Crystalline Fe and Mn Oxyhydroxides

Amorphous and crystalline oxyhydroxides minerals are a dominant controlling solid fraction for metals in the environment because of their high reactivity, their ubiquitous nature, and their association commonly with smaller grained particles where they often form surface coatings which may cover other metal-reactive surfaces such as carbonates, organic matter, clays or bacteria (Brown et al., 1999; Small et al., 1999; Warren and Zimmerman, 1994). Oxyhydroxides can also exist as nodules, concretions or cement between particles (Tessier et al., 1979). The production of surface coatings, in particular, allows for a greater surface area to volume ratio, which allows for greater metal uptake associated with surface sorption reactions, despite their relatively small concentration in solid fractions (Warren and Haack, 2001).

Amorphous oxyhydroxides tend to be more reactive and are able to adsorb more metal than their crystalline counterparts (Nelson et al., 2002). Amorphous oxyhydroxides tend to be formed first: they are quickly precipitated or biogenically formed, and are generally poorly structured and small in size (Nelson et al., 1999; Stumm, 1992). As amorphous oxyhydroxides age they become more structured and stable forming crystalline oxyhydroxides, which tend to be less soluble and larger in size (Stumm, 1992). The enhanced adsorption qualities of amorphous oxyhydroxides are primarily due to their high surface area and high density of defect sites to which metals can easily sorb (Brown et al., 1999).

Iron oxyhydroxides are rapidly formed abiotically above pH 3, while Mn oxidation is predominantly a bacterially mediated process below pH 9; abiotically, Mn oxidation occurs on a time scale of months to years (Stumm and Morgan, 1996). Mn oxyhydroxides that are formed biogenically and Fe oxyhydroxides that are either formed biogenically or abiotically are more amorphous than those precipitated over slowly changing conditions or longer time scales (Nelson et al., 2002). Both Fe and Mn reduction occurs more quickly with bacterially mediated catalysis (Nealson and Little, 1997; Lovely, 1991; Brown et al., 1999b; Brown et al., 1998 and Warren and Ferris, 1998). Changes in redox potential can reduce Fe and Mn oxyhydroxides, causing them to become more soluble, releasing Fe, Mn and other metals associated with the oxyhydroxides (Tessier et al., 1979; Stumm and Morgan, 1996).

Oxyhydroxides possess amphoteric surfaces: their surfaces can be both net positively or net negatively charged depending on system pH and thus surface metal sorption processes (e.g. nature of metal sorbed, pH at which oxyhydroxides effectively sorb metals) change depending on pH, (Stumm, 1992; Warren and Haack, 2001). At a certain pH, called the pHzpc these minerals carry a net neutral charge; the sum of their positive surface charges equals the sum of their negative surface charge. As the pH increases above the pHzpc the surface functional groups lose the protons bound to the surface to remain in equilibrium with the solution and the surface becomes increasingly net negatively charged. As the pH decreases below the pHzpc, the surface sorbs greater protons, increases its net positive charge and becomes a net positive surface. Thus metal sorption is pH dependent for oxyhydroxides and will depend on which oxyhydroxide and metal are involved. Oxyhydroxide pHzpc is mineral dependent. The pHzpc for a typical Fe oxyhydroxide is 7.8 and for Mn oxyhydroxide values of between reported to range from 3.2 to 6.8 (Kennedy et al., 2004; Stumm, 1992).

Further, metal speciation is element specific and some metals are cationic whilst others are anionic in aqueous systems. Thus some metals are more efficiently sorbed at low pH as they form oxyanion species, e.g. CrO_4^{2-}, while divalent cationic species, such as Cd^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} will sorb more effectively at higher pH values to oxyhydroxides as their surfaces become increasingly negatively charged. If the surface of the oxyhydroxide is positively charged, sorption of other negatively charged species, such as bacterial cells or other organic matter, is also possible which will induce a charge reversal of the mineral surface to which it is sorbed as any organic surface is always negatively charged in aqueous systems due to the extremely low pKa values of their carboxylic functional groups (Au et al., 1999).

1.2.7.4 Organic Matter

Organic matter is composed of any biological materials, including humic and fulvic acids, algal and bacterial cells, bacterial surfaces - both dead and alive – and the extracellular polysaccharides associated with bacteria (Leppard et al., 2003; Ledin, 2000; Buffle et al., 1990). Humic and fluvic substances can exist in both dissolved and particulate form, and both are forms of refractory organic matter. Metals bind to organic matter because it possesses a variety of highly reactive functional groups, most notably carboxylic, phenolic, alcohol and amine groups (Stumm, 1992; Cox et al., 1999). These functional groups have unique metal binding properties and each possess different pK_as. Because of the complex mixture of these functional groups, organic matter is able to maintain a net negative charge throughout the range of pH values found in natural waters providing the high affinity of organic matter for cationic species, as well as sorption of Fe

1.4 Metal Specific Behavior

In a metal contaminated system it is important to recognize that metal behavior is dependent on the element(s) involved. Sorption is influenced by the affinity of a metal for a particular sorbent and speciation in solution is influenced by specific metal properties such as the number of oxidation states that the metal atom possesses and the structure of the atom. Specific metal characteristics dictate the affinity and necessity of a metal for the metabolic pathway of a particular organism, and the affinity of a metal for a particular sorbent, thus influencing bioavailability and toxicity of that metal.

Twelve metals were chosen in this study: Cr, Mn, Co, Cu, Sn, Ag, As, Ni, Zn, Cd, Se and Fe. There are many metals of interest in Hamilton Harbour due to the various anthropogenic activities in the surrounding area. This particular suite of metals was chosen to represent a range of toxicity to organisms, abundance in the system and biogeochemical behavior in the environment.

1.4.1 Chromium

Cr is a redox sensitive species, the oxidized form, Cr(VI), is found in solution as a dissolved anion, commonly chromate or dichromate (CrO_4^{-2} or $Cr_2O_7^{-2}$), while under intermediate and reducing conditions Cr occurs as Cr(III) and is generally less mobile and strongly absorbed, intermediates Cr(IV) and Cr(V) are unstable in normal conditions (Drever, 1997). Reduced forms of Cr are more easily oxidized at higher pH and the oxidized form is more stable with increasing pH, however it is soluble at all pHs (Kimbrough, 1999). Cr commonly associates with Fe and Mn oxyhydroxides and organic matter (Moore, 1991). Metal alloy commonly employs Cr production (Moore and Ramamoorthy, 1984).

1.4.2 Manganese

Mn is used in the production of iron alloys and non-ferrous alloys and is also found in geogenic particulate, as such, it is often found in the carbonate fraction (as a geogenic component) and in the oxyhydroxide fraction (Moore, 1991). The most important oxidation states of manganese are Mn(II) and Mn(IV), however, oxidation states of Mn range from (-III) to (VII). Mn is an essential element for both animals and plants and, generally, does not present direct toxicological significance in aquatic systems; however Mn is of great importance in the control of other metals as it forms a constituent of a ubiquitous and important metal-reactive fraction, the oxyhydroxides. These mineral fractions are discussed previously (see Section 1.2.8.3). In addition, Mn is present in large quantities in Hamilton Harbour and, therefore, important to quantify (HHRAP, 1992).

1.4.3 Cobalt

Co is an essential element for many organisms and has not been identified as an environmentally significant contaminant for fish, however, it can be found in high, potentially toxic concentrations in some contaminated environments (Moore, 1991). Normal concentrations are from 0.02μmol/g – 0.2μmol/g and concentrations in Hamilton Harbour have been reported to be as high as 0.64μmol/g (Poulton, 1987). Sources of Co are commonly found in runoff from mining operations and urban stormwater as well as industrial effluents (Triantafyllou et al., 1999). The most common oxidation state of Co is Co(II), but there is also a Co(III) oxidation state. Co concentrations in water are correlated with pH and Co is also shown to be scavenged by manganese oxides and therefore, Co concentrations in water are effected by redox (Talliefert et al., 2002; Lienemann et al., 1997; Moore and Ramamoorthy, 1984).

1.4.4 Copper

Cu has three oxidation states, however the Cu(II) is the most common. Cu and alloys of Cu are often found in applications for electrical energy use and plumbing also it was once used as a component of marine biocide however, use of this substance has been phased out (Moore and Ramamoothy, 1984). The behavior of Ni, Zn, Cd, Cu and Co are similar, they are all present in solution as a divalent, positively-charged ion, and are commonly investigated in other studies. Cu is often incorporated in organic matter (Mahony et al., 1996).

1.4.5 Tin

Tin is of interest particularly because it is often used as an antifouling agent in paint, inhibiting the attachment of aquatic organisms that may foul the hauls of large commercial vessels (Haggartt et al., 1992), however, Sn is also used to form steel alloys. The tributyl form of tin is the most toxic form (Macguire, 1987) and this form continues to be found in the paint on larger commercial vessels; however, its use has been discontinued in smaller vessels (Haggartt et al., 1992). Tin is also found in inorganic forms as Sn^{4+}, Sn^{2+}, Sn^{4-} and Sn^0. It is reported to associate with oxyhydroxides and clay minerals in aqueous environments (Moore, 1991). Contributions of tin and its toxic constituents may occur by sloughing-off of paint as the hulls of larger vessels scrape the bottom of the Harbour en route to the various industries on the south shore.

1.4.6 Silver

Silver is included in this study because of the known toxicity of this element to biota, the Ag^+ ion is one of the most toxic substances found in surface waters (Moore, 1991). Common sources of Ag are mining and milling of ores, photographic chemical waste and municipal waste. Efforts are often made to recover Ag from waste products and thus, concentrations in water are not often high. The principal form of Ag in water is

Ag^+ and it is known to associate with organic matter (Leppard et al., 2003), oxyhydroxides and clays (Moore and Ramamoorthy, 1984).

1.4.7 Arsenic

As is a redox sensitive species, found in four oxidation states As^{-3}, As^0, As^{+3} and As^{+5}, depending on redox status and pH (Moore, 1991). As^{+3} and As^{+5} are the most common ionic forms (Moore and Ramamoorthy, 1984). The As^{+3} form is more toxic and more mobile than the As^{+5} form (Jonnalagadda and Rao, 1993; Mandal and Suzuki, 2002, and references therein) which may be a consequence of the high sorption affinity of As^{+5} for immobile oxyhydroxides (Martin and Pedersen, 2002; Martin and Pedersen, 2004) or it is possible that reducing conditions simply favour the reduction of both the oxyhydroxides and As^{+5} (Harrington et al., 1998). As is often associated with oxyhydroxides, carbonates and less frequently to organic matter (Moore, 1991).

1.4.8 Nickel

Ni occurs primarily as Ni(II), however, oxidation states ranging from Ni(-I) to Ni(IV) have been reported (Moore, 1991). Ni inputs from anthropogenic sources are found in the production of Ni alloys, including steel alloys, and from mining and smelting operations (Moore, 1991). Ni is more toxic to plants than other organisms and is generally found in low concentrations in surface waters (Moore and Ramamoorthy, 1984). It is often found bound to oxyhydroxides, carbonates and organic matter in oxidizing conditions and sulfur in reducing conditions (Moore and Ramamoorthy, 1984).

1.4.9 Zinc

Zinc is investigated because (HHRAP, 1992; Poulton, 1987). This metal is used in the production of steel as a protective coating and in other metal production processes; it is also a component of fertilizer and cement (Moore, 1991). It is also important because of the known abundance of this metal in the Harbour. Zn has been shown to partition primarily to the oxyhydroxide fraction and is found as a carbonate mineral from geogenic sources (Moore, 1991). The only oxidation state of Zn is Zn(II), however the speciation of Zn is dependent on pH and redox conditions: Zn forms various hydroxide species, depending on pH, under oxidizing conditions and ZnS under anoxic conditions regardless of pH (Moore, 1991).

1.4.10 Cadmium

Cd sources are smelting, refining of nonferrous metals and in domestic waste (Moore, 1991). The only oxidation state of Cd is Cd(II). Cd is often associated with manganese oxyhydroxides, and carbonate fractions (Moore, 1991). Cd and the Cd(II) ion are particularly toxic to plants and animals at concentrations as low as 0.008µmol/L causing mortality in some fish species (Moore, 1991).

1.4.11 Selenium

Selenium has four oxidation states Se(-II), Se(0), Se(IV) and Se(VI). Reduced conditions favour the solubility of the Se(-II) and Se(0), while oxidizing conditions favour the solubility of Se(IV) and Se(VI) and the oxidation of Se species is relatively rapid (Masscheleyn et al., 1990). Conditions that favour Se solubility are high pH, oxidizing conditions, and high concentrations of additional anions in solution (Masscheleyn et al., 1990). The solubility of Se is highly influenced by redox potential and insoluable in anoxic conditions, however, Se may become available from anoxic sediment if the sediment is oxidized via even small turbulent events in the sediment (Peters et al., 1999). Se is found in the organic matter fraction, the oxyhydroxide fraction and the exchangeable fraction (Peters et al., 1999). Anthropogenic sources of Se are burning of fossil fuels, smelting and refining processes (Moore, 1991). Se is highly bioavailable and can bioaccumulate to potentially toxic levels in aquatic organisms (Moore, 1991).

1.4.12 Iron

Fe pollution is common in areas where steel and iron are manufactured (Moore, 1991) so it is not surprising that Fe is the most abundant metal in Hamilton Harbour (HHRAP, 1992; Krantzberg, 1995). Fe is an essential element for many organisms and is therefore, not highly toxic (Moore, 1991). It has two oxidation states Fe(II) and Fe(III). Fe(III), which is practically insoluable under oxidizing conditions and dominates in aerobic conditions and the Fe(II), a soluable form, dominates in anaerobic conditions (Moore, 1991); therefore, it is highly influenced by redox processes. Fe(III) forms oxyhydroxide minerals and, often associated with Mn oxyhydroxide, is important in the sorption and control of other elements, most notably in this context, metals. The importance of Fe as a metal sorbent has been discussed (section 1.2.8.3). Because of the importance of iron as a trace metal sorbent, a change in redox status may reduce insoluble Fe (III) to soluable Fe (II) and release the associated metals to the surrounding water, making Fe cycling an extremely important process.

1.5 Research Directions

There are a great number of metals of interest in Hamilton Harbour many of which have been investigated in studies on bed sediment (e.g. Krantzberg, 1994; Diamond and Ling-Lamprecht, 1996), SPM (Mayer and Manning, 1990) and dissolved metals (e.g. Poulton, 1987; Diamond and Ling-Lamprecht, 1996). A suite of 12 metals, specifically, Cr, Mn, Co, Cu, Sn, Ag, As, Ni, Zn, Cd, Se and Fe, was chosen for this research based on toxicity to biota, redox behavior, abundance in the system, and importance as components of reactive solids.

To date, a number of studies have investigated metals in Hamilton Harbour, several dealing with bioavailability of metals (Krantzberg, 1994; Krantzberg and Boyd, 1995), spatial variability of total metals in SPM (Mayer and Manning, 1990) and bed sediments (HHRAP, 1988) and fractionation of metals in sediments (Krantzberg, 1994; McIsaac et al., 1981). However, there is a paucity of information investigating the dynamics of metal movement among the three important aquatic compartments, SPM, bed sediment and dissolved compartments at a high resolution temporal and spatial scale either in Hamilton Harbour or in other freshwater bodies.

Therefore, the goals of this study are to 1) determine the concentrations of a suite of 12 metals (Cr, Mn, Co, Cu, Sn, Ag, As, Ni, Zn, Cd, Se and Fe) in three compartments ((i) surficial bed sediments, (ii) SPM, and (iii) dissolved), at two sites; 2) characterize the geochemical fractionation of these 12 metals with the two solid (surficial bed sediment and SPM) compartments; 3) evaluate dynamic exchange of metals amongst these three compartments; and 4) identify controlling factors in metal behavior at two sites in Hamilton Harbour at a high resolution spatial and temporal scale.

Chapter 2: Materials and Methods

2.1 Study Site

Hamilton Harbour is located at the western end of Lake Ontario (Figure 2.1). The Harbour is separated from Lake Ontario by a sand bar which has been reinforced during the last two centuries by the addition of a beach community and a well-used roadway. The Burlington Ship Canal is the only entrance for shipping traffic to the Harbour and a means of water exchange with Lake Ontario (Barica, 1989). A large volume of industrial shipping traffic enters the Harbour to service the two large steel mills on the south shore and there are also recreational vessels that frequently use the Harbour.

Discharge from two large steel mills and other industries, input from the urban, industrial and agricultural watershed, and treated sanitary sewage and combined sewer outflows carry a variety of contaminants to the Harbour. As a result, the suspended sediment and bed sediment in the Harbour have high concentrations of metal contamination. In the 1980's, Hamilton Harbour was designated by the International Joint Commission as an "Area of Concern", meaning that it fails to meet criteria set out by the IJC to maintain biological integrity of the ecosystem (IJC, 1987). Due to this appointment, a Remedial Action Plan (HHRAP) was developed to identify objectives specific to Hamilton Harbour. The RAP identifies metals (specifically, arsenic, cadmium, iron, copper, nickel, manganese and zinc) as priority contaminants and substances that "pose a risk to fish and wildlife" (HHRAP, 2004).

Reductions in loading to the Harbour have aimed to bring many of the metal concentrations in the water at, or below the provincial guidelines by 2001; however, the sediment remains a significant sink/source for metals in the Harbour (Persaud et al., 1992).

2.2 Site Selection

During the summer of 2003 preliminary data, including bed sediment samples, water samples and physical-chemical profiles were gathered from seven sites within Hamilton Harbour. Two sites were selected based on metal concentrations found at the sites, physico-chemical conditions and anthropogenic inputs. The shallow site (UTM: E590502 N4792698), with an average depth of 1.5m, is located in the northwestern corner of the Harbour in a shallow bay that has a well-mixed water column the deep site, with an average of 6.9m depth, is near the boat slip for one of the steel mills. The epilimnion at the deep site (UTM: E597704 N4792185) was at approximately 5.5m depth (Figure 2.1). A more rigorous sampling regime for comparison of these two sites was begun in the spring of 2004.

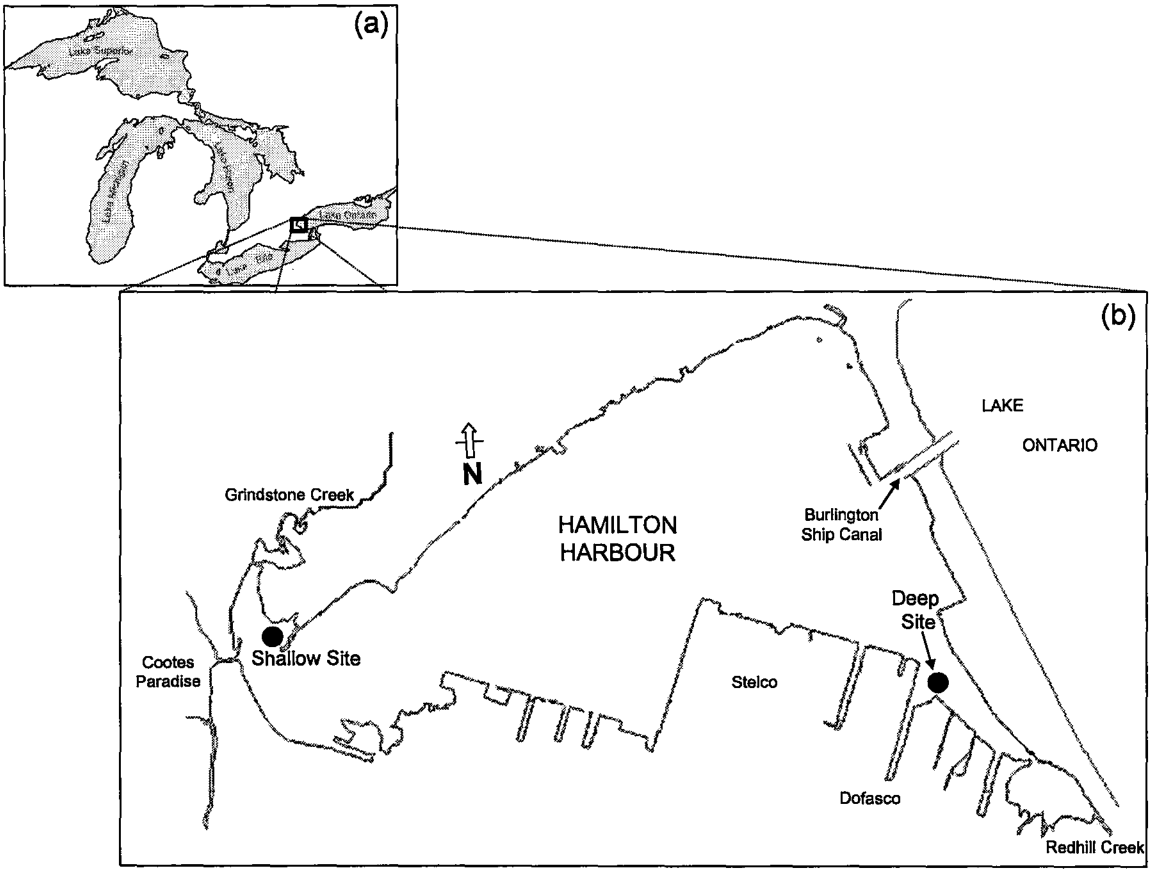

Figure 2.1: Map showing the location of Hamilton Harbour in the Laurentian Great Lakes area (a) and the location of the shallow and deep sites within the Harbour (b).

2.3 Sample Collection

Sampling occurred from May to August of 2004 over a period of three days each month. During each three-day period, two sites were visited a total of three times each. During the first day the shallow site was sampled in the morning (AM: between 8am and 9:30am) and in the afternoon (PM: between 4pm -5pm), the second day the shallow site was sampled in the AM and the deep site was sampled in the PM. On the final day, the deep site was sampled in the AM and PM. Sampling in August was adjusted to avoid unsafe weather conditions: on the second day of sampling the deep site sample was taken prior to the shallow site in the AM, instead of the PM, therefore the deep site was taken at approximately 8:30am and the shallow site was taken at approximately 10:00am.

Sampling protocol included physico-chemical profiles of the water column, water samples collected for dissolved-phase metal analysis, bed sediment samples, suspended particulate matter (SPM) samples and sediment pore water samples (in July and August only) (Figure 2.2). Dissolved organic carbon and SPM concentration samples were also collected and analyzed by Environment Canada.

2.3.1 Sample Container Preparation

Sampling equipment that came in contact with samples (i.e. VanDorn bottle, sediment core tubes, sediment-extruding implements and all sample containers) was acid washed and rinsed using ultra-pure water (UPW: Millipore Milli-Q Gradient system, 18.2mΩ/cm) using the following procedure: 1) soak in dilute soap solution (Sparkleen1, Fisher Scientific catalogue #04-320-4) rinse with UPW several times 2) rinse with 95% ethanol and rinse with UPW at least 7 times 3) immerse in 4% HCl solution for at least 8 hours and rinse at least 7 times with UPW 4) then stored immediately in clean plastic bags.

2.3.2 Physico-chemical Profiles

A Hydrolab Datasonde 4 was used to obtain temperature (temp), per cent dissolved oxygen (DO%), pH, oxidation-reduction potential (ORP) and specific conductivity (SPC) profiles from each site. Light irradiance was measured with a Li-Cor spherical quantum sensor. Irradiance values were used to calculate extinction coefficients to obtain the depth of the 1% light penetration.

2.3.3 Dissolved Metal Sampling

Discrete water samples were collected for dissolved metal analysis at approximately 0.5m - 1.0m above the sediment/water interface (congruent with SPM sampling), using a trace metal clean, acid washed Van Dorn water sampler. Water was poured into an acid washed syringe and filtered through a 0.45μm and 0.2μm sterile in-line syringe filter and subsequently preserved with nitric acid (2%). The 0.45μm filter is a pre-filtration step and the 0.2μm size removes suspended particles, bacteria, algae and most colloids (Stumm and Morgan, 1996).

2.3.4 Surficial Bed Sediment Sampling

Polycarbonate sediment core tubes and all other sampling implements were acid washed prior to use. Three separate sediment core samples were obtained at each sample time for triplicate analysis. Cores were taken by SCUBA divers to ensure the integrity of the structure of the sediment/water interface. Sediment samples were taken from the top 2 - 4mm of the core and extruded within 20 minutes upon arrival at the surface into a Whirlpak sample bag. Bagged samples were frozen immediately on dry ice for transport back to the laboratory.

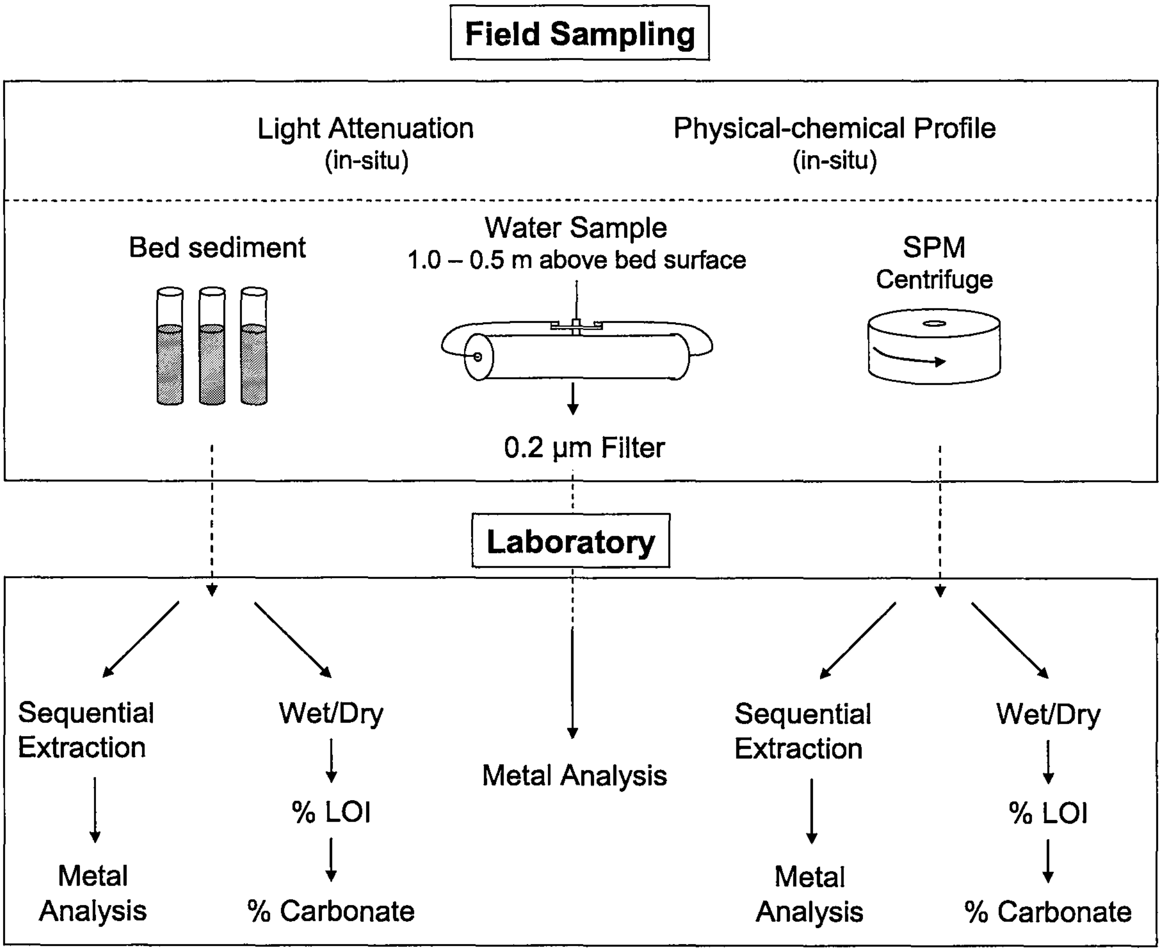

Figure 2.2: Method summary of the sampling procedure for all three compartments.

2.3.5 SPM Sampling

SPM samples were collected from 1m above the sediment/water interface by NWRI staff in a continuous flow centrifuge (Alfa-Laval Model WSB 103B). Water was pumped to the centrifuge by a 5C-MD March submersible pump located 0.5m above the bed sediment surface. The centrifuge was adjusted to a flow rate of 4L/min for optimal efficiency. The stainless steel centrifuge bowls were then transported back to NWRI in Burlington, Ontario for sample removal. Samples were removed from the bowl as aqueous slurry, placed in acid washed polypropylene bottles and refrigerated. Samples were subsequently centrifuged in an ultracentrifuge (Sorvall RC-5C Plus) at 10 000 RPM for 30 minutes and stored frozen until analysis. Water samples were taken for SPM concentrations (in mg/L) and analysed by NWRI staff.

2.4 Sediment Analysis

Bed sediment and SPM were analyzed in the laboratory for metal content, water:dry ratio, loss on ignition (%LOI) and carbonate content. Once thawed, samples were centrifuged for 10 minutes at 12 000 rpm prior to analysis, due to high water content. Sediment samples were then homogenized by stirring and separated into two aliquots: one for wet:dry ratio, %LOI and carbonate analysis and the other for determination of metal fraction association.

2.4.1 Wet:Dry, %LOI and Carbonate Content Analyses

The same sediment sample was used for these three analyses. Each sample was analysed in triplicate, in the case of bed sediment three separate samples were obtained in the field at each sample time and each sample was analysed to make triplicate samples, while for water samples and SPM samples three separate samples were taken from the single field sample taken for triplicate analysis. Wet:dry ratios were obtained by placing a sediment sample in a pre-weighed aluminum dish and, after weighing the dish and wet sediment, placing it in a drying oven overnight at 105°C. Dish and dry sediment were weighed and wet:dry ratio was obtained by dividing the weight of the wet sediment by the dry sediment weight.

%LOI was determined according to the procedure in Bengtsson and Enell, (1986) with ignition time recommended by Heiri et al. (2001). Dried sample from the wet:dry analysis was placed in a pre-weighed porcelain crucible and placed in a muffle furnace for one hour at 450°C. The samples were allowed to cool in a dessicator and subsequently weighed. The loss of mass was converted to a per cent value. Samples were placed back in the muffle furnace at 950°C for one hour. After removal from the oven and cooling in a dessicator, samples were weighed and the difference in mass between this weight and the weight of the sample after %LOI analysis was converted to a per cent value to determine the carbonate content of the sediment.

2.4.2 Metal Fractionation Analysis

All sediment and SPM samples were processed in triplicate using a microwave digestion sequential extraction procedure from Haack and Warren, 2003. This uses a procedure adapted from Tessier et al. (1979), and includes an additional extraction step that allows the differentiation between the amorphous and crystalline oxides (Table 2.1).

Reagents were added to 1g of wet sediment in approximately a 20:1, reagents-to-wet-sediment ratio and samples were subjected to the conditions specified by the procedure. The resulting slurry was then centrifuged for 20 minutes at 16 000 rpm and the supernatant was decanted. The subsequent reagent in the procedure was added to the remaining sediment pellet, subjected to extraction conditions and centrifuged until the process was completed. Each run was accompanied by a reagent blank to correct for contamination during the procedure. Total metal concentrations were determined by summing the metals obtained from the extraction of each fraction unless otherwise identified.

2.5 Metal Analysis

Dissolved metal samples, bed sediment and SPM extraction steps were diluted in a 2% Nitric acid solution and analyzed for Cr, Mn, Co, Cu, Sn, Ag, As, Ni, Zn, Cd, Se and Fe content using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS: PerkinElmer Elan® 6100). Dissolved metal samples were analysed in triplicate (while bed sediment and SPM samples were sequentially extracted in triplicate). An internal standard (Y^{89} in-line at 2ppb) was used to detect instrument drift and matrix effects were corrected for using standard solutions made in the same matrix. Total metal concentrations were determined by summing the concentrations of the six extraction phases.

2.6 Data Analysis

All statistical analyses were performed using SigmaPlot 9.01 (Systat Software, Inc., 2004). All metal data were shown as the mean +/- the standard error (S.E.) which is defined as the standard deviation of the mean divided by the square root of the sample size. Coefficents of variation, reported as per cent values, were often used as a measure of variability and were calculated as: standard deviation divided by the mean, multiplied by 100. Regression analysis was performed using logarithmically transformed data to improve normality and homoscedasticity. ANOVA analyses were performed, followed by a post hoc multiple comparison procedure to determine variables that were significantly different. Unless otherwise stated, the total number of bed sediment and dissolved samples at each site was 12 and the total number of SPM samples at each site was 11. Each of these samples was analysed in triplicate.

2.6.1 Determination of Amorphous and Crystalline Oxyhydroxide Concentrations

An estimate of the per-gram mass of the Amorphous oxides and Crystalline oxides was determined by converting the Fe and Mn that was extracted from the amorphous and crystalline sequential extraction steps, respectively, into a 'grams of oxyhydroxide per gram of sediment' value using the molar mass of the most common oxyhydroxide, FeOOH (Ferrihydrite) and MnOOH (Manganite).

Table 2.1: Outline of reagents used and conditions for the reaction of each fraction in the sequential extraction procedure. Reagents were added in a 20:1 ratio reagents-to-dry weight sediment sample. Samples were extracted in triplicate. Procedure developed by Haack and Warren (2003).

Fraction	**Reagents**	**Conditions**
Exchangeable	1M sodium acetate, pH 8.2 (with HOAc)	1hr shaking, room temperature
Carbonates	1M sodium acetate, pH 5.0 (with HOAc)	Microwave Program 1 (MP-1): Heat to 150°C over 8 minutes. Maintain temperature for 5 minutes. 30 minute cool-down.
Reducible: Amorphous Fe/Mn Oxyhydroxides	0.25M Hydroxylamine hydrochloride in 0.25M HCl.	MP-1
Reducible: Crystalline Fe/Mn Oxyhydroxides	1.0M Hydroxylamine hydrochloride in 25% (v/v) acetic acid.	MP-1
Oxidizable: Organic and Sulfides	3:2 ratio 30% H_2O_2: 0.02M HNO_3 + 1:4 ratio 3.2M NH_3OAc:UPW	MP-1
Residual	Concentrated HNO_3	Microwave Program 2 (MP-2): Heat to 180°C over 20 minutes. Maintain temperature for 10 minutes. 45 minute cool-down.

Chapter 3: Results and Discussion

3.1 System Chemistry and Total Metals

3.1.1 Water Column Physico-Chemical Characteristics

Physico-chemical conditions in the bottom 1m of the water column are generally similar for both sites. Water column mean May to August temperature, pH, specific conductivity (SPC) and per cent dissolved oxygen (DO%) were not significantly different ($p<0.05$) between the deep and shallow sites (19°C± 3°C, 7.7±0.4, 635μS/cm^2 ± 40μS/cm^2 and 73% ± 26% for the shallow site and 18°C± 4°C, 7.6±0.3, 637μS/cm^2 ± 53μS/cm^2 and 67% ± 13% at the deep site). Water column mean May to August per cent dissolved oxygen (DO%) at the deep site oxygen profiles show greater consumption in bottom waters above the sediment water interface (approximately 5-6m depth), typically indicative of greater consumption of oxygen in sediments and, consequently, a net diffusion of oxygen into sediments that is not replenished by mixing of water.

The mean water column oxidation-reduction (redox) potential from May to August for the deep site was significantly lower (236mV ± 87mV) compared to the shallow site (326mV ± 174mV; $p<0.001$, d.f. = 164, t = 4.3) consistent with the lower dissolved O_2 conditions, particularly in bottom waters at this site, and decreased through the season at both sites. Mean water column pH increased and DO% decreased at the deep site from May to August; however the trends were reversed at the shallow site for these parameters. At both sites the highest SPC and redox potential were recorded in May and generally decreased from May to August while the highest temperatures were found in August and increased from May to August. Thermal stratification occurred during all months at the deep site, more often during afternoon sampling times, however there were intermittent periods of a mixed, unstratified water column (in the morning sampling times and some afternoon sampling times). The shallow site, at a total of 2m depth, showed typically isothermal profiles and a temperature differential of no greater than 1.9°C from the surface to the bottom was observed. The afternoon sample in July was the only exception where there was evidence of typical thermal stratification with a thermocline between 0.6-1m, however the profile was isothermal by the next morning. Profiles in May and the afternoon in June show a thermal structure, where there is a temperature difference between 2.2 and 3.8 degrees, and does not follow the pattern of typical thermal stratification, instead there is a warmer band of water, approximately 30cm deep, near the bottom of the profile (at approximately 1.0m – 1.3m, and increases the water temperature 1°C - 2°C). This may be influenced by Grindstone Creek inflow and caused by a density difference in the water, caused by differences in temperature, that is coming in from this source which appears to be warmer at some sampling times.

The shallow site was always lighted to the bottom, but the 1% light level at the deep site ranged between 4m and 6m or approximately 1m to 3m from the bottom and showed no seasonal-based pattern.

Suspended particulate matter (SPM) concentrations at 1m above the bottom were within the concentrations found at other sites in the tributaries to the St. Lawrence River, Canada (Rondeau et al., 2005), the Don River, Canada (5mg/L – 160mg/L; Warren and Zimmerman, 1994) and a database reporting values from European and United Kingdom Rivers (range: 1mg/L - 201mg/L, mean: 28mg/L; Hakanson et al., 2005). SPM concentrations range from 2mg/L – 35mg/L for both sites with the shallow site showing a greater range (10mg/L – 35mg/L) and the highest concentration (17mg/L). The deep site had an average concentration of 6.6mg/L and a smaller range of 2.3mg/L – 11mg/L. The SPM contribution from Grindstone Creek has been shown to increase with an increase in flow rate which is influenced by precipitation events during the months of May to August: the largest values of SPM at the shallow site occur in May and coincide with a rain event of 34mm in total during the three days prior to sampling and may indicate that there is an important precipitation-associated runoff contribution to the SPM from Grindstone Creek and Cootes Paradise at this location. According to loading estimates for 2002 Grindstone Creek and Cootes Paradise contribute on average, 2403kg/day and 10071kg/day of SPM, respectively, to the Harbour or a total of approximately 47% of the total SPM to the Harbour (O'Connor, 2004). These two sources are influenced by Sewage Treatment Plant (STP) inputs (Dundas STP discharges into Cootes Paradise and Waterdown STP discharges into Grindstone Creek) as well as urban runoff.

In general water column profiles for both sites indicate isothermal, oxygenated, high pH conditions occurred over the sampling period. The shallow littoral site is always lighted to the bottom, with greater SPM concentrations and higher oxygen concentrations compared to the deep site. The deep site shows more reducing conditions, with greater O2 consumption evident in the water overlying the sediments (indicative of oxygen diffusion into the sediments against a consumption gradient) and a lighted depth to 1m - 3m above the interface.

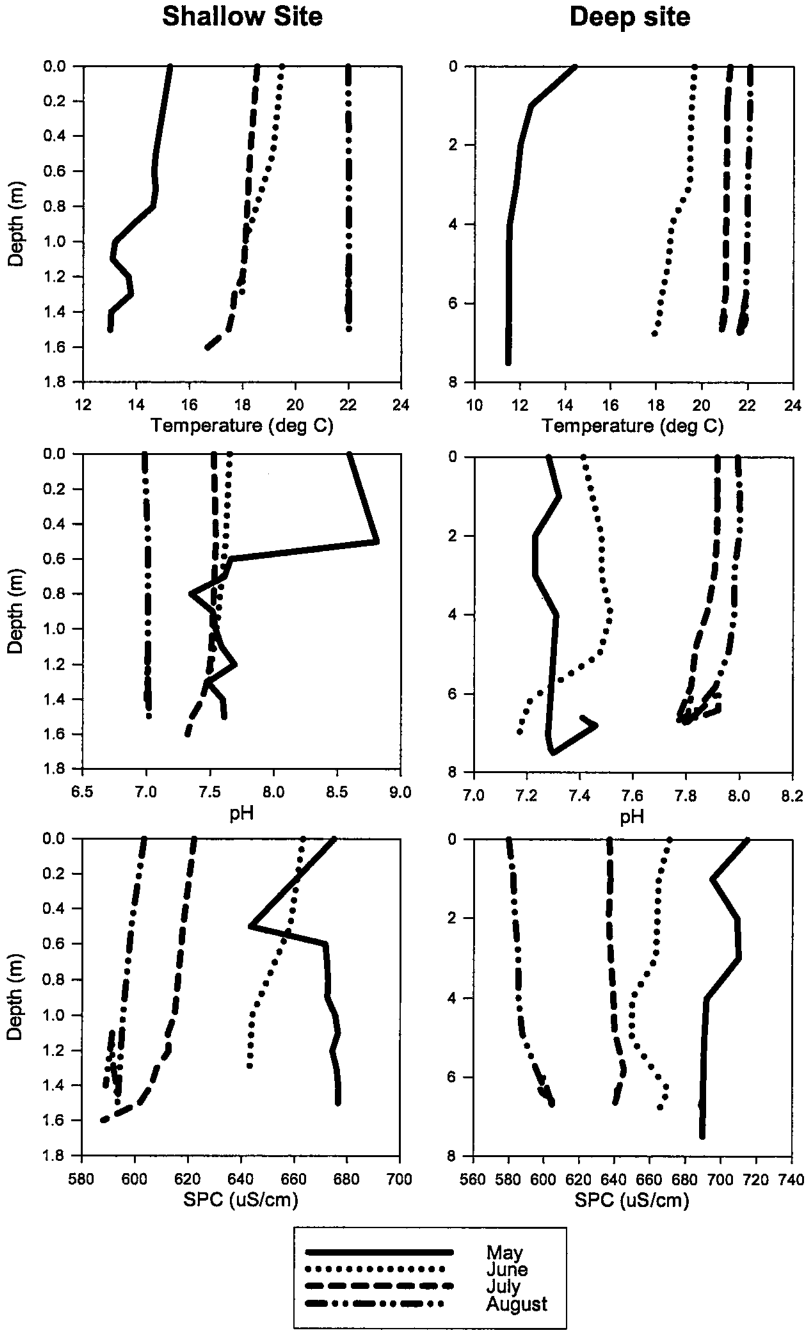

Figure 3.1.1: Temperature (°C), pH and Specific Conductivity (SPC; uS/cm) of the water column at shallow and deep sites. Each plot shows one morning sample from each month. Not all profiles were included for clarity.

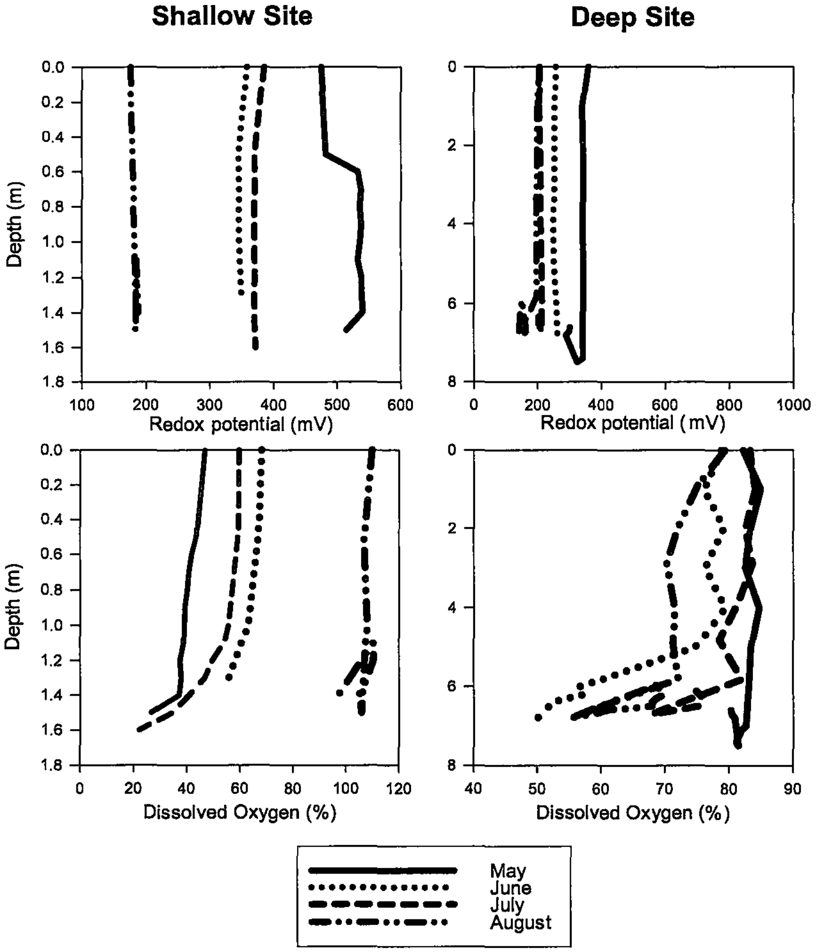

Figure 3.1.1 (continued): Redox (mV) and % Dissolved Oxygen of the water column at shallow and deep sites. Each plot shows one morning sample from each month. Not all profiles were included for clarity.

Comparing morning (AM) and afternoon (PM) samples, there was an increase in DO% in the PM sampling times at the shallow site in June, July and August which likely reflects photosynthetic processes producing oxygen during the day. This is especially evident in August when DO% is above saturation (approx. 120%) throughout the water column. There were no other consistent diel trends in the other physico-chemical parameters (Figure 3.1.1).

The differences in water column physico-chemical characteristics reflect the nature of the two sites the deep site being in a less lighted, intermittently mixed location and the shallow site being in a lighted-to-the-bottom, well-mixed location.

3.1.2 Site Associated Total Metal Abundance in Dissolved Metal, Bed Sediment and SPM Compartments

Metal trends within each of the three compartments are element specific, as discussed in more detail below. However, among the three compartments metals tend to follow similar trends in abundance i.e. metals that are abundant in the dissolved compartment are, generally abundant in the bed sediment and SPM compartments.

3.1.2.1 Metal Abundance in the Dissolved Compartment

As might be expected in an anthropogenically impacted system, dissolved metal concentrations were high, ranging from μM (Fe, Zn, Se) to nM (Mn, Cr, Ni, Cu, As, Co , Cd and Sn) and pM (Ag; Figure 3.1.2). Mean dissolved concentrations for May to August followed the same order of abundance at both the shallow and deep site: Fe (May to August mean: 18μM, shallow and 19μM, deep; note – this pattern is followed for all metals in this list, except where noted) > Zn (7μM, 8μM) > Se (2μM for both sites) > Mn (190nM, 200nM) > Cr (89nM, 93nM) > Ni (25 nM, 33nM) = Cu (24nM, 27nM) > As (8nM, 8nM) > Co (2nM, 2nM) = Cd (2nM, 1nM) > (at shallow site only, = at deep site) Sn (1nM, 1nM) > Ag (0.2nM, 0.2nM) (note "=" between metals in this list indicates no significant difference between these metals, and ">" indicates difference that is larger than one standard error of the mean, n=12). Fe and Cr were the only metals to show a significant difference between the two sites, with slightly higher concentrations at the deep site, in the dissolved compartment possibly pointing to a source of these metals that is specific to the deep site ($n=12$, $p<0.05$; Mann-Whitney Rank Sum Test); no other significant differences in dissolved concentrations were found between the two sites suggesting a reasonably well mixed epilimnion in Hamilton Harbour.

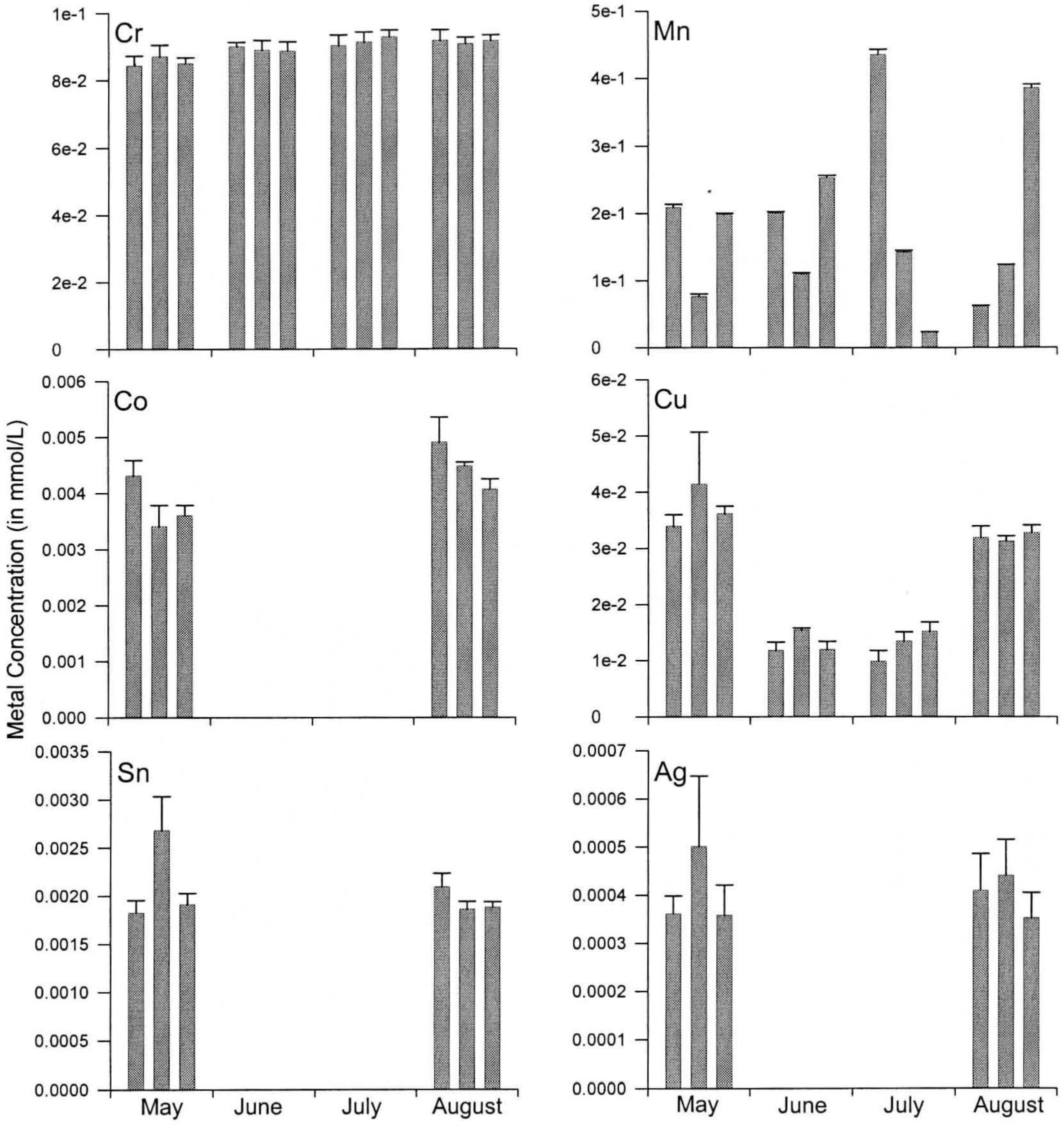

Figure 3.1.2 (a): Metal concentrations in the dissolved compartment (in mM) at the shallow site from May to August 2004. No bar means that the sample was below detection limits.

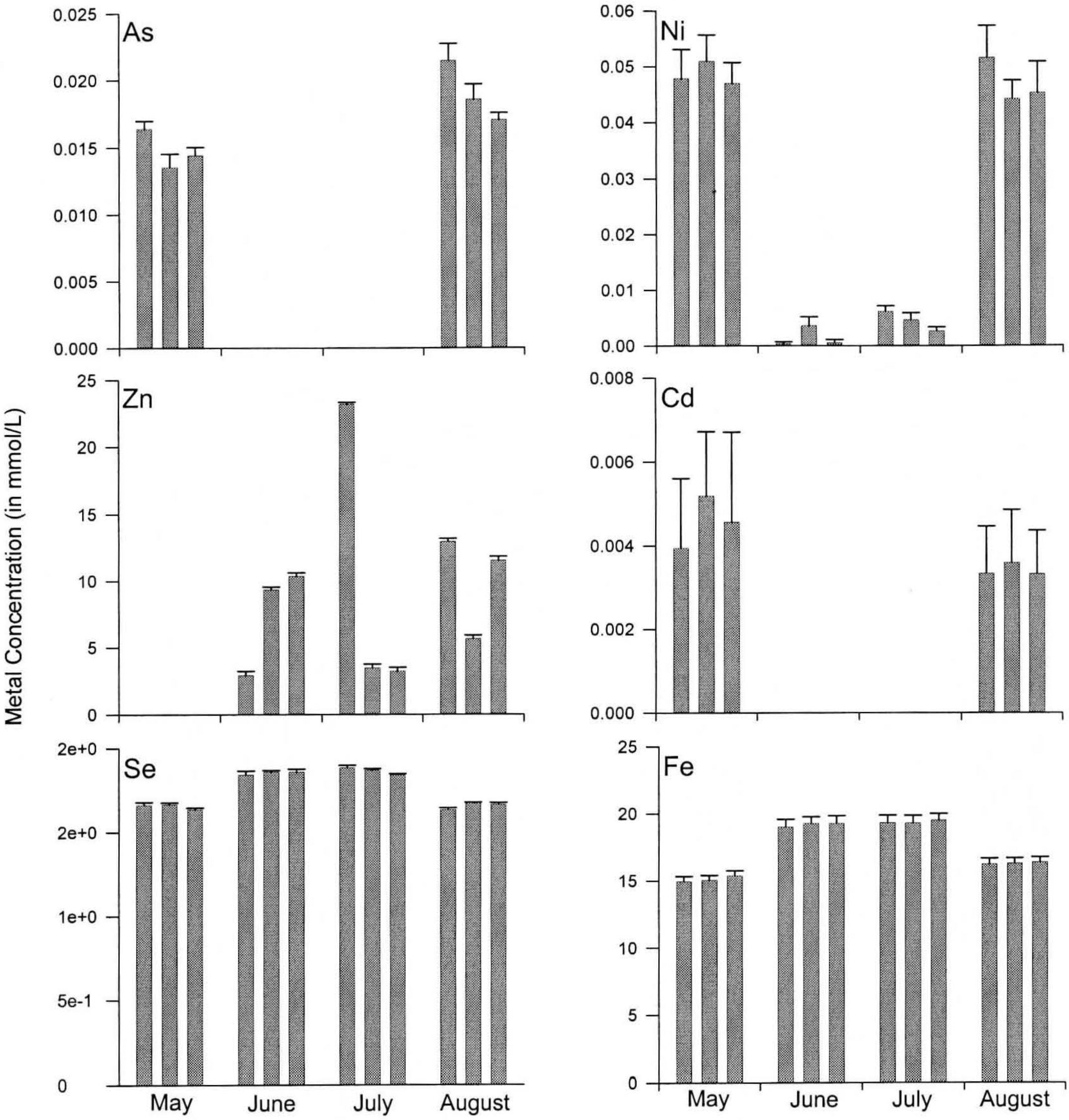

Figure 3.1.2 (b): Metal concentrations in the dissolved compartment (in mM) at the shallow site from May to August 2004 (continued from previous page). No bar means that the sample was below detection limits.

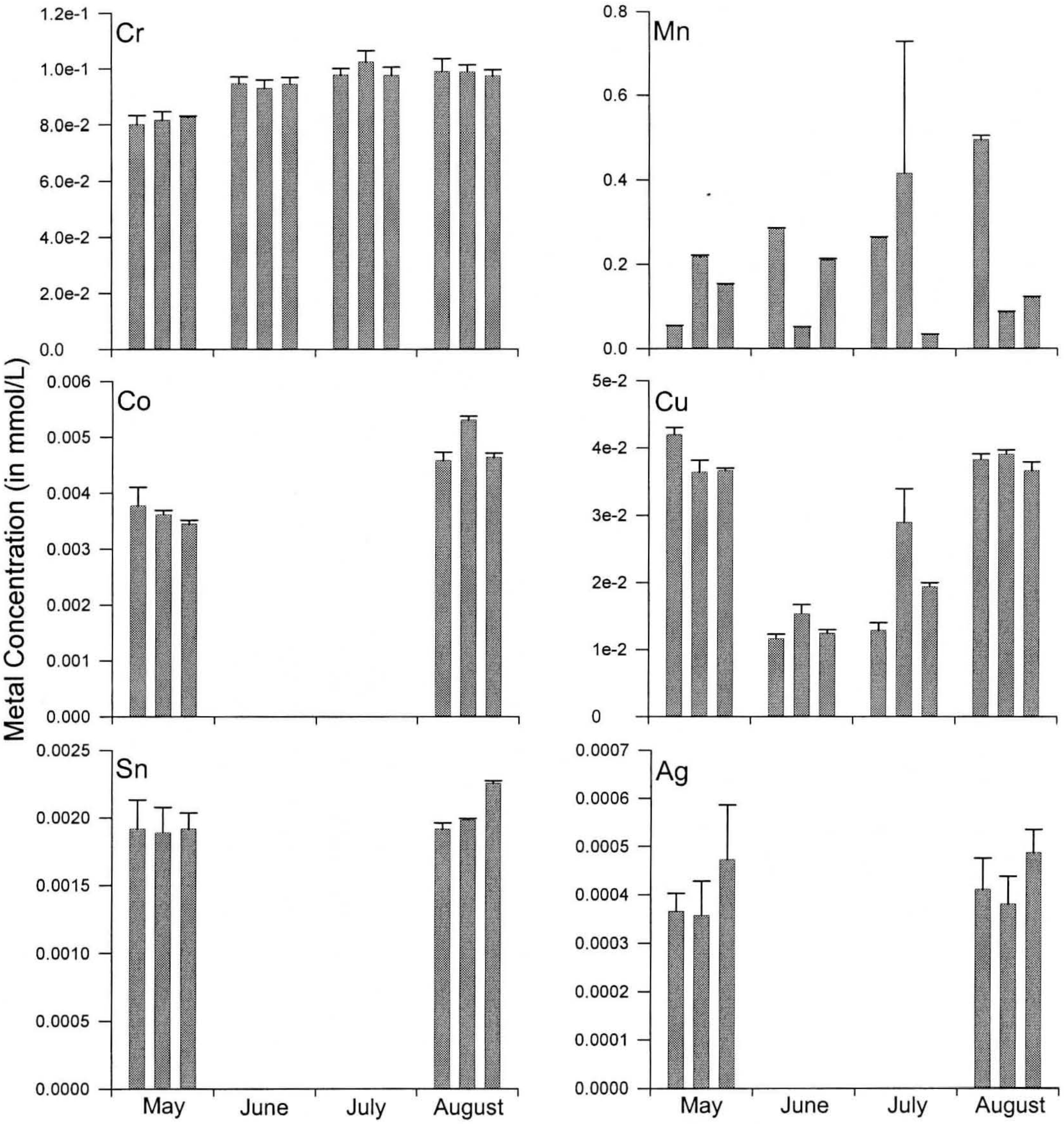

Figure 3.1.3 (a): Metal concentrations in the dissolved compartment at the deep site (in mM) from May to August 2004. No bar means that the sample was below detection limits.

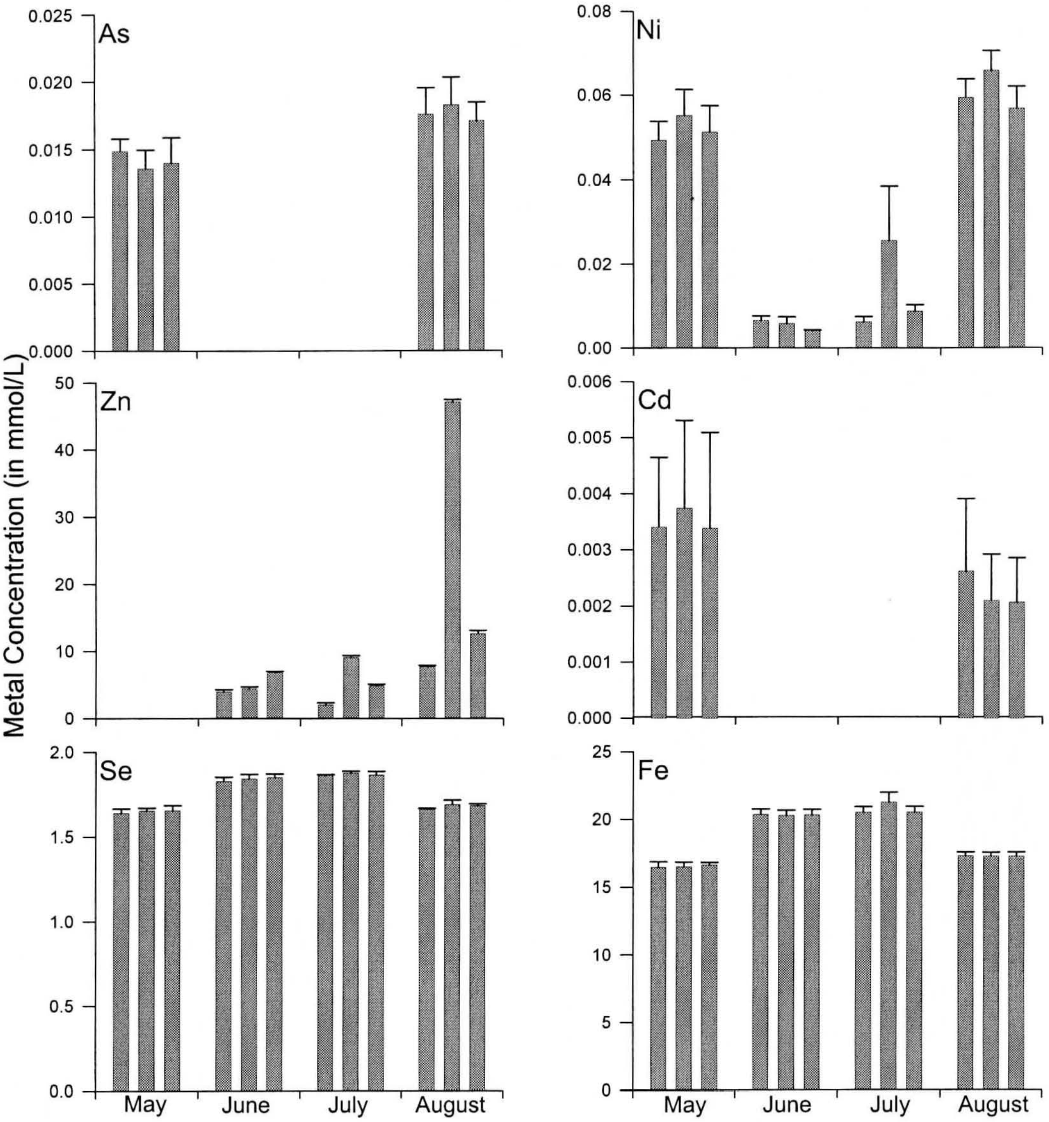

Figure 3.1.3 (b): Metal concentrations in the dissolved compartment at the deep site from May to August 2004 (in mM) (continued from previous page). No bar means that the sample was below detection limits.

Other studies have reported similar, higher and lower values than results from this study for dissolved metals in Hamilton Harbour. For instance, results from this research for dissolved Cu, As, Ni and Cd are within the range of values reported (previously reported values for Cu 25nM – 47nM; As <13nM; Ni 35nM – 68nM; Cd <2nM), while my results for Cr and Fe concentrations are about 6 times higher than previous reported values (previously reported values for Cr 17nM, and Fe 3.5μM), Zn concentrations were, on average, an order of magnitude larger than previous reported values (260nM – 140nM), and those for Mn values were approximately 3 times lower compared to studies done previously (1.5μM; Diamond and Ling-Lamprecht, 1996; HHRAP, 1992; HHRAP, 1988). There were no published values for Co, Sn, Ag and Se for which to compare my results.

These results present some historical comparison, and while some elements show increases, others show decreases and some no change, it is difficult to draw any conclusions about whether dissolved metal contamination levels in the Harbour have improved or degraded further. Differences in time (i.e. seasonal or time of day) or location within the Harbour may also play a role in the observed differences between previously reported results and results from this research.

In a broader context of metal contaminated systems, Hamilton Harbour is clearly highly anthropogenically impacted. The range of reported dissolved metal concentrations from other contaminated water bodies are within the same order of magnitude of the Hamilton Harbour dissolved metal concentrations for most metals, for example: dissolved Cr, Mn, Co, Cu, As, Ni and Cd concentrations from tributaries to Chesapeake Bay, USA are within one order of magnitude of concentrations in Hamilton Harbour; however, Zn and Se were 2 – 3 orders of magnitude greater in Hamilton Harbour and Fe was 1-2 orders of magnitude greater. Reported Mn values from Chesapeake Bay are up to one order of magnitude larger than results of this research (Miller et al., 2003). Dissolved metal concentrations for the St. Lawrence River and tributaries are within the same order of magnitude as Hamilton Harbour dissolved metal concentrations for Mn, Co, Cu, and Ni; however, concentrations of Fe and Cd are 1-2 orders of magnitude larger in this study and Zn is 2-3 orders of magnitude larger (Rondeau et al., 2005).

3.1.2.2 Total Metal Abundance between Bed Sediment and SPM

For all metals, bed sediment and SPM compartments (the solid compartments) are a repository for metals in Hamilton Harbour. Mean total metal concentrations (in μmol/g) of the solid compartments were 3-5 orders of magnitude larger than dissolved compartment metal concentrations depending on metal, compartment and site for 11 of the 12 elements evaluated. Se however, showed solid compartment concentrations only one order of magnitude greater compared to the dissolved compartment. Se is known to be soluble under oxidizing conditions and may be released to the water column during disturbance events that cause the oxidation of sediment and result in the dissolution of Se (Peters et al., 1999). Therefore, under oxidizing conditions, a greater proportion of this element typically partitions to the dissolved compartment compared to the solid compartments.

Differences in metal concentrations between the two solid compartments and the direction of the difference (i.e. is the metal concentration higher in the bed sediment or the SPM) may be indicative of processes affecting metal concentrations in these compartments or sources of certain metals to the water column. Differences between mean seasonal concentrations of a specific metal in the bed sediment and the SPM at the same site were no larger than two fold for any of the metals. Shallow site mean seasonal total metal concentrations of Co were significantly higher in the bed sediment compared to the SPM ($n=11$, $p>0.05$). All other metals were not significantly different between the two compartments at the shallow site, further supporting the argument for well-mixed conditions at the shallow site.

At the deep site 7 of the 12 metals studied were significantly different between the two compartments: total Se was the only metal with significantly higher concentrations, approximately 1.4 times larger in the SPM compared to the bed sediment ($n=11$, $p<0.05$). Cr, Ag, As, Zn and Cd total metals were significantly higher ($n=11$, $p<0.05$) in the bed sediment (approximately 1.5 times larger) while there was no significant difference ($n=11$, $p>0.05$) between SPM and bed sediment concentrations for Mn, Co, Cu, Sn, Ni and Fe.

Total mean metal concentrations in solid compartments were, generally, significantly greater at the deep site compared to the same compartment at the shallow site ($n=12$ for bed sediment and $n=11$ for SPM, $p<0.05$). Co and Ni concentrations in the bed sediment and SPM were not significantly different at the deep site compared to the shallow site ($n=11$ for SPM and $n=12$ for bed sediment, $p>0.05$). Higher total metal concentrations in the deep site solid compartments likely reflect the proximity of the deep site to a significant metal point-source. These include CSOs and the high concentration of steel-oriented industrial activity on the south shore of the Harbour (Curran et al., 2000; Droppo et al., 1998).

Studies of total metals from the HHRAP (1988) examined several sites in the Harbour for Cr, Co, Cu, As, Ni and Zn and found that most of the total metal concentrations were 3.5 (Cu) – 7 (Zn) times higher in the proximity of the deep site compared to the proximity of the shallow site with the exception of Co (0.17 at the shallow site compared to 0.20 at the deep site) and Ni (0.63 at the deep site compared to 0.43 at the shallow site), consistent with findings in this study.

3.1.2.2.1 Total Metal Abundance in Bed Sediment Compartments

Bed sediment compartment total mean seasonal metal concentrations range over µmol/g to nmol/g at the shallow site and mmol/g to nmol/g at the deep site. Mean total seasonal metal abundances in the shallow site bed sediment decrease in the order: Fe (711µmol/g) > Mn (20µmol/g) > Zn (7µmol/g) > Cu(916nmol/g) > Cr (811nmol/g) > Ni

(628nmol/g) > Co (215nmol/g) > As (121nmol/g) > Se (45nmol/g) > Sn (24nmol/g) >Cd (13nmol/g) > Ag (5nmol/g). The deep site followed a similar pattern: Fe (2mmol/g) > Mn (47μmol/g) > Zn (25μmol/g) > Cr (4μmol/g) > Cu (2μmol/g) > Ni (729nmol/g) = Sn (676nmol/g) > Co (193nmol/g) = As (188nmol/g) > Se (84nmol/g) > Cd (34nmol/g) = Ag (24nmol/g; an "=" sign means there was less than one standard error between means and a > sign means the difference between means was greater than one standard error).

Comparison of these results with available literature on Hamilton Harbour show no consistent higher or lower metal concentration trends, rather element specific patterns emerge suggesting that the differences in metal concentrations between results from this study and previous research cannot be attributed to either increased or decreased water quality. Instead, it is possible that these element-specific differences reflect a change in specific sources and affect certain elements, alternatively, these results may reflect differences in time, location and analyses of the metal data reported.

Concentrations of Co and Cu were within the range of the values reported from previous studies on Hamilton Harbour. All of the other metals had lower concentrations at the shallow site compared with values from previous studies: bed sediment compartment concentrations of Mn, Ni and Fe from the shallow site were approximately 2 times smaller than the reported values; Cr, As and Zn were 3-5 times lower; and the concentration of Cd was approximately 9 times lower (HHRAP, 1992; Krantzberg, 1994). Measurements of Sn, Ag and Se were not available from previous studies on Hamilton Harbour. Previous studies on bed sediment concentrations near the Cootes Paradise channel (close to the shallow site) have been reported as having lower total metal concentrations in the bed sediments compared to other parts of the Harbour (HHRAP, 1988).

Bed sediment metal concentrations of Cr, Mn, Co, Cu, Ni and Fe at the deep site of Harbour-wide averages previously reported in the literature were within the range of concentrations measured in this study, however, concentrations of As, Zn and Cd from this study were approximately 2 times lower than those previously reported (HHRAP, 1992; Krantzberg, 1994).

Previous studies have noted that the sediment near the Cootes Paradise channel, i.e. near the shallow site, can be 1/3 of the concentrations in other parts of the Harbour for many metals (HHRAP, 1988). Because the metal concentrations from previous studies on Hamilton Harbour are Harbour-wide averages, metal concentrations from the shallow site may be expected to be lower than values reported in these studies, therefore it is appropriate to compare the two sites to metal concentrations reported in previous studies from locations in the Harbour from similar locations to the shallow site and deep sites in this study. In comparison to metal concentrations reported in the HHRAP (1988) from a specific site in a similar location to the shallow site in this study Cr and Co total mean seasonal bed sediment metal concentrations are within the range of values in the present study and Cu, As, Ni and Zn total metal concentrations were 2, 3, 1.5 and 2 fold greater, respectively, in this study. Concentrations of Mn, Sn, Ag, Cd, Se and Fe were not given.

Total metal concentrations in bed sediment of Cr, Co, Cu, As, Ni and Zn from a previous study on Hamilton Harbour for a specific site in a similar location to the deep site in this study were within the range of values reported in the present study (HHRAP, 1988).

Generally, total mean metal concentrations for most metals at the deep site in Hamilton Harbour were within an order of magnitude higher than total metal concentrations reported for contaminated systems and shallow site bed sediment metal concentrations were within the range of values found for other contaminated systems (Lake St. Claire: Rossman, 1988; Lake Ontario: Poulton et al., 1988; Chesapeake Bay: Paul et al., 2002), Australia (Roach, 2005), and Turkey (Alemdaroglu et al., 2003; Table 3.1.1). Exceptions at the shallow site were Zn which was approximately 2 times greater at the shallow site and Cd concentrations in Lake Macquarie (Australia) were approximately 4 times larger than Hamilton Harbour.

Some exceptions in deep site bed sediment metal concentrations were Zn, which was 1-2 orders of magnitude larger in Hamilton Harbour compared to Lake St. Clair sediment (19μmol/g-29μmol/g in Hamilton Harbour and 0.63μmol/g in Lake St. Clair) and Ag, also 1-2 orders of magnitude larger in the Australian Lake sediment (15nmol/g – 28nmol/g in Hamilton Harbour and 1nmol/g in Lake Macquarie). Concentrations of bed sediment metals at the deep site were generally larger, but within one order of magnitude of metal concentrations in other contaminated systems. Specifically, concentrations in Hamilton Harbour were within the range of other systems for As (other systems: 0.15μmol/g – 0.13μmol/g) but Cd concentrations in Lake Macquarie (0.06μmol/g) were approximately 2 times the deep site concentration in Hamilton Harbour. Concentrations of Cu, Ni and Se were approximately 2 times greater in Hamilton Harbour compared to other systems (In other systems - Cu: 0.18μmol/g – 1.0μmol/g; Ni: 0.17μmol/g – 0.53μmol/g; Se: 0.03μmol/g) and concentrations of Cr, Mn, Ag, Zn and Fe were up to 10 times greater in Hamilton Harbour compared to other systems (In other systems - Cr: 0.59μmol/g – 1.3μmol/g; Mn: 12μmol/g, Ag: 0.001μmol/g – 0.007μmol/g, Zn: 0.63μmol/g – 4.2μmol/g and Fe: 370μmol/g).

With respect to most metals in bed sediments, the deep site in Hamilton Harbour has high levels of contamination compared to other contaminated water bodies, while the shallow site is, typically within the range of other contaminated Harbours.

3.1.2.2.2 Total Metal Abundance in SPM Compartments

The total mean metal concentrations in SPM compartment from May to August at the shallow site decreased in the order: Fe (700μmol/g) > Mn (30μmol/g) > Zn (5μmol/g) >Cr (987nmol/g) > Cu (820nmol/g) > Ni (647nmol/g) > Co (176nmol/g) > As (107nmol/g) > Se (58nmol/g) > Sn (42nmol/g) > Cd (7nmol/g) > Ag (4nmol/g). The total mean metal concentrations from May to August for the SPM at the deep site decreased in the order: Fe (1mmol/g) > Mn (86µmol/g) > Zn (20µmol/g) > Cr (3µmol/g) > Cu (2µmol/g) > Sn (682nmol/g) = Ni (674nmol/g) > Co (170nmol/g) > As (145nmol/g) > Se (115nmol/g) > Cd (27nmol/g) > Ag (20nmol/g).

SPM total metal concentrations from previous studies were within range of values measured in this study at the shallow site for Mn, Ni and Fe. Concentrations of Cu and As, Cr and Cd, and Zn, however, were approximately 2, 4 and 6 times lower, respectively, in this study (HHRAP, 1988; Diamond and Ling-Lamprecht, 1996; Mayer and Manning, 1990).

Deep site SPM concentrations of Cr, Mn, Cu, Ni, Zn, Cd and Fe were within the range of the previously reported values, while As concentrations were less than 2 times previous values (HHRAP, 1988; Diamond and Ling-Lamprecht, 1996; Mayer and Manning, 1990). Total metal concentrations in SPM from previous studies in Hamilton Harbour were not available for Co, Sn, Ag and Se.

3.1.2.2.3 Comparison to Guidelines

There are two sets of guidelines for sediments in Ontario set by the Ministry of the Environment (1993). The Lowest Effect Level (LEL) is defined as the level at which ecotoxic effects become apparent and the Severe Effect Level (SEL) is the level above which sediments are considered heavily polluted and likely to affect the health of benthic organisms. Management decisions and plans may be based on these sediment quality guidelines. For instance, sediment that is above the LEL guidelines may require further testing or the implementation of a management plan and sediment metal concentration measurements that are above the SEL metal concentrations may require the implementation of controls on contaminant inputs or the removal of the sediment (MOE, 1993). Seven of the twelve metals (Cr, Cu, As, Ni, Zn, Cd and Fe) are above the LEL at the shallow site and Mn was the only metal above the SEL. Three of the twelve metals (As, Ni and Cd) were above the LEL and five of the twelve metals (Cr, Mn, Cu, Zn and Fe) were above the SEL at the deep site. There are no Ontario guidelines for sediment concentrations of Co, Sn, Ag and Se. Further, there are currently no guidelines for SPM metal concentrations in Ontario, however, if the guidelines for sediment quality are applied to Hamilton Harbour sediment the metals that exceed these guidelines in the SPM are the same as the metals that exceed the guidelines in the bed sediment.

3.1.3 Temporal Trends in Total Metal Abundance among Dissolved Metal, Bed Sediment and SPM at Two Sites

No temporal trends were observed for all metals within a given compartment. However, temporal trends emerge for subgroups of the total suite of metals analyzed in each compartment. This result would suggest that there is not one physico-chemical factor controlling metal behaviour in an independent manner, i.e. element identification is required. The apparent differences in observed behavior among this suite of elements, likely reflects a dynamic interplay of physico-chemical parameters, variation in metal sources (industry, urban or agricultural runoff) and element specific solid-solution partitioning in controlling their individual behaviours.

3.1.3.1 Temporal Trends in Dissolved Metal Concentrations

No evident temporal trend (i.e. through sampling season from May to August), emerged that was common for all metals studied in dissolved compartment concentrations (Figure 3.1.2 (a)-(b) for shallow site and 3.1.3 (a)-(b) for deep site). Further, no evident diel trends (morning 10-12am, afternoon 4-6pm) emerged in dissolved concentrations for any of the analyzed metals. However, groups of metals did show similar temporal trends. For example, dissolved Fe and Se concentrations showed similar temporal trends in both the shallow site and the deep site. They exhibited similar values for each metal in May and August and similar, but higher values in June and July. This may indicate a similar source for the two metals to the water column perhaps due to their association and subsequent dissolution within sediments (Belzile et al., 2000) or a common source in the steel and metallurgy industries (George, 2005).

In addition, seven of the twelve metals (Co, Cu, Sn, Ag, As, Ni, Cd) show a large amount of variability between samples in May and August compared to samples in June and July at both sites (coefficient of variation (COV) 43% - 93%). Extreme variability for these aforementioned metals is a result of June and July dissolved metal concentrations at both sites being significantly lower than concentrations in May and August ($n=6$, $p<0.001$ for all metals). For example, dissolved metal concentrations of Co (difference: 4 fold at shallow site and 2.5 fold at deep site), Cu (difference: 2.5 fold at shallow site and deep site), Sn (difference: 2.5 fold at shallow site and 2.5 fold at deep site), Ag (difference: 4 fold at shallow site and 4.5 fold at deep site), As(difference: 12 fold at shallow site and 12 fold at deep site), Ni (difference: 15 fold at shallow site and 6 fold at deep site) and Cd (difference: 4.5 fold at shallow site and 3 fold at deep site) were increased up to 15 fold in May and August compared to June and July.

Dissolved concentrations of Zn were also extremely variable, although they did not follow the same temporal trend, they were below detection limits at both sites in May, while maximum concentrations were measured in July (23μM) at the shallow site and August (47μM) at the deep site, resulting in coefficient of variation (COV) values of 101% at the shallow site and 157% at the deep site. High variability in dissolved metal concentrations can cause problems for dissolved metal monitoring and management programs in Hamilton Harbour, possibly resulting in inappropriate planning decisions, depending on the timing of the sample. Provincial Water Quality Objectives (PWQO) are set by the Ministry of Environment and Energy (MOEE, 1999) and management decisions are made based on these concentrations: a concentration that is measured over the guideline may result in more stringent management procedures. The dissolved metal concentrations measured in this study indicate that many metal concentrations are time-dependent; therefore, inappropriate management procedures may be undertaken, in the worst case, resulting in further degradation of a system that is already in need of better management. For example, in comparison to the PWQA for Ontario, average dissolved concentrations of Cd are above the guideline at the shallow site and below the guideline at the deep site, however, at both sites the dissolved concentrations of each sample exceed the guidelines 50% of the time (May and August samples) and are below the guidelines 50% of the time (June and July samples). Average dissolved concentrations of Zn exceed the PWQA, however, 25% of the time the dissolved concentrations of the samples were below the guidelines and due to the variability in these samples the dissolved concentration may exceed the PWQA by up to 2.5 orders of magnitude.

Dissolved average metal concentrations for Zn, Cd (shallow site only), Se and Fe exceed the guidelines and dissolved average concentrations of Cr, Co, Cu, Ag, As, Ni and Cd at the deep site are below the guidelines. Guidelines do not exist for Mn and Sn in dissolved compartments.

3.1.3.2 Temporal Trends in Total Bed Sediment and SPM Metal Concentrations

There were no trends that were seen in total metal concentrations in either bed or SPM compartments that were consistent for all metals in one or both sediment compartments at the shallow site (Figures 3.1.4 (a) and (b) for shallow site and Figures 3.1.5 (a) and (b) for deep site). However, there are groups of metals that show similar trends. Co, Cu and Fe show high concentrations in shallow bed sediment in May. Reasons why these metals have high concentrations in May are not clear, however, deep site concentrations of Cr, Co, Cu, As and Fe are also high in bed sediment in May.

Mn and Fe concentrations were significantly higher in June in the SPM of the shallow site and Mn, Cu, Ni and Fe were higher in June at the deep site. Fe, Co, Cu concentrations were highest in May in the bed sediment of the deep site than in the other months. Patterns in Ni concentration in the SPM and bed sediment followed Fe concentration patterns closely.

There was variability between the metal concentrations in the samples taken in the AM (first and last sample each month) compared to the samples taken in the PM (second sample each month) of both bed sediment and SPM however, there was not a consistent difference between the two sampling times for any of the metal.

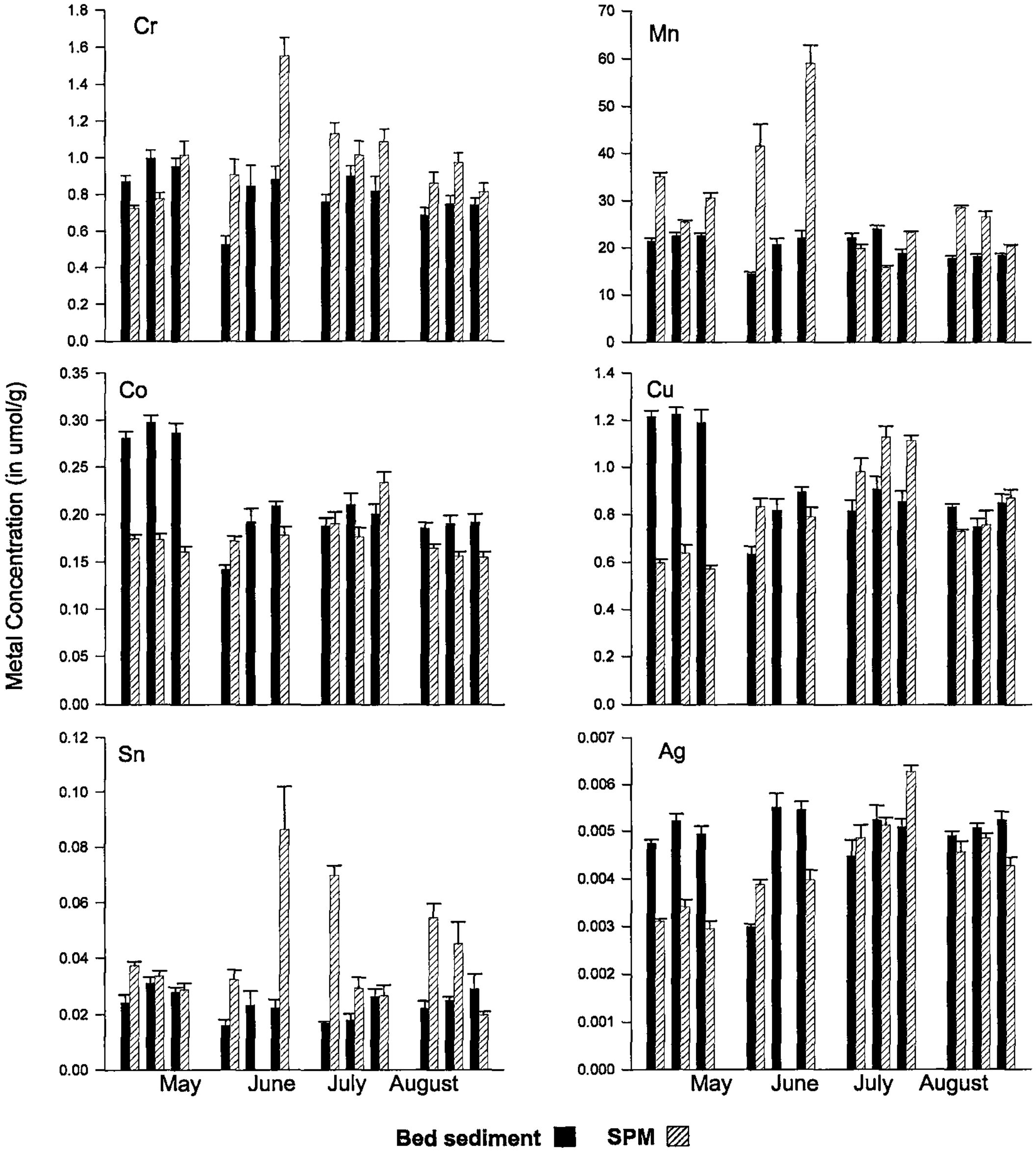

Figure 3.1.4 (a): Bed sediment and SPM associated metals at the shallow site (in μmol/g).

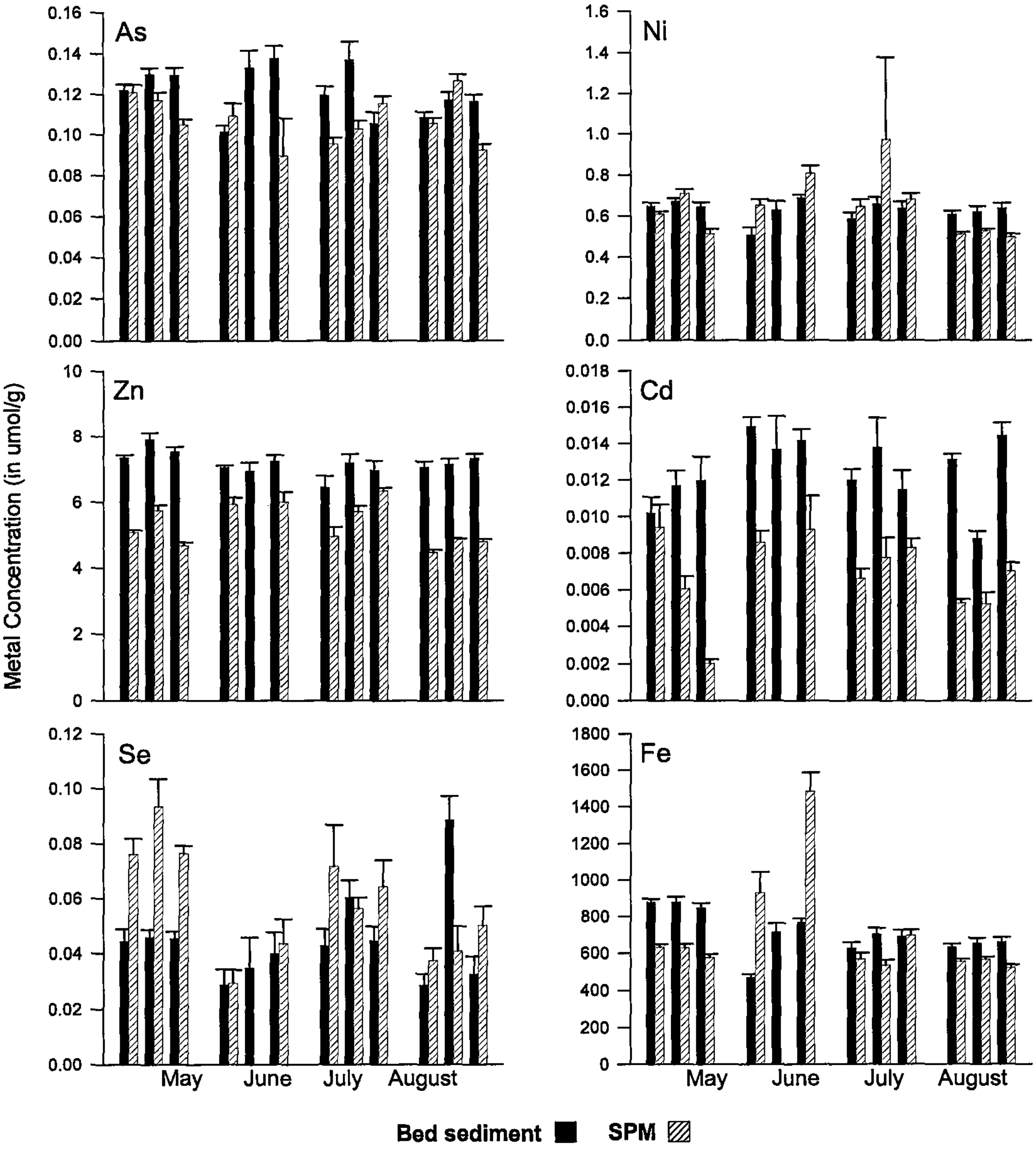

Figure 3.1.4 (b): Bed sediment and SPM associated metal concentrations at the shallow site (continued from previous page) from May to August (in μmol/g).

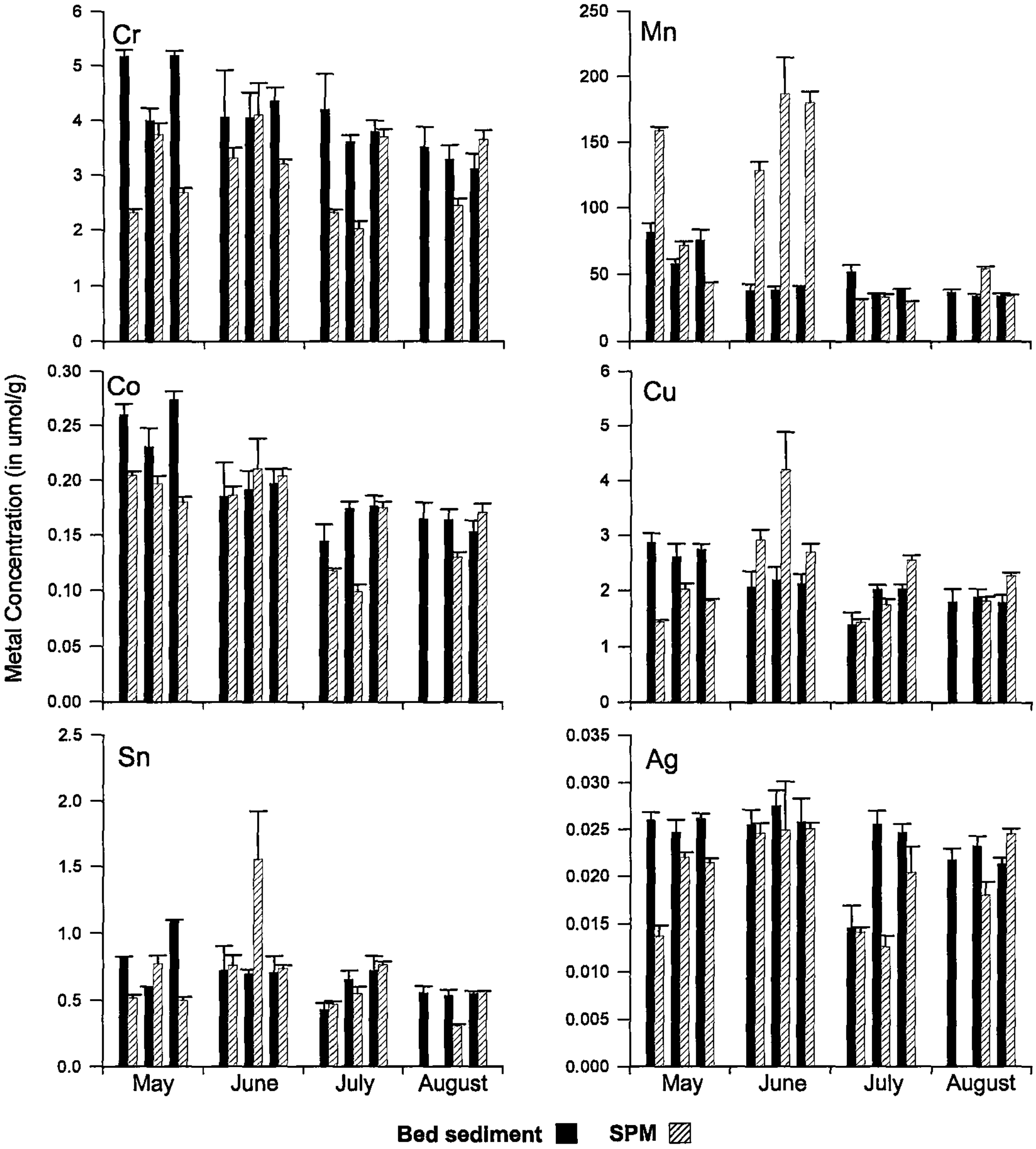

Figure 3.1.5 (a): Bed sediment and SPM associated metals at the deep site (in µmol/g).

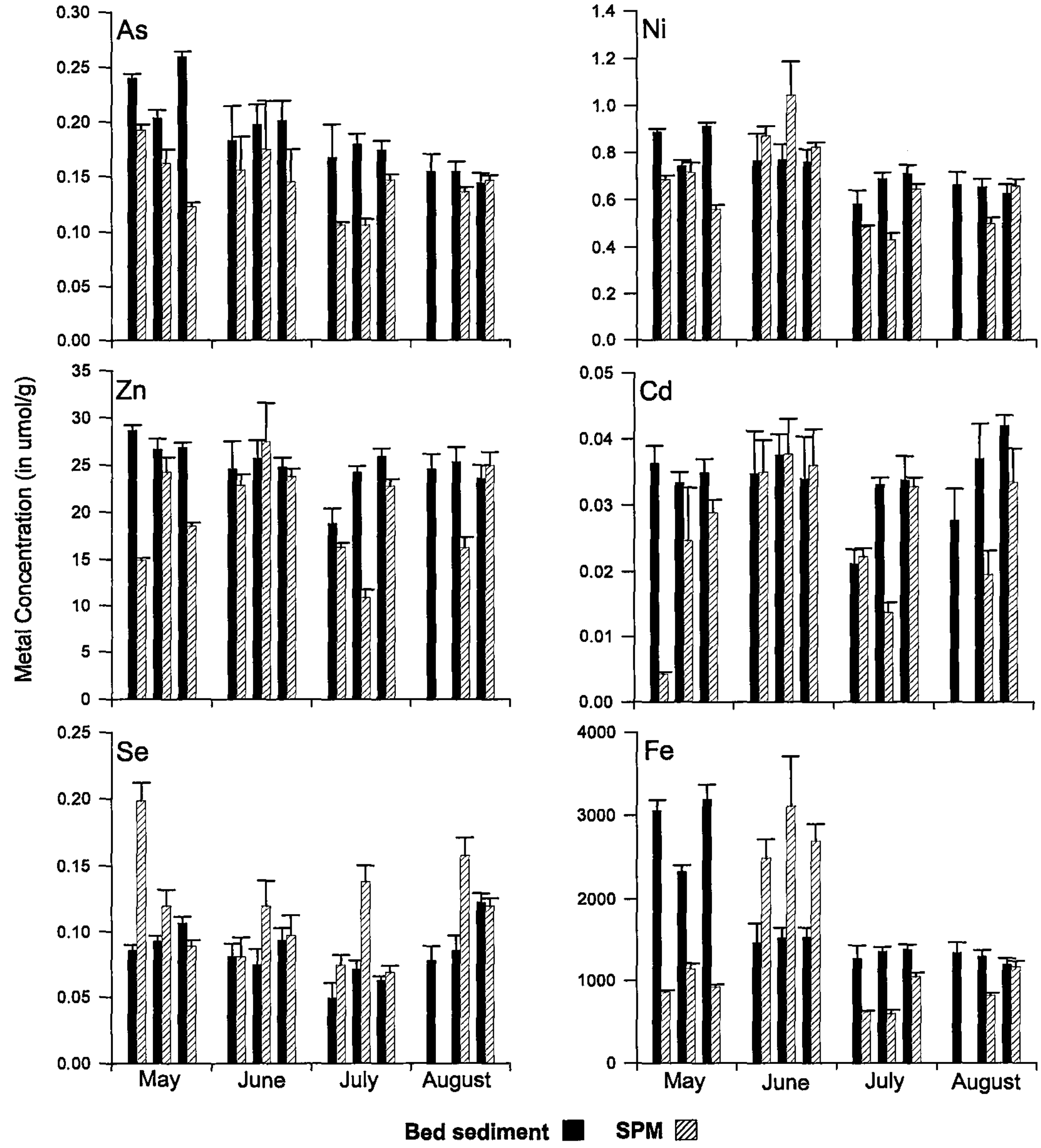

Figure 3.1.5 (b): Bed sediment and SPM associated metal concentrations at the deep site (continued from previous page) from May to August (in μmol/g).

3.2 Metal Fractionation in Solid Compartments

Sediments are typically a sink for metal contaminants in aqueous systems and thus, the higher the sediment associated metal loads, typically the greater the degree of metal contamination. Thus, total sediment associated metal concentrations provide a means to assess changes in metal contamination with time in a given system as well as acting as a scale to assess relative metal contamination across systems. However, sediments are variably composed of heterogeneous mixtures of minerals and organic matter i.e. detritus, bacteria and associated extracellular polymeric substances, each of which present differing processes for metal uptake, and differing reactivities and affinities for particular metals. Sequential extraction techniques provide the means to characterize these metal associations and provide insight to the nature of metal sorption processes and controls on bioavailability or mobility of metals. This section will first discuss the sediment composition in terms of these important fractions for metal sorption and then discuss the spatial and temporal distribution of metals that are associated with these fractions.

3.2.1 Sediment Composition

As outlined in Sections 2.4.1 and 2.6.1, the sediment was analyzed for the following components: organic matter, carbonates, amorphous Fe and Mn oxyhydroxides and crystalline Fe and Mn oxyhydroxides. These fractions represent significant metal sequesters in most aqueous systems (Tessier et al., 1979; Warren and Zimmerman, 1993) and have been shown to play a role in Hamilton Harbour (McIsaac et al., 1981; Krantzberg, 1994; HHRAP, 1988) for some elements. In order to comparatively assess their relative affinities for the elements analyzed here, their relative abundances over time and space were also evaluated.

3.2.1.1 Specific Sediment Fractions Abundance in Both Solid Compartments

The mass of specific sediment fractions in the SPM compartment (mean seasonal concentrations in g/g) decrease in the following order: organic matter (mean: 0.23g/g±0.010) > carbonates (mean: 0.08g/g±0.005) > amorphous oxyhydroxide (mean: 0.04g/g±0.003) > crystalline oxyhydroxide (mean: 0.01g/g±0.002) at the shallow site and at the deep site: organic matter (mean: 0.28g/g±0.008) > amorphous oxyhydroxide (0.08g/g±0.010) = carbonates (mean: 0.07g/g±0.008) > crystalline oxyhydroxide (mean: 0.02g/g±0.003; n.b. a ">" sign denotes a significant difference and an "=" sign denotes a non-significant difference, ANOVA on Ranks, H=39.0, $p<0.001$ for shallow site and H=33.6, $p<0.001$ – both tests followed by a Student-Newman-Keuls All Pairwise Multiple Comparison Procedure, $P<0.05$ to determine differences between individual fractions; Figure 3.2.1). Mean concentrations of the carbonate and organic matter fractions are always significantly greater ($p<0.05$) than the concentrations of the amorphous oxides and the crystalline oxyhydroxides with the exception of the deep SPM, where the concentrations of the amorphous oxyhydroxides were not significantly

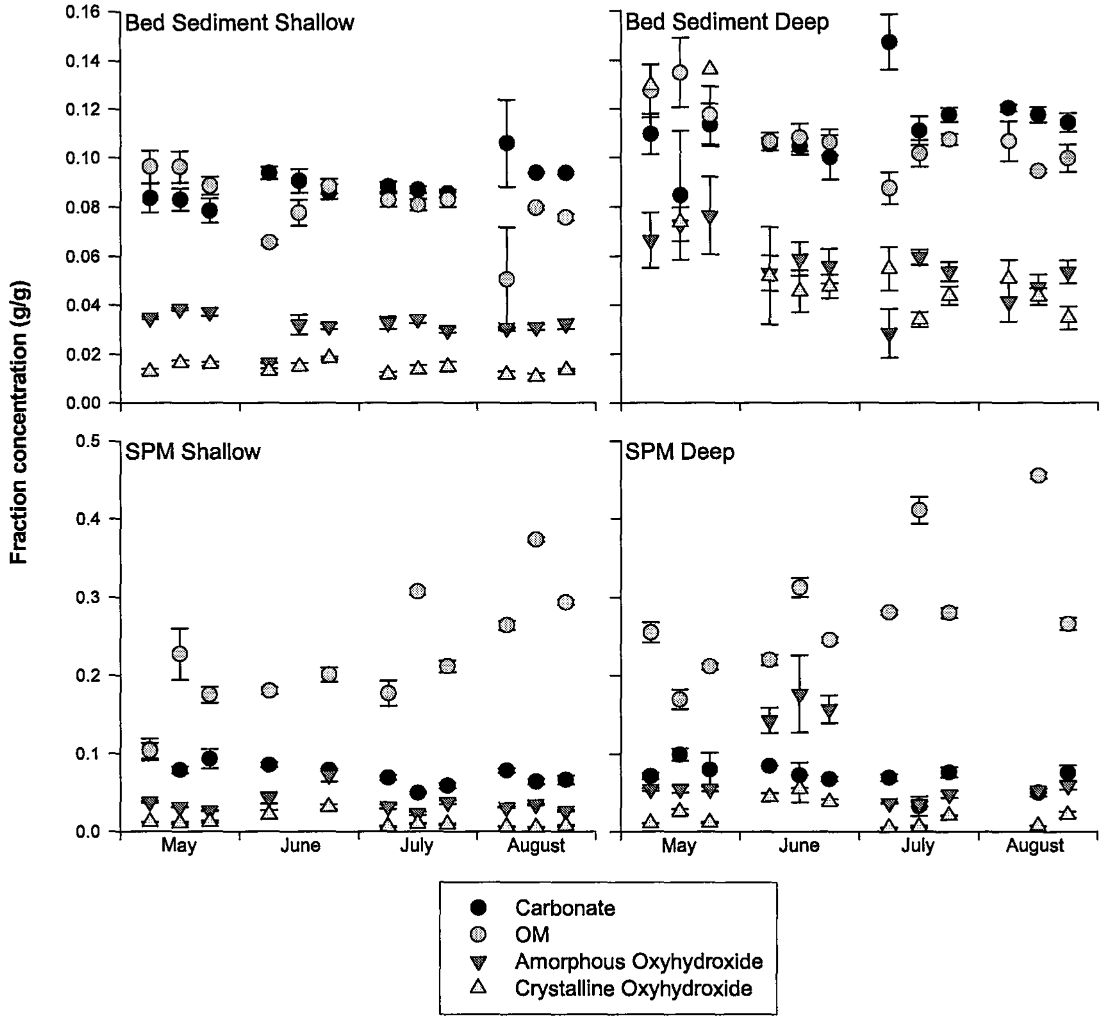

Figure 3.2.1: Mass of important fractions for metals sorption in solid compartments at both sites through the sampling season in g of fraction / g of sediment. Note the difference in scale for the bed sediment and SPM compartments.

3.2.1.2 Temporal Trends in Fraction Content

The concentrations of amorphous and crystalline oxyhydroxides followed similar patterns from May to August within each compartment at each site (Figure 3.2.1). SPM concentrations of amorphous and crystalline oxyhydroxides were 2-3 times greater in the month of June compared to the other months (0.058g/g ± 0.007shallow site and 0.159g/g ± 0.028 deep site amorphous oxyhydroxide, 0.026g/g ± 0.004 shallow site and 0.046g/g ± 0.009 deep site crystalline oxyhydroxide for June samples, versus 0.031g/g ± 0.001 shallow site and 0.050g/g ± 0.003 deep site amorphous oxyhydroxide, 0.009g/g ± 0.001 shallow site and 0.014g/g ± 0.001 deep site crystalline oxyhydroxide in other months). The highest concentrations of amorphous oxyhydroxides and crystalline oxyhydroxides at the deep site occurred in the month of May in the bed sediment (0.072g/g ± 0.011amorphous oxyhydroxide and 0.113g/g (S.E. not available, sample lost) crystalline oxyhydroxide in May vs. 0.050g/g ± 0.006 amorphous oxyhydroxide and 0.045g/g ±0.007 crystalline oxyhydroxide in other months).

The organic matter concentration in SPM increased substantively from May to August within each sediment compartment at each site. The deep site showed approximately a three-fold increase (0.17gOM/g in May to 0.46gOM/g in August) and the shallow site approximately a four-fold increase (0.10gOM/g in May to 0.37gOM/g in August) in organic matter concentration from May to August. As the season progresses through the warm months of the summer productivity increases the biomass of the system contributing to the organic matter in the system. There are also contributions to biomass from bacterial populations that grow with the increasing temperatures (O'Connor, 2004) and may contribute large amounts of organic matter in the form of in-situ growth of populations as well as inputs from sewage treatment plant outflows found near both sites.

Concentrations of carbonate are highest in May at both sites and there was approximately a two-fold difference in the range at the shallow site and a three fold range at the deep site in carbonate concentrations. The carbonate nature of the watershed (Hough, 1962) and contributions from anthropogenic carbonate particulate matter in the watershed (Vermette et al., 1991) may have been contributed to the Harbour by the rainstorm in the days prior to the sample period in May (34mm of rain).

3.2.1.3 Spatial Trends in Fraction Concentration in Compartments

To assess whether concentrations of these sediment fractions differed significantly between sediment compartments and sites, two-way ANOVA analyses, with site and compartment as the two treatment variables were performed using a post-hoc test (Holm-Sidak All Pair-wise Multiple Comparison Procedure) to identify specific compartment and site relationships which significantly differed ($p<0.05$). A schematic is presented in Figure 3.2.2, where one-way arrows denote a significant relationship and point in the direction of the higher concentration of a fraction; two-way arrows denote a non-significant difference. Sediment fractions are symbolized by the letter on the arrow:

C – carbonate, A – amorphous oxyhydroxide, Y – crystalline oxyhydroxide and O – organic matter.

The composition of the SPM and bed sediment at the shallow site was more similar than the composition of the two compartments at the deep site, evidenced by a greater number of significant differences in the fraction content between the compartments at the deep site (two-way ANOVA n=10, $p<0.05$). This result may indicate two things: one, sediment at the shallow site is resuspended with greater frequency compared to the deep site causing a more similar composition between the SPM and surficial bed sediment at this littoral site, and/or two, the shallow site has a greater sedimentation rate than the deep site, burying the bed sediment quickly and replacing the surficial bed sediment with newly deposited SPM-like sediment. It is difficult to determine the more likely scenario and it is also possible that a combination of both processes is taking place at the shallow site, keeping SPM and surficial bed sediment compartments well-mixed. Thus, if sediment characteristics (i.e. concentrations of specific sediment fractions) are an important control on metal scavenging, then the shallow site would be expected to show more similarity in metal solid associations between the two solid compartments than the deeper site.

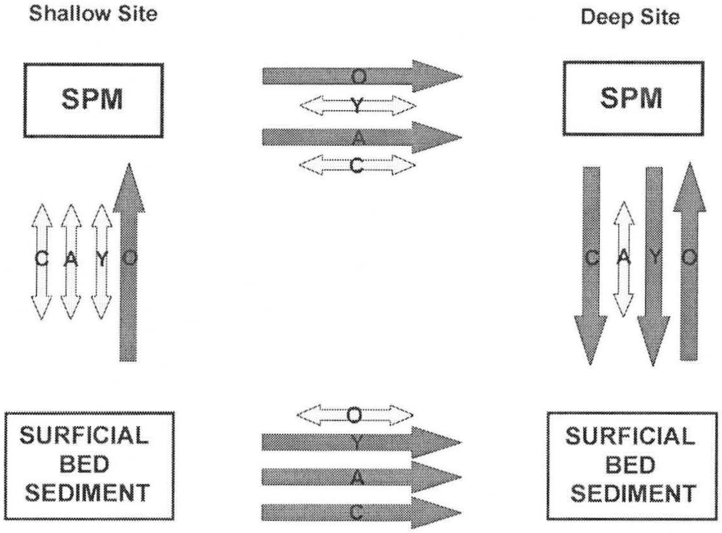

Figure 3.2.2: Schematic of concentrations of important metal sorbent fractions in solid compartments. One-way arrows point to the compartment with the significantly larger concentration of the fraction; two-way arrows indicate that there was no significant difference. Fractions are abbreviated as follows - "E": Exchangeable, "C": Carbonates, "A": Amorphous Oxyhydroxides, "Y": Crystalline Oxyhydroxides, and "O": Organic Matter (Two-way ANOVA: n=40, $p<0.05$).

All significant differences between the two sites indicate that there are consistently greater concentrations of four sediment fractions: carbonate, amorphous oxyhydroxide, crystalline oxyhydroxide, and organic matter at the deep site. Thus, if sediment fraction abundance is a controlling factor in sediment metal uptake, the deep site sediment compartments should have a greater ability to sequester metals than sediment compartments at the shallow site.

Similar concentrations of carbonate in the SPM of both sites may be indicative of a similar carbonate source for both sites. A large source of the carbonates is likely the limestone and dolomite based bedrock in the watershed (Hough, 1962) and buildings composed of carbonate based building material i.e. cement (Droppo et al., 1998) providing a non-point source that is similarly distributed between both sites.

At both sites there is a larger proportion of organic matter in the SPM compartment compared to the bed sediment compartment, which may reflect greater decompositional activity mineralizing organic carbon in the bed sediment. This result may also reflect a size associated settling factor, i.e. organic matter occurs as smaller sized particles in the solid compartment and therefore, remains in the water column rather than settling out. The increased organic matter abundance in the SPM compartment may also reflect increased microbial colonization and growth rates associated with the SPM in the water column as water temperature increases. While not specifically examined in this study, other systems have shown such a phenomenon (Wetzel, 1983). In addition, there is typically a doubling of metabolic rates with every 10°C increase in temperature and thus, bacterial populations are likely to increase in number with seasonal warming water temperatures (Campbell, 1996).

The SPM at the deep site has a significantly higher concentration of amorphous oxyhydroxides (0.080g/g ± 0.010g/g) compared to the shallow site SPM (0.036g/g ± 0.003g/g). However, no significant difference in the crystalline oxyhydroxide concentration in SPM was observed between the two sites (0.012g/g ± 0.002g/g at the shallow site, 0.022g/g ± 0.003g/g at the deep site). There is also significantly less crystalline oxyhydroxide in the deep site SPM (0.022g/g ± 0.003g/g) compared to the deep site bed sediment (0.062g/g ± 0.005g/g). However, the amorphous oxyhydroxide concentrations are not significantly different between SPM (0.080g/g ± 0.010g/g) and bed sediment (0.056g/g ± 0.007g/g) at the deep site. The steel industry close to the deep site is a likely source of Fe and Mn for the formation of oxyhydroxides (Moore, 1991; Droppo et al., 1998). Larger particles of crystalline oxyhydroxides may settle out of the water column quickly at the deep site and become part of the bed sediment; in addition, diagenetic processes over time will convert amorphous oxyhydroxides to a more crystalline form (Morel and Herring, 1993) possibly contributing to an accumulation in crystalline oxyhydroxide after deposition and aging of amorphous oxyhydroxide in the bed sediment. The lighter, smaller portion of the crystalline oxyhydroxide particles may remain in the water column as mobile SPM which may also explain the similarity of the crystalline oxides between the SPM compartment concentrations at the two sites.

3.2.2 Metal Associations with Sediment Fractions

Seasonal mean metal concentrations associated with each of six solid fractions indicate that the amorphous oxyhydroxide and crystalline oxyhydroxide fractions are the most important fractions for scavenging for a majority of the metals in both compartments at both sites (the combined averages of amorphous and crystalline associated metals as a per cent of the total concentration are as follows: Cr: 59% shallow bed, 78% deep bed, 58% shallow SPM and 75% deep SPM (n.b. the following are presented in the same format); Mn: 32%, 59%, 28%, 30%; Co: 73%, 70%, 74%, 65%; Cu: 77%, 83%, 54%, 64%; Sn: 60%, 70%, 52%, 51%; Ag: 81%, 91%, 70%, 89%; As: 70%, 73%, 57%, 63%; Ni: 71%, 70%, 72%, 67%; Zn: 66%, 74%, 72%, 73%; Cd: 69%, 76%, 63%, 73%; Se: 18%, 5%, 33%, 21% Fe: 71%, 74%, 79%, 80%; Figures 3.2.3a-d). This result is consistent with a report on Hamilton Harbour by McIsaac et al., (1981) where the oxyhydroxides were found to be the most important fraction for metal uptake. Research on other systems has also widely evidenced the role of oxyhydroxides in metal uptake (Tessier et al., 1985; Zoumis et al., 2001; Haack and Warren, 2003). Metal uptake by oxyhydroxides is typically attributed to their high surface area, partly resulting from their ability to form surface coatings on other particles, and their highly reactive surface sites, allowing for greater uptake of associated metal despite their smaller concentrations compared to other important metal sorbents such as organic matter and carbonates (Dzombak and Morel, 1990; Dong et al., 2000; Triverdi and Axe, 2000). Consistent with these literature observations, metals in this study, with the exception of Mn and Se, show greater than 50% association with amorphous and crystalline oxyhydroxide fractions.

Mn does not exhibit a high association with the oxyhydroxide fraction typical of most of the other metals in this study. Rather, Mn shows a strong affinity for the Carbonate fraction (61% in shallow bed sediment, 33% in deep bed sediment, 47% in shallow SPM and 52% in deep SPM). Strong Mn associations with the carbonate fraction are also seen in studies by Zachara et al., 1991, and Tessier et al., 1979. Research by Xiao-Quan and Bin (1993) and Arunachalam et al. (1996) has shown that Mn is often associated with Carbonate minerals and can substitute for Mg^{2+} in dolomite or Ca^{2+} in calcite. Given the dolomite nature of the Hamilton Harbour watershed (Hough, 1962), high Mn association with carbonate is a likely scenario.

In this study, Se was largely sorbed to the organic matter fraction (47% in shallow bed sed, 45% in deep bed sediment, 31% in shallow SPM and 36% in deep SPM) and is typically evenly distributed among the remaining fractions. Other researchers have found that Se is commonly found in the organic matter fraction (Moore, 1991) as well as the exchangeable and oxyhydroxide fractions (Peters et al., 1999) although Se has been shown to have less than 10% of total Se associated with oxyhydroxide fractions (Cutler, 1989).

The sum of metals in all fractions except the residual fraction indicates the concentration of bioavailable metals. In Hamilton Harbour, more than 80% of Mn, Co, Cu, As, Ni, Zn, Cd and Se in solid compartments at both sites and, Ag and Cr in deep site solid compartments, can be considered bioavailable and bioavailability of Sn, and Fe in solid compartments at both sites and Ag and Cr in shallow site solid compartments ranged from 84% to 50% bioavailable.

The smallest concentrations of metals were typically found in the exchangeable fraction for most metals and often accounted for less than 2% of the total metal. Se was the only metal that showed consistently higher exchangeable associated proportions of total metals in all solid compartments at both sites (8% in shallow bed sediment, 10% in deep bed sediment, and 15% at both sites in the SPM). Selenium has been shown to be released from sediments under oxidizing conditions (Masscheleyn et al., 1990). Peters et al., (1999) found that Se showed a continuum of increasing mobilization/dissolution; Se that was bound to organic matter under reducing conditions moved into both the dissolved compartment and into the more labile Fe and Mn oxyhydroxide and exchangeable fraction under increasingly oxidizing conditions.

There was an increase of one order of magnitude or greater in the proportion of exchangeable associated Mn, As and Ni in the SPM compartment compared to the bed sediment compartment, with the exception of Mn at the deep site where there was a 7-fold increase in the proportion of Mn in the exchangeable fraction of the SPM compared to the exchangeable fraction of the bed sediment. This may be a result of the increased mobility of the SPM compartment. Greater mobility should increase the uptake of dissolved metals to the SPM due to the increased exposure to potential sorbents; also, SPM generally has an increased accessible surface area for potentially greater metal uptake - particularly to the exchangeable fraction where metals are loosely associated with solids compared to the, relatively stationary, bed sediment - assuming that sorption is a key mechanism of association in the exchangeable fraction. Alternatively, it is possible that there is a movement of metal from other, more tightly bound fractions to the exchangeable fraction. In this scenario, less competitive metals are desorbed from inner sphere sorption sites in favour of more competitive sorbents, some of these less competitive metals may become part of the loosely bound exchangeable metals.

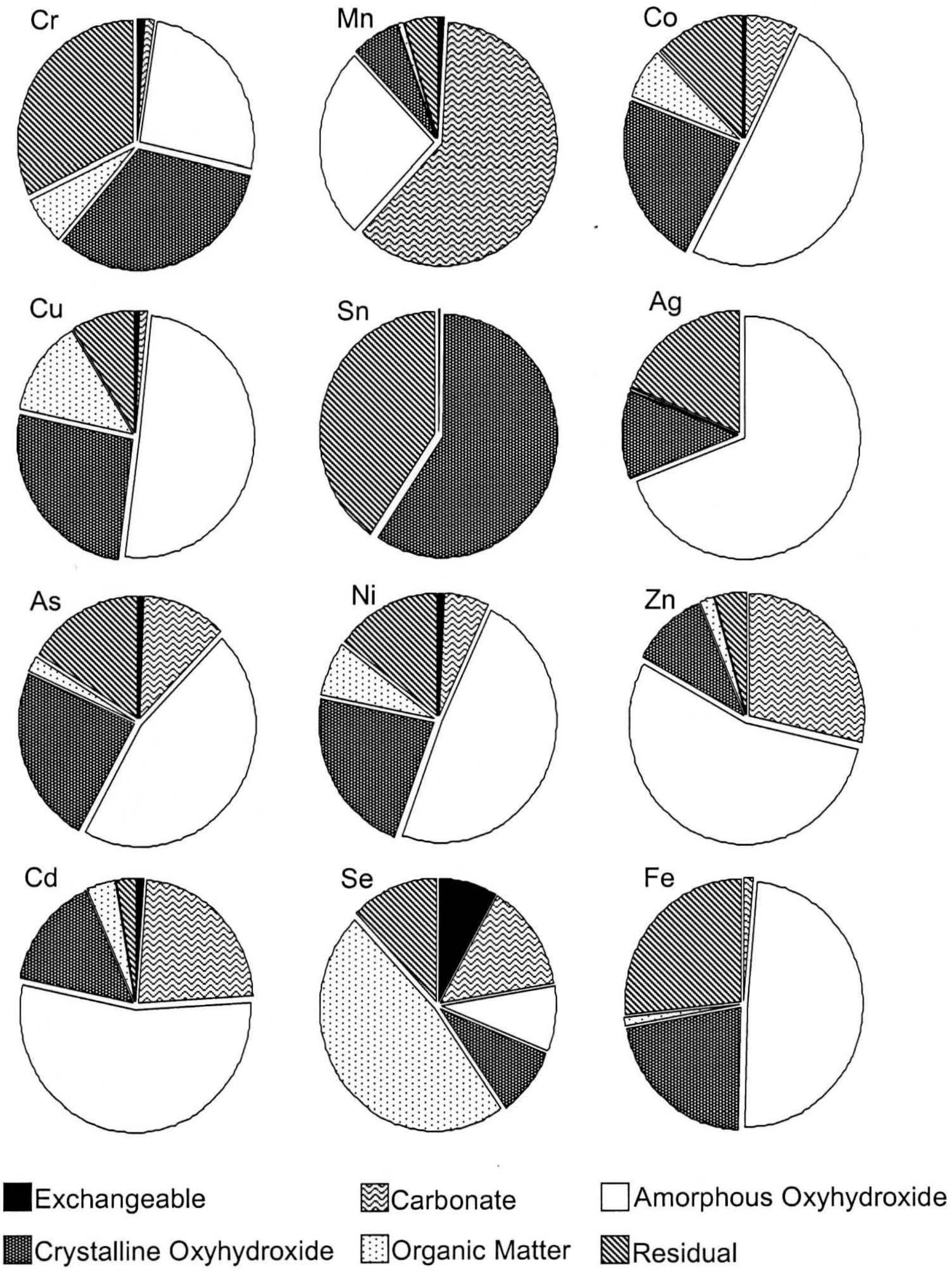

Figure 3.2.3a: Pie diagrams showing the proportion of metals in each of six fractions for the bed sediment at the shallow site.

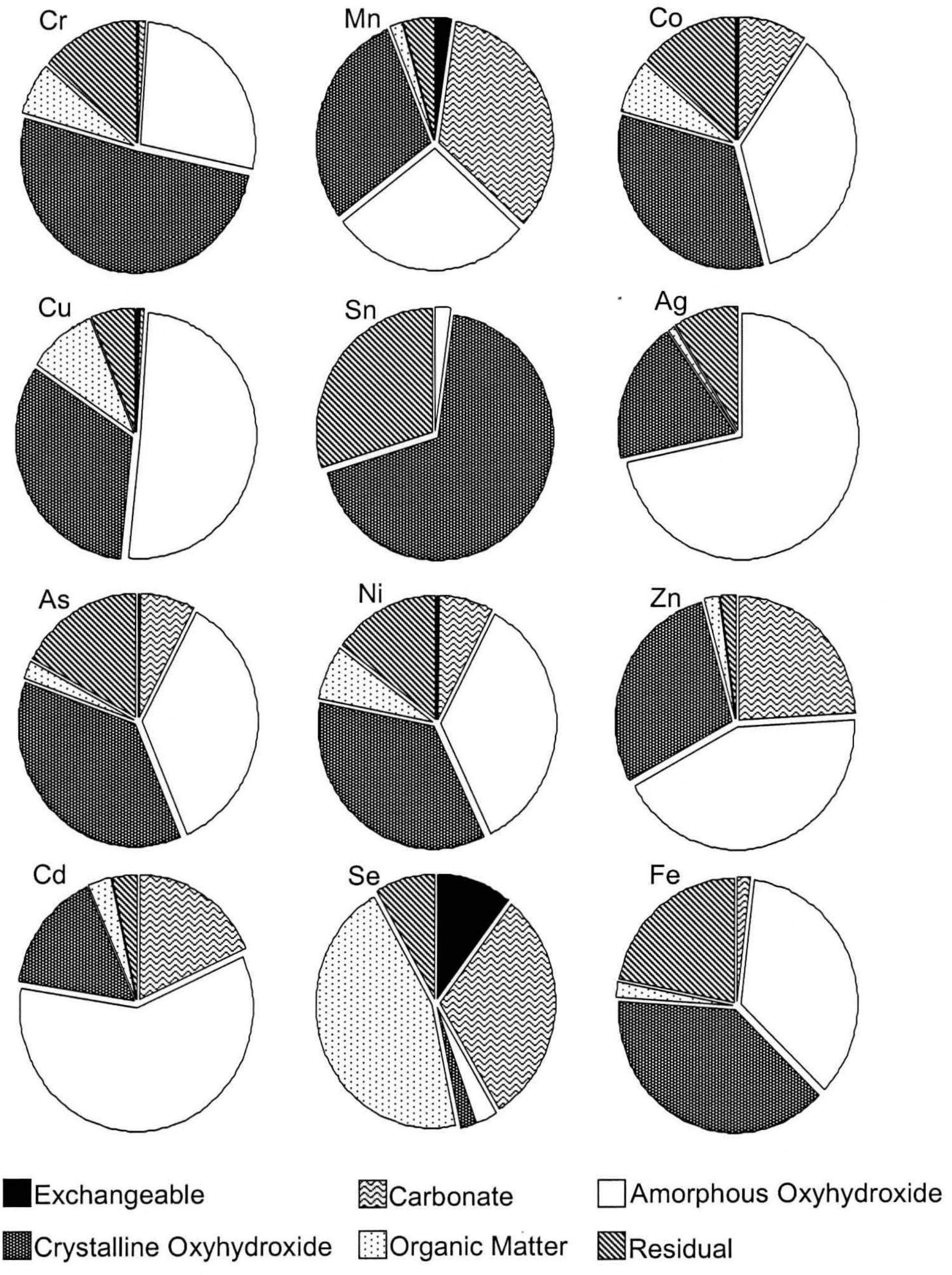

Figure 3.2.3b: Pie diagrams showing the proportion of metals in each of six fractions for the bed sediment at the deep site.

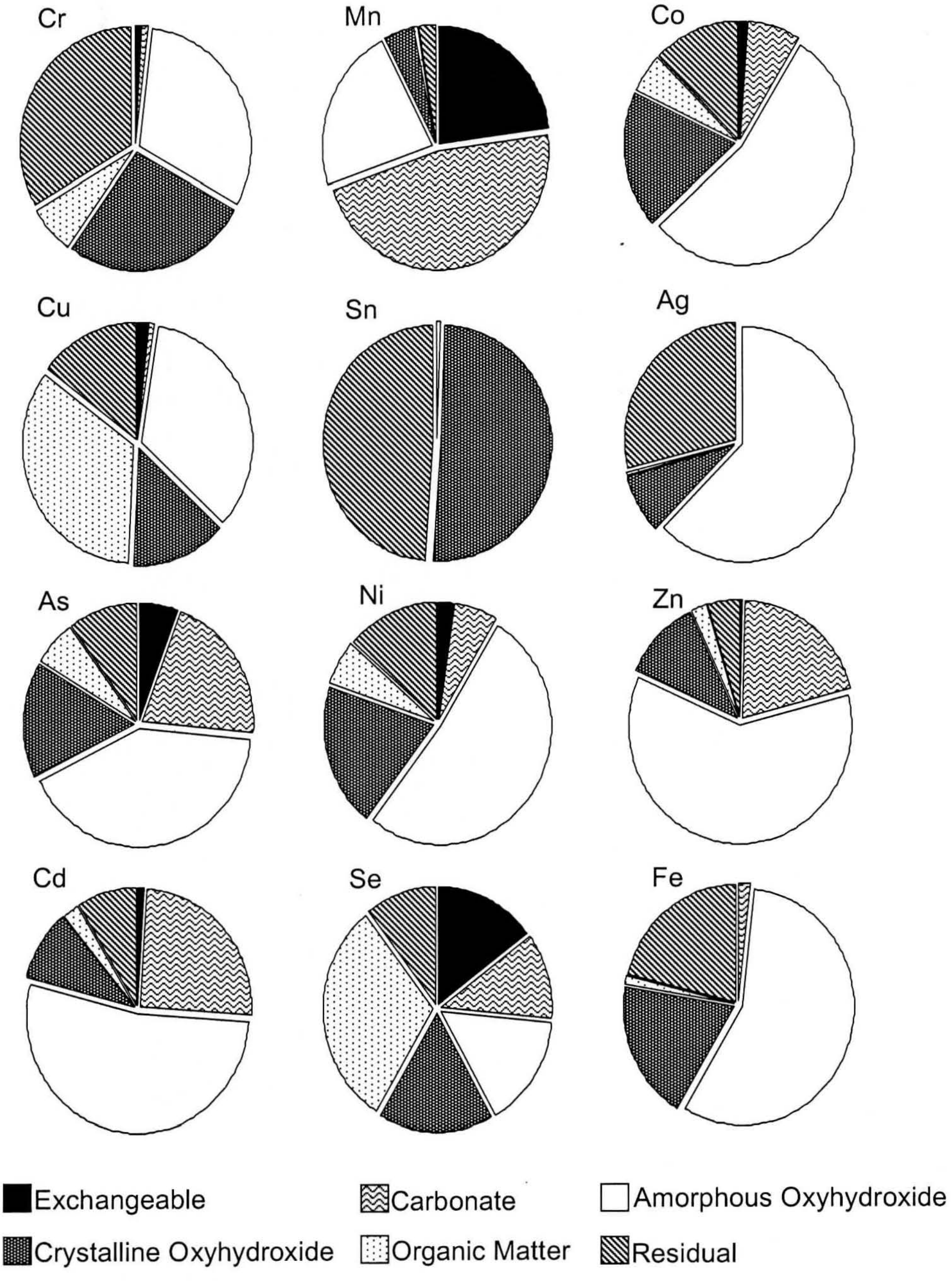

Figure 3.2.3c: Pie diagrams showing the proportion of metals in each of six fractions for the SPM at the shallow site.

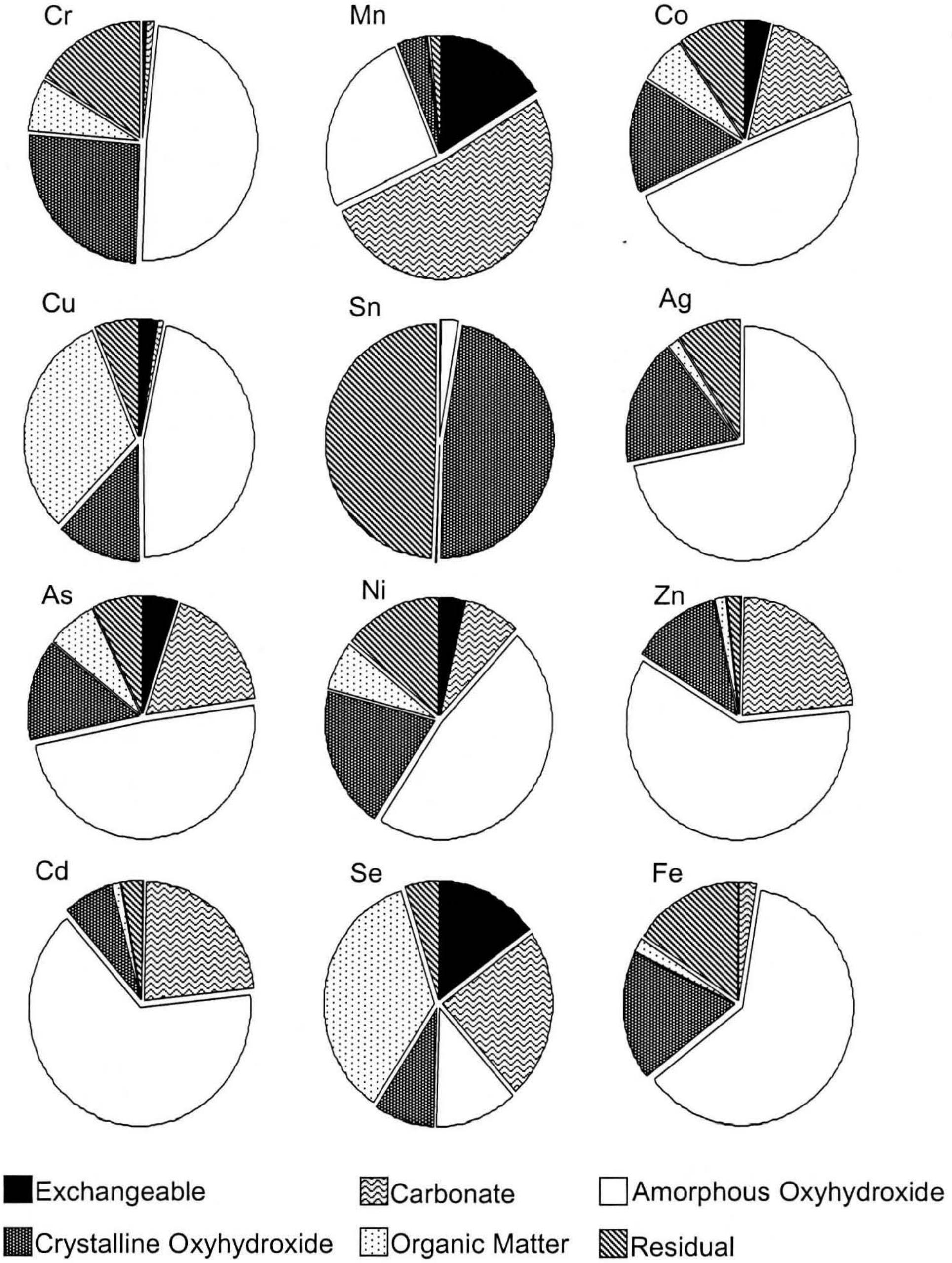

Figure 3.2.3d: Pie diagrams showing the proportion of metals in each of six sediment fractions for the SPM at the deep site.

3.2.3 Temporal Trends in Fraction Associated Metals

There were no consistent seasonal trends in concentrations of metals in each of the six sequential extraction fractions or in the per cent (%) of total metal in each of the six sequential extraction fractions (Figure 3.2.4 a - l). Further, there were no consistent diel trends in concentrations of metal in any of the fractions, or any of the metal concentrations as a % of the total metal for any of the metals.

3.2.3.1 Temporal Trends in Fraction-Associated Metal Concentrations

Metal concentrations for Cr, Co, Cu, Sn, Ag, As, Ni, Zn, Cd and Fe were dominated by the concentrations of amorphous oxyhydroxide or crystalline oxyhydroxide or both throughout the season from May to August; however, Mn was dominated by carbonate associated metal concentrations and Se was dominated by organic matter metal concentrations (Figure 3.2.4 a – l, metal concentration graphs). These results correspond to results reported previously for mean seasonal proportions (see section 3.2.2). Temporal trends in metals associated with oxyhydroxide fractions for metals with high concentrations in these fractions mirror total metal temporal trends in absolute concentrations, reported in section 3.1.3.2, while metal concentrations in carbonate fractions and crystalline oxyhydroxide fractions (in deep site bed sediment only) for Mn are similar to temporal trends in total metals and there was not one fraction that dominated temporal trends in Se concentrations.

Overall, most metals associated with each fraction exhibited substantial temporal variability. Coefficients of variation (calculated as: (standard deviation / mean) x 100%) for most metals in most fractions ranged from 21% – 196% for exchangeable metals, 15% – 235% for carbonate associated metals, 9% – 208% for amorphous oxyhydroxide associated metals, 12% – 169% for crystalline oxyhydroxide associated metals, 10% – 303% for organic matter associated metals, 15% – 135% for residual associated metals in both compartments and sites. Overall, variability of the amorphous and crystalline oxyhydroxide fractions at both sites in both compartments was less than 50% for all metals, except Se in all compartments (Se ranged from 75% - 208% for amorphous oxyhydroxide and 70% – 169% for crystalline oxyhydroxide), Mn (59%) and Fe (56%) in bed sediment, crystalline oxyhydroxides at the deep site Mn (53%) and Fe (64%) in crystalline oxyhydroxides in shallow site SPM and Mn (52%), Sn (55%), As (53%), Ni (53%), Zn (52%), Cd (58%) and Fe (75%) in crystalline oxides in deep site SPM. Residual variability was also typically less than 60% for all metals with the exception of Cd and Se at both sites and in both compartments.

Mean coefficients of variation for shallow bed sediment are: 83% exchangeable, 44% carbonate, 50% amorphous oxyhydroxide, 25% crystalline oxyhydroxide, 47% organic matter, and 33% residual; in deep site bed sediment mean coefficients of variation are 53% exchangeable, 48% carbonate, 33% amorphous oxyhydroxide, 42% crystalline oxyhydroxide, 45% organic matter, and 42% residual; in shallow site SPM:

60% exchangeable, 47% carbonate, 42% amorphous oxyhydroxide, 44% crystalline oxyhydroxide, 58% organic matter, and 44% residual; and in deep site SPM: 89% exchangeable, 77% carbonate, 38% amorphous oxyhydroxide, 57% crystalline oxyhydroxide, 66% organic matter, and 47% residual. Metal concentrations in each fraction for each compartment show the greatest variability, represented by the mean of coefficients of variation for each fraction in each compartment, in the exchangeable fraction in all compartments. The exchangeable fraction represents, the most readily available, loosely bound solid-associated fraction of metals and may be the most susceptible to changes in physico-chemical conditions and hence, the most variable concentrations of associated metals (Tessier et al., 1979).

3.2.3.2 Temporal Trends in Fraction-Associated Metals as a Per Cent of Total

From May to August the proportions of each metal in each fraction were variable through the season (Figure 3.2.4 a – l, stacked bar graphs). Variability ranged from 17% – 217% in % exchangeable metal, 4% - 226% in % carbonates metal, 7% – 193% in % amorphous oxyhydroxide metal, 10% – 168% in % crystalline oxyhydroxide metal, 12% – 315% in % organic matter metal and 13%-107% in % residual metal.

Mean coefficients of variation of metal proportions in each fraction for shallow bed sediment are: 75% exchangeable, 43% carbonate, 40% amorphous oxyhydroxide, 23% crystalline oxyhydroxide, 49% organic matter, and 29% residual; in deep site bed sediment mean coefficients of variation are 44% exchangeable, 47% carbonate, 29% amorphous oxyhydroxide, 31% crystalline oxyhydroxide, 39% organic matter, and 35% residual; in shallow site SPM: 66% exchangeable, 40% carbonate, 29% amorphous oxyhydroxide, 32% crystalline oxyhydroxide, 52% organic matter, and 33% residual; and in deep site SPM: 85% exchangeable, 71% carbonate, 20% amorphous oxyhydroxide, 40% crystalline oxyhydroxide, 60% organic matter, and 37% residual.

This indicates that the proportions of a metal in each fraction at a single sample time will not necessarily give an accurate account of the fractionation of the metal throughout the season; therefore, variability in fractionation must also be taken into account on a metal specific basis, but also on a temporal basis. This is particularly true for the exchangeable metals, the most bioavailable fraction, which for Cd in all compartments, Cr, Mn, Co, Ni and Zn in shallow site bed sediment, Cr and Sn in deep site bed sediment, Cu, Sn, Ag, Ni and Zn in shallow site SPM and Cu, Sn, Ag, As, Ni, Zn and Fe coefficients of variation were greater than 50% (i.e. the standard deviation was greater than 50% of the mean from May to August). Exchangeable fraction associated metals are more easily released to the dissolved compartments and therefore, variability in these concentrations may impact the dissolved compartment concentrations, potentially impacting ecosystem health.

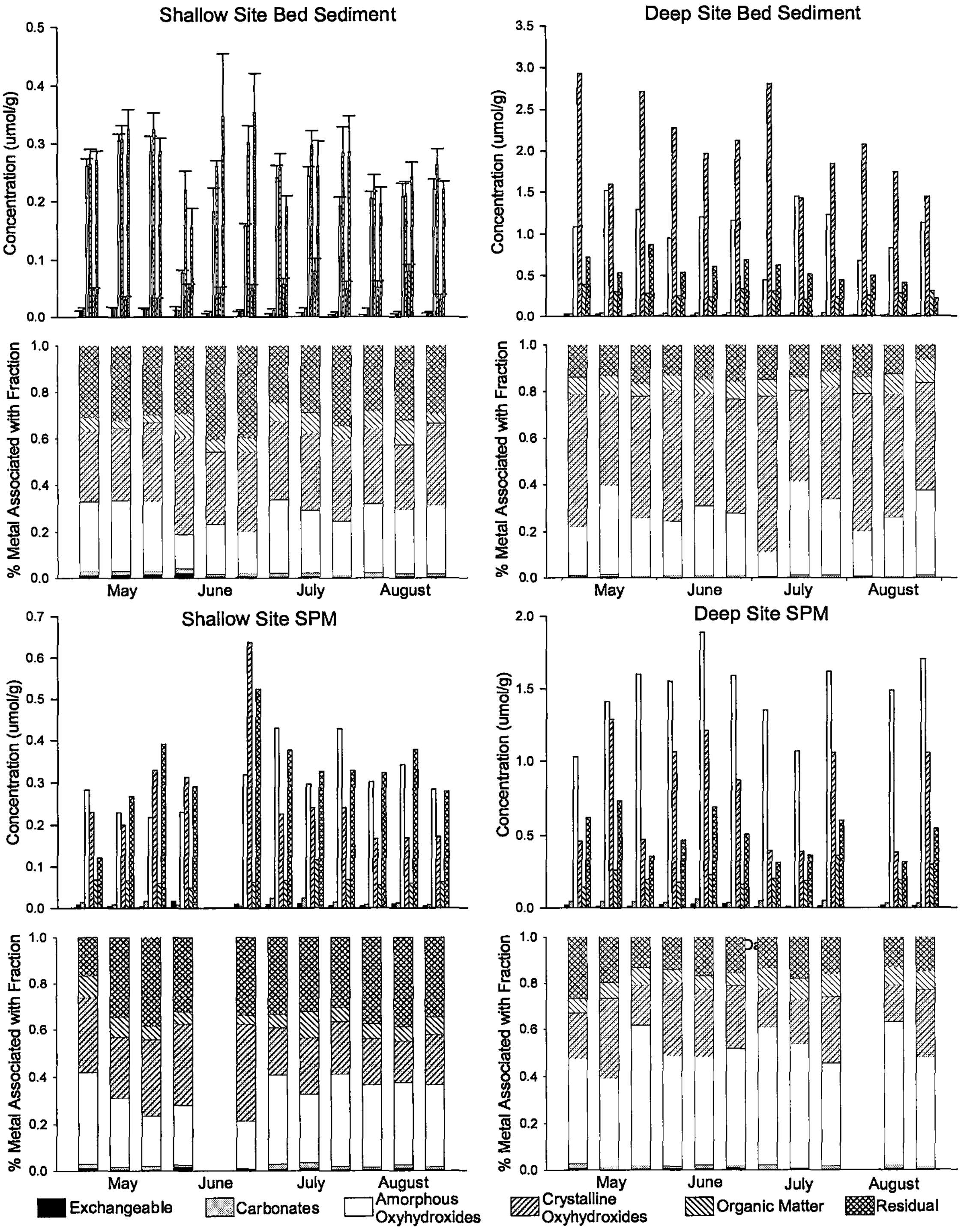

Figure 3.2.4a: Cr concentrations and per cent values in bed sediment and SPM from May to August. Values represent sample means (n=3).

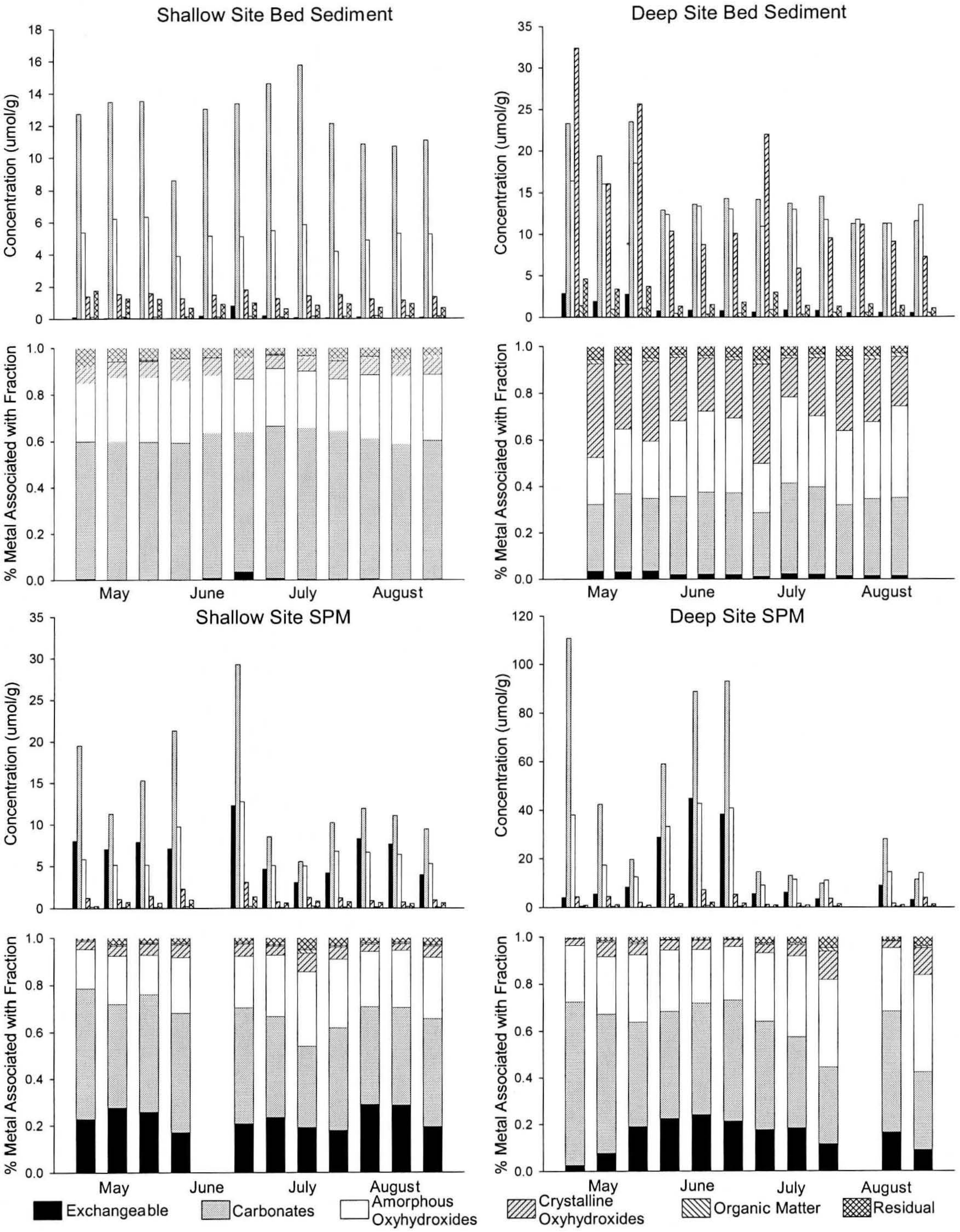

Figure 3.2.4b: Mn concentrations and per cent values in bed sediment and SPM from May to August. Values represent sample means (n=3).

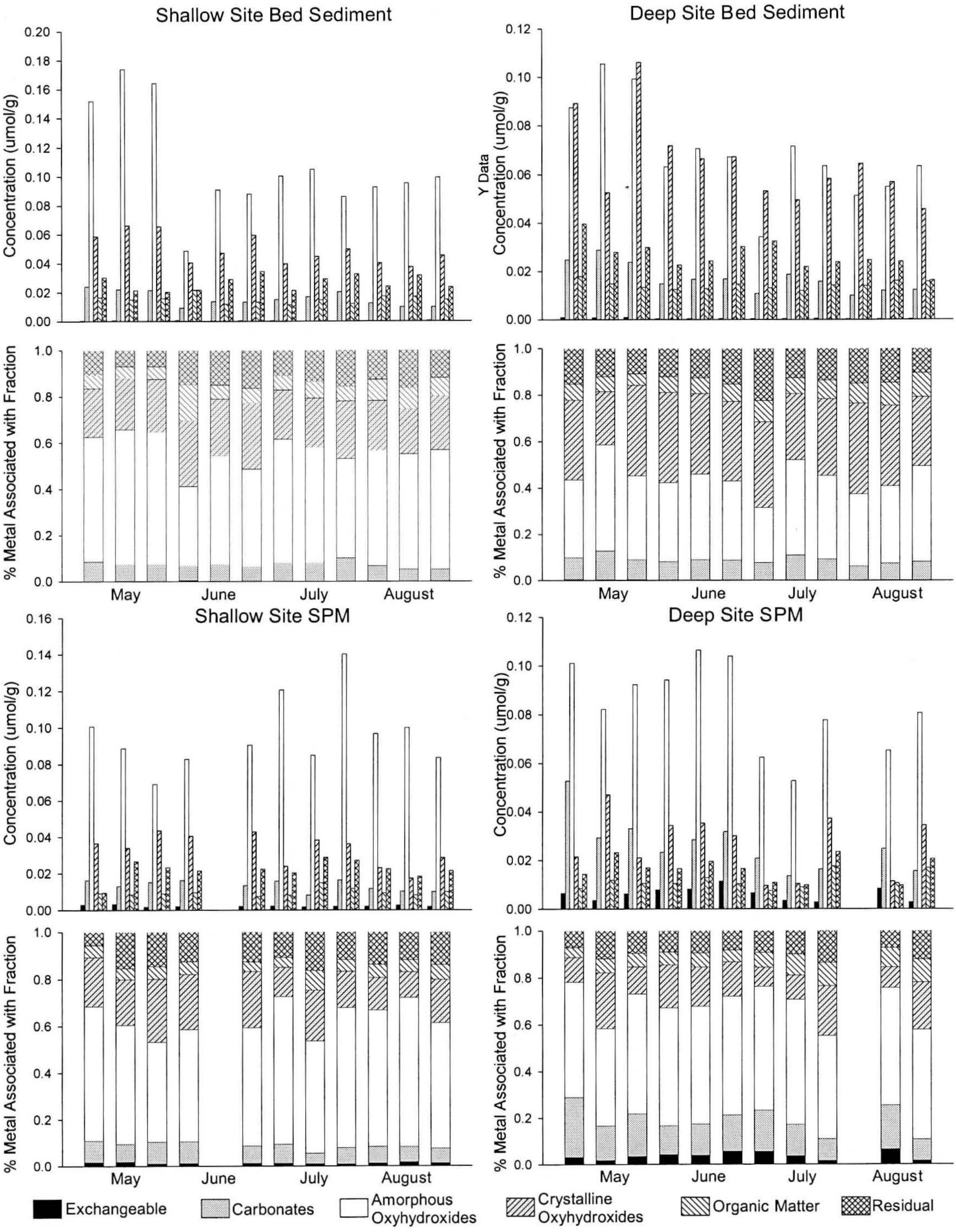

Figure 3.2.4c: Co concentrations and per cent values in bed sediment and SPM from May to August. Values represent sample means (n=3).

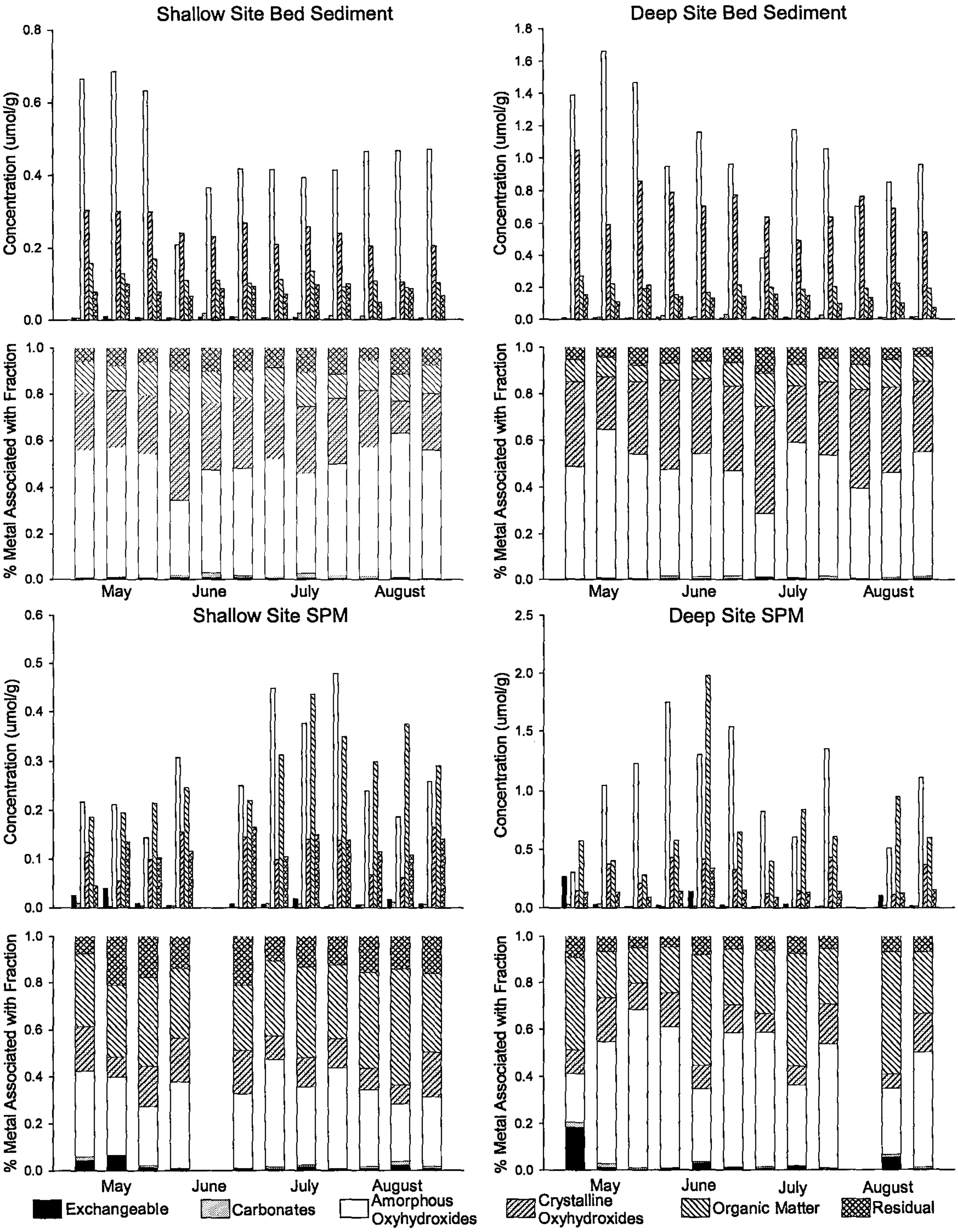

Figure 3.2.4d: Cu concentrations and per cent values in bed sediment and SPM from May to August. Values represent sample means (n=3).

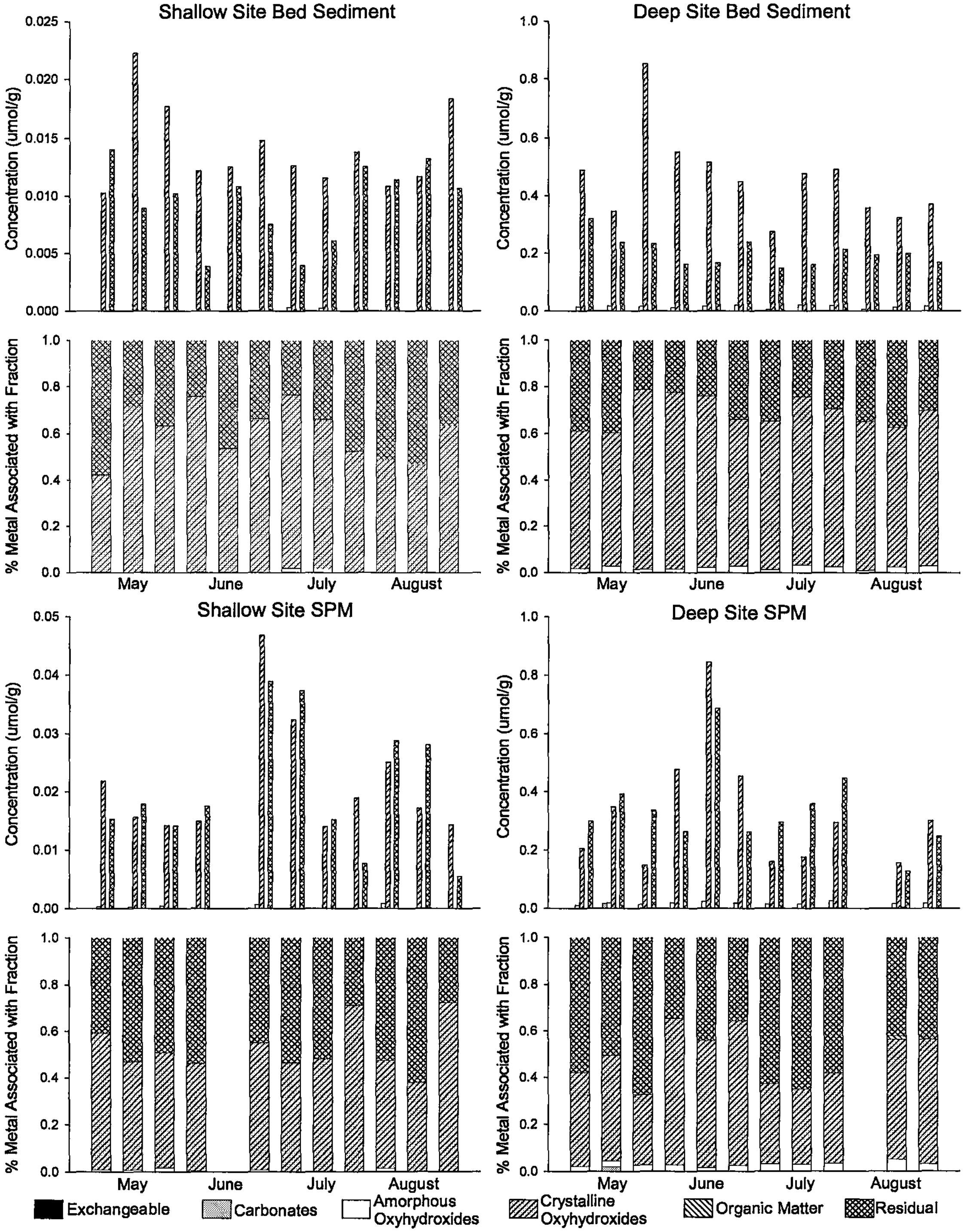

Figure 3.2.4e: Sn concentrations and per cent values in bed sediment and SPM from May to August. Values represent sample means (n=3).

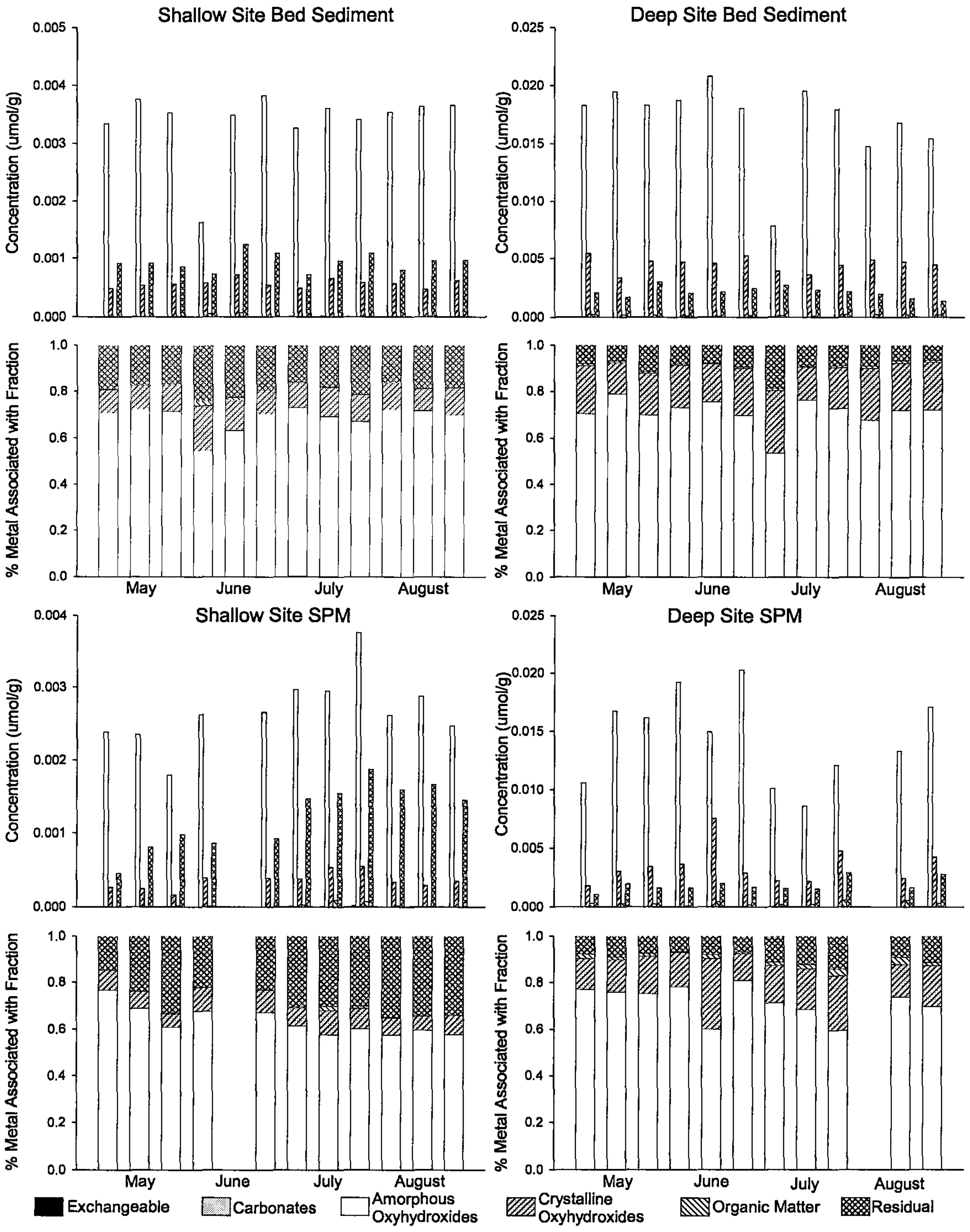

Figure 3.2.4f: Ag concentrations and per cent values in bed sediment and SPM from May to August. Values represent sample means (n=3).

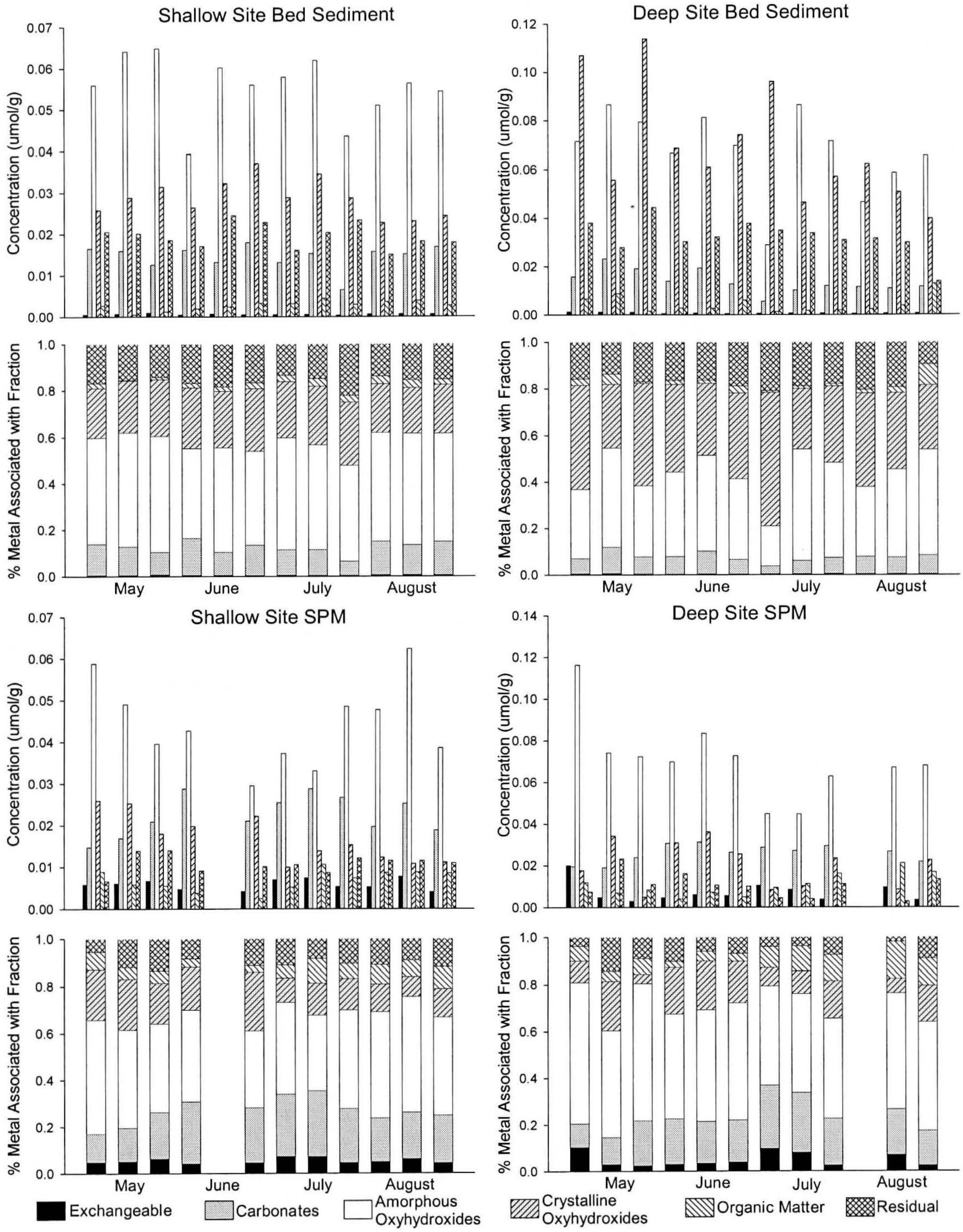

Figure 3.2.4g: As concentrations and per cent values in bed sediment and SPM from May to August. Values represent sample means (n=3).

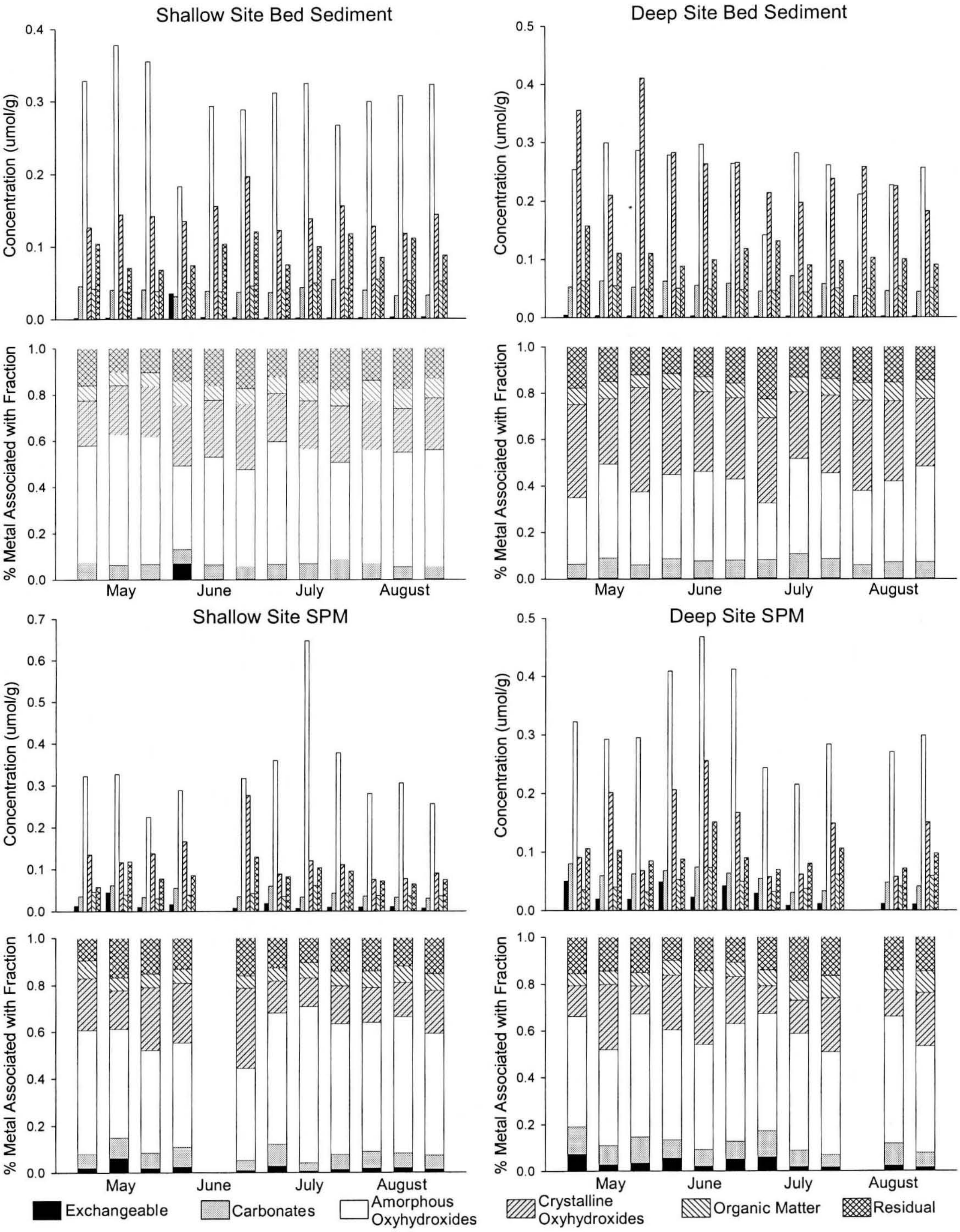

Figure 3.2.4h: Ni concentrations and per cent values in bed sediment and SPM from May to August. Values represent sample means (n=3).

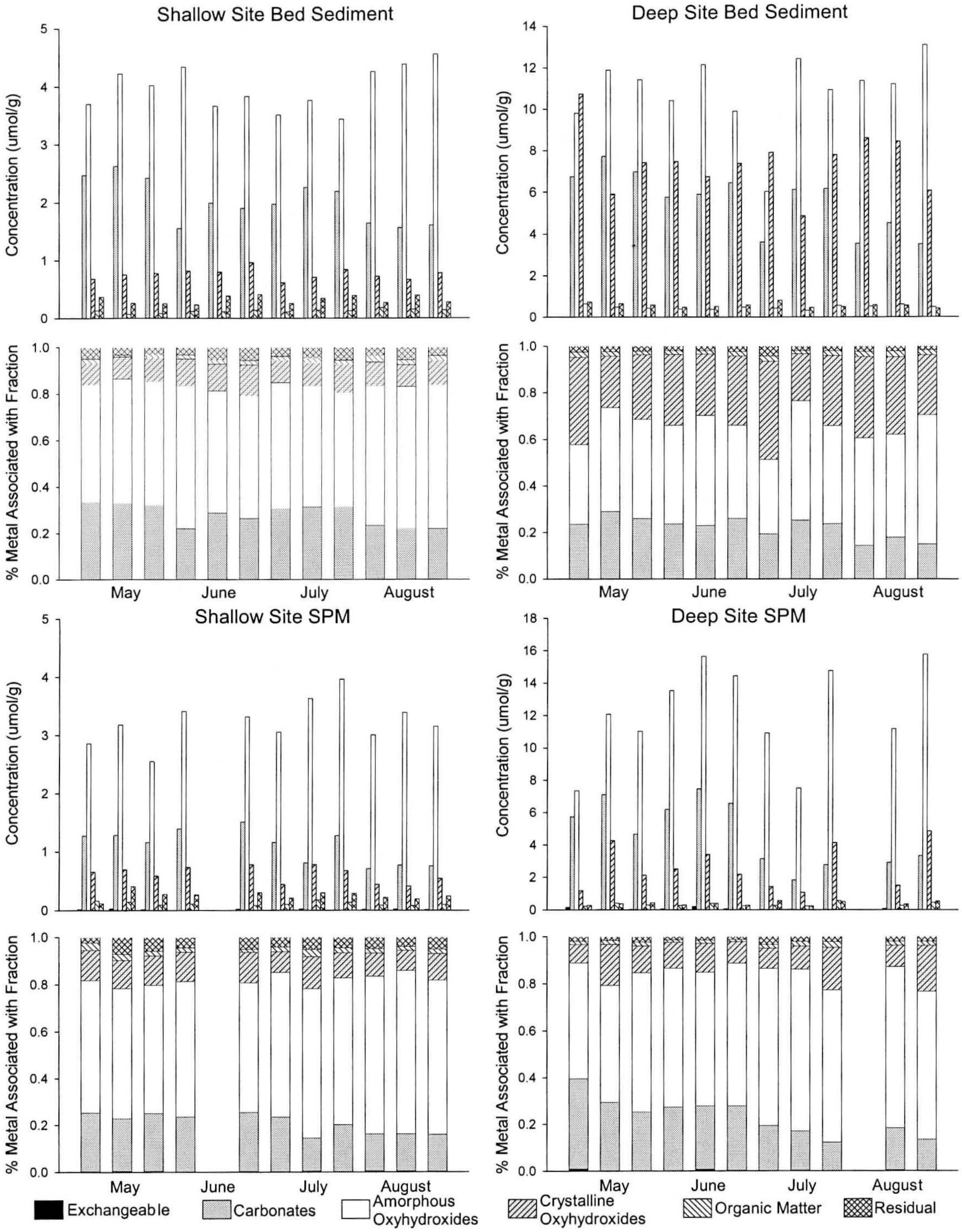

Figure 3.2.4i: Zn concentrations and per cent values in bed sediment and SPM from May to August. Values represent sample means (n=3).

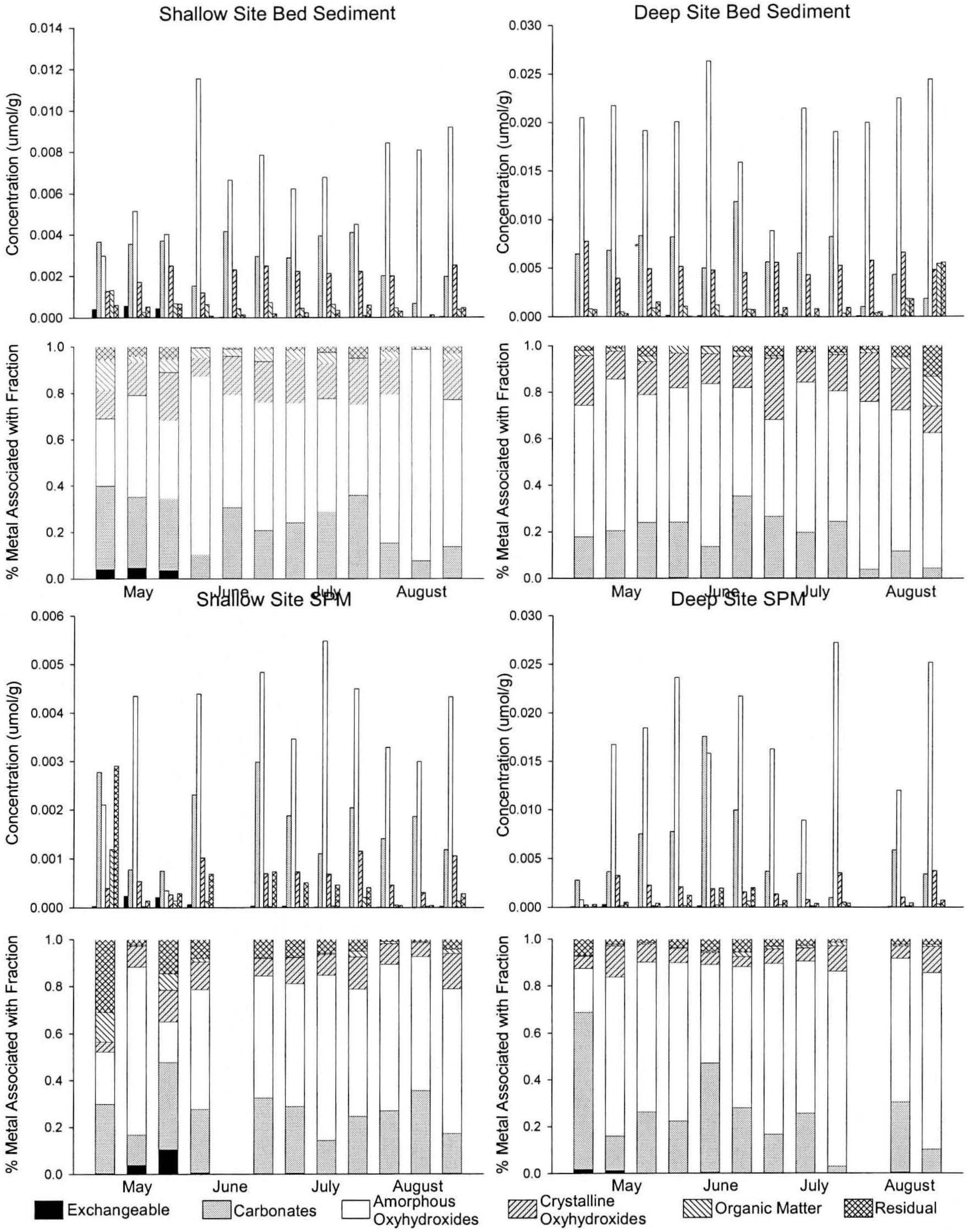

Figure 3.2.4j: Cd concentrations and per cent values in bed sediment and SPM from May to August. Values represent sample means (n=3).

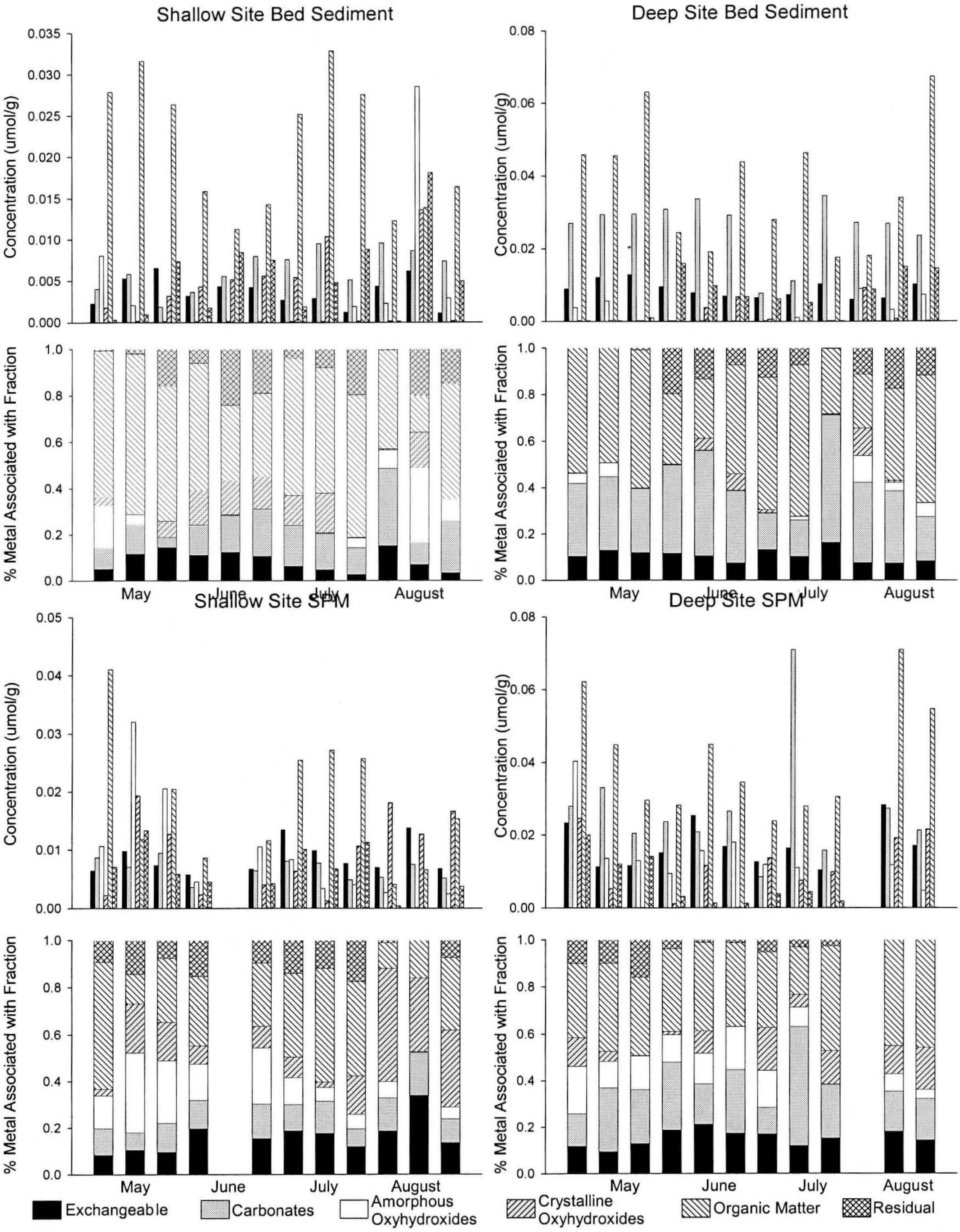

Figure 3.2.4k: Se concentrations and per cent values in bed sediment and SPM from May to August. Values represent sample means (n=3).

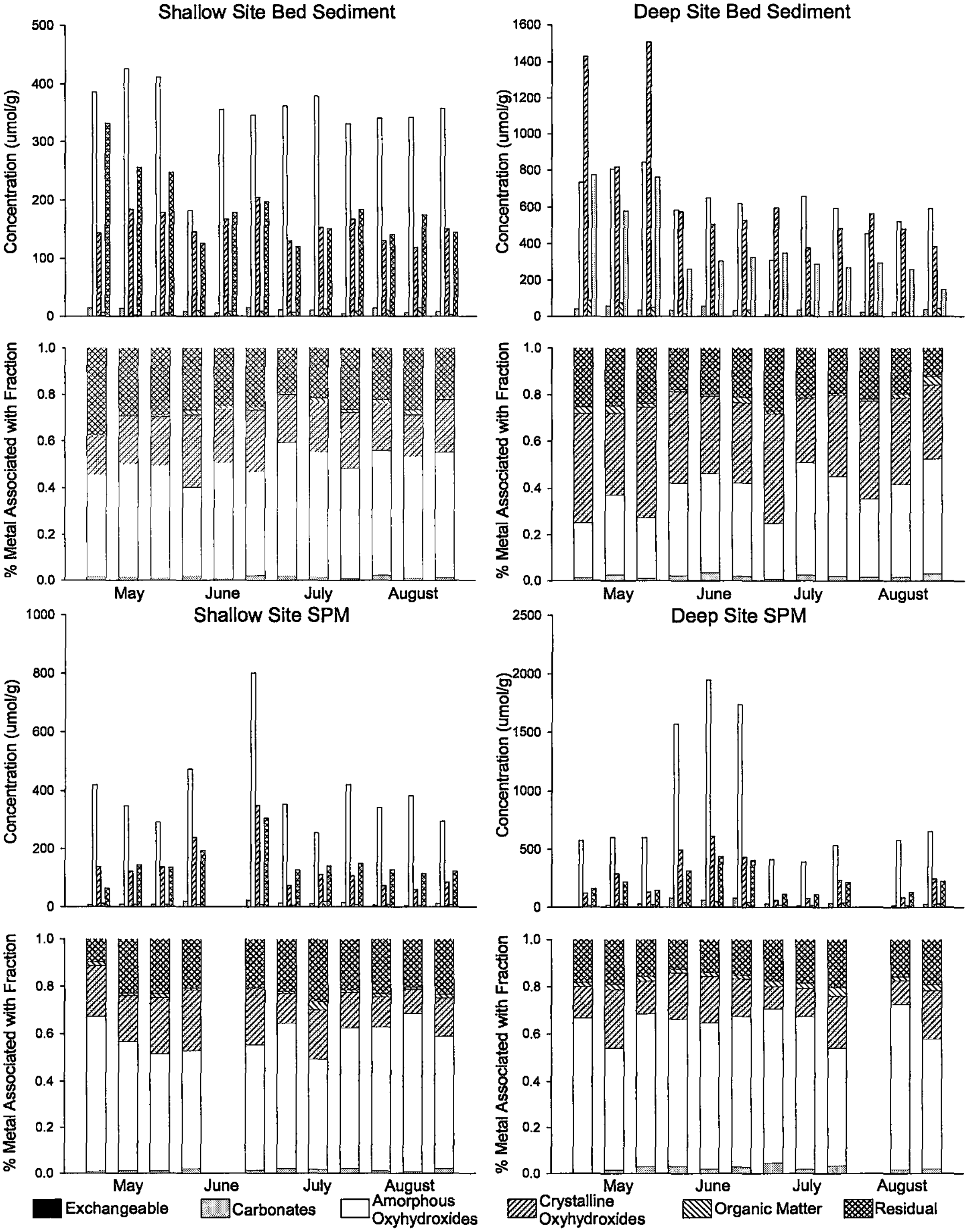

Figure 3.2.41: Fe concentrations and per cent values in bed sediment and SPM from May to August. Values represent sample means (n=3).

3.2.4 Metal Distributions in Compartments

To examine trends in sediment fraction associated metal concentrations two-way ANOVA analyses were used to determine effects of compartment and/or site with a post-hoc multiple comparison procedure to identify specific compartment or site significant differences (i.e. $p<0.05$). Figure 3.2.5 summarizes these differences in metal concentrations in each fraction between the two compartments at the two sites in this study using the results of the ANOVA (n.b. this figure is similar to Figure 3.2.2, in the manner by which results are presented). In these figures one-way arrows represent significant differences, determined from two-way ANOVA, and point in the direction of the significantly greater concentrations of a particular metal in a fraction. Two-way arrows are between compartments that did not have significantly different metal concentrations in a particular fraction. Fractions are represented by single letters for simplicity: E - exchangeable metal concentrations, C – carbonate metal concentrations, A – amorphous oxyhydroxide metal concentrations, Y – crystalline oxyhydroxide metal concentrations, O – organic matter metal concentrations and total – total metal concentrations. Metals in the residual fraction were not included in this analysis because metals in this fraction are part of the crystalline lattice of primary or secondary minerals and are not considered labile or bioavailable (Tessier, 1979).

Several trends can be observed from Figure 3.2.5:

1) There were always higher concentrations of metals in all of the potentially bioavailable fractions at the deep site i.e. when a significant difference in metal concentration exists between sites there is a larger concentration of metal in the deep site compartment. The higher concentrations of metals at the deep site may be partially explained by the higher concentration of some of the reactive fractions at this site - if fraction content is linked to metal concentration (see Figure 3.2.2) - concomitant with a direct input from point and non-point sources of most metals at the deep site, providing a potential increased scavenging ability and a larger source concentration compared to the shallow site (HHRAP, 1988; HHRAP, 1992; Droppo et al., 1998). These factors, combined with varying physico-chemical conditions i.e. deeper water column and lower dissolved oxygen concentrations and an increased likelihood of thermodynamic disturbances from shipping traffic at the deep site are possible contributors to the increased metals found at this site.

2) At the deep site, there is a greater concentration of metal sorbed to crystalline oxyhydroxides in the bed sediment compared to the SPM with the exception of Se, which, as discussed previously, does not have a high affinity for the oxyhydroxide fractions. Again this pattern of metal behavior is consistent with higher relative concentrations of crystalline oxyhydroxide in the deep site bed sediment compared to the deep SPM or shallow bed and SPM compartments (see Figure 3.2.2 and Section 3.2.1.4)

3) When a significant difference occurred, the metals associated with amorphous oxyhydroxides were always higher in the SPM compared to the bed sediment

compartment at both sites; however in contrast to the results summarized above, no significant difference in amorphous oxyhydroxide fraction concentration occurred between the two compartments at each site (see Figure 3.2.2). The decreased metal concentration associated with bed sediment oxyhydroxides, may reflect a decreased sorption ability of the amorphous oxyhydroxides in the bed sediment. Sorption of other non-metal material such as, organic matter and bacteria (Warren and Zimmerman, 1994; Brown et al., 1999) or carbonates (Appelo et al., 2002; Villalobos et al., 2001) may mask sites on the oxyhydroxide surface decreasing the ability of amorphous oxyhydroxides to sorb metals in solution or alternatively, differing physicochemical conditions within the bed sediment compartment may decrease relative sorptive abilities of the amorphous oxyhydroxides.

4) Greater similarity occurred between metal concentrations in the SPM and bed sediment at the shallow site than at the deep site; sediment fraction concentrations also reflect this trend possibly linking fraction concentrations to associated metal concentrations. Similarities between both the SPM and bed sediment composition and the concentrations of metals associated with these compartments at the shallow site are consistent with the hypothesis that greater mixing occurs at this site with greater similarity between the compartments.

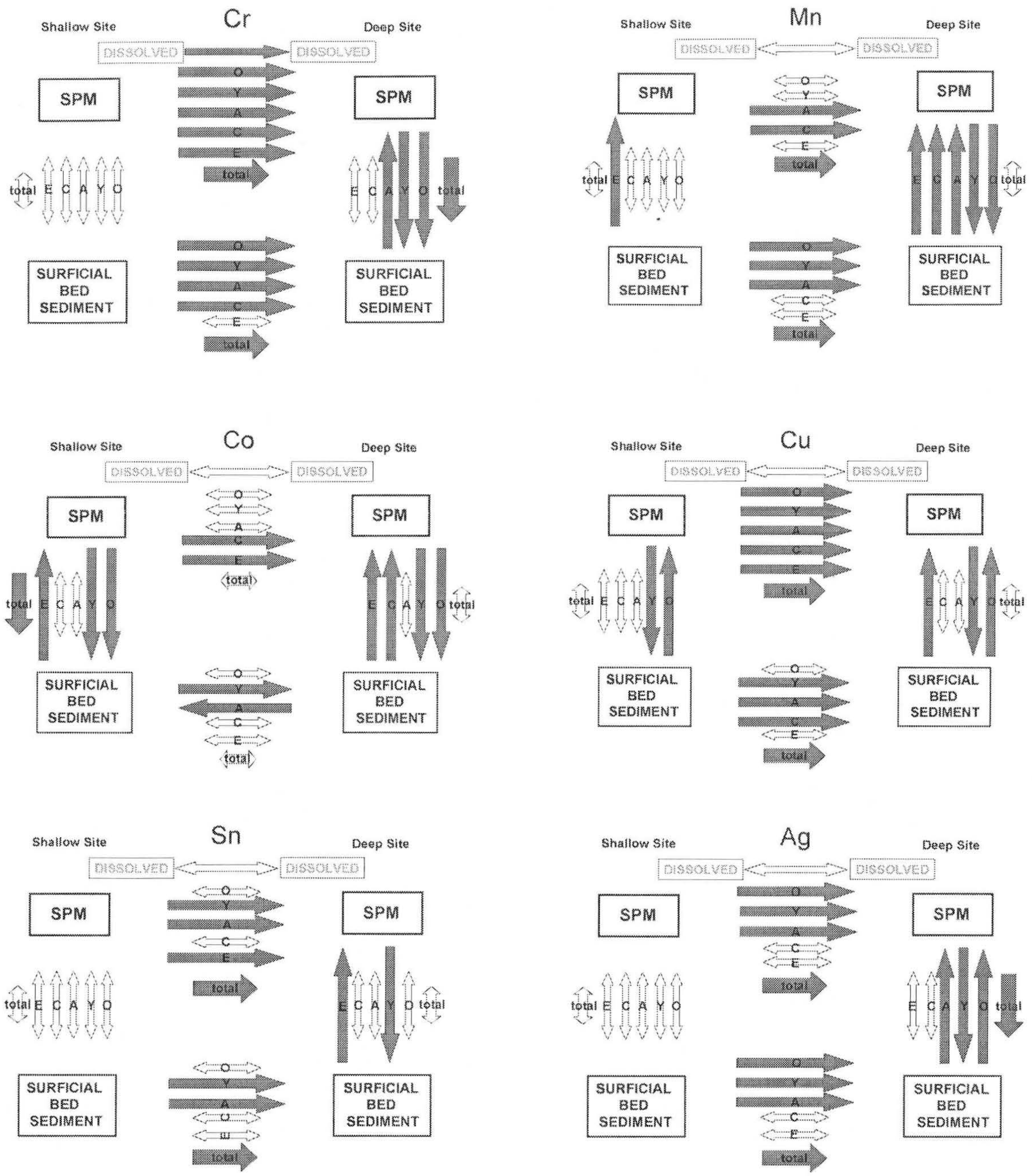

Figure 3.2.5: Schematic of site and compartment variation in metal concentrations within each fraction. Two-way arrows indicate no significant difference and one-way arrows point toward the compartment that contains the greater concentration of metal. "E": Exchangeable, "C": Carbonates, "A": Amorphous Oxyhydroxides, "Y": Crystalline Oxyhydroxides, "O": Organic Matter and "total": total of all fractions.

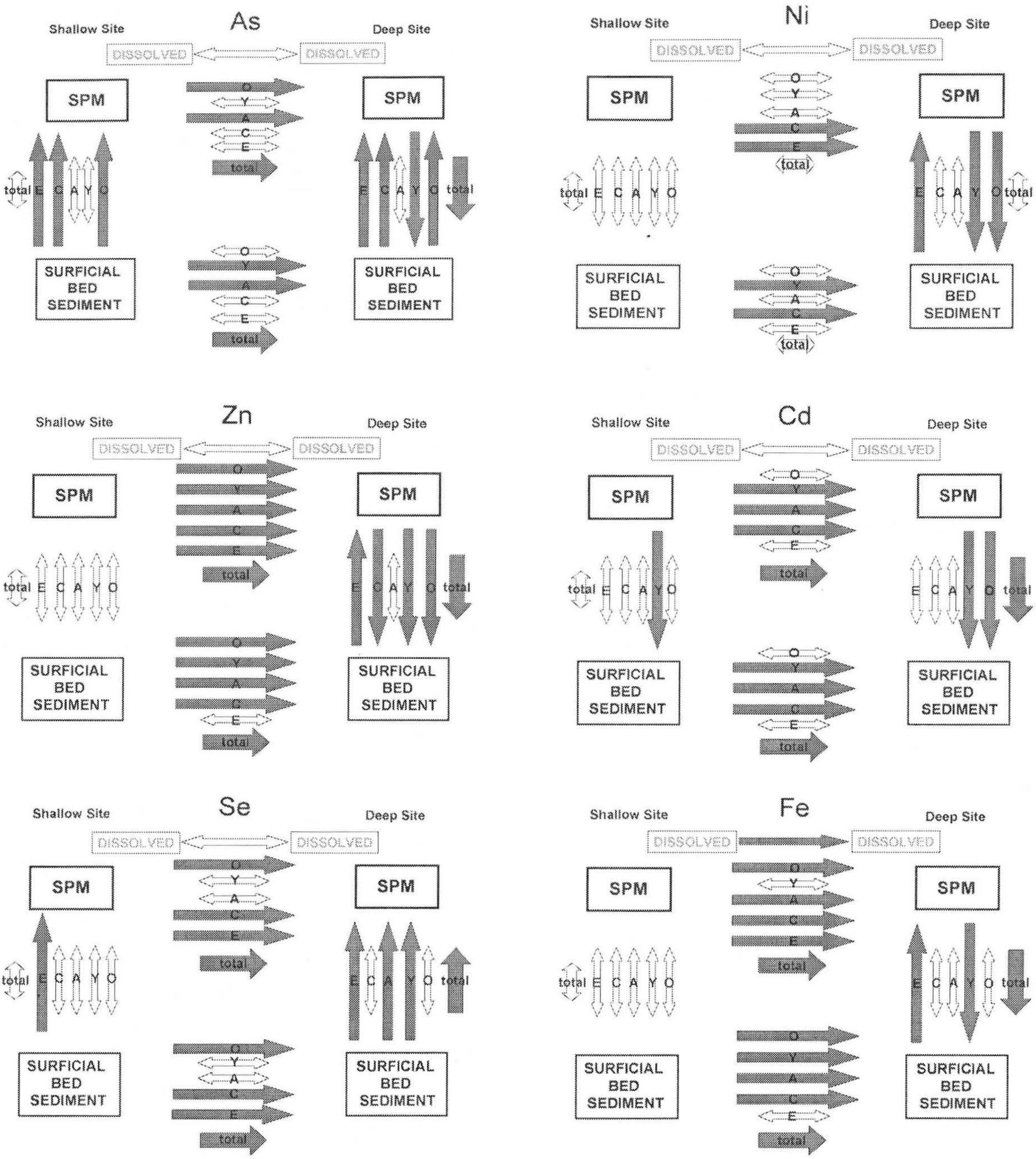

Figure 3.2.5 (continued from previous page): Schematic of site and compartment variation in metal concentration within fractions. Two-way arrows indicate no significant difference and one-way arrows point toward the compartment that contains the greater concentration of metal. "E": Exchangeable, "C": Carbonates, "A": Amorphous Oxyhydroxides, "Y": Crystalline Oxyhydroxides, "O": Organic Matter and "total": total of all fractions.

3.2.4.1 The Importance of Fraction Concentration

A number of trends in metal concentrations in fractions are also reflected in the trends in the concentrations of the fractions themselves i.e. when there is a greater concentration of a fraction within the sediment pool, there is typically also a greater concentration of metal associated with that fraction. For example, there are typically higher concentrations of metals in the deep site bed sediment and SPM compartments and this is also mirrored in the fraction concentrations where significant differences indicate higher concentrations at the deep site. Indeed, metal concentrations are significantly positively correlated ($r^2>0.50$, $p<0.05$) with fraction content, particularly in the oxyhydroxide fractions, for a great number of the metals i.e amorphous oxyhydroxide fraction concentrations are correlated with up to 10 metals (Cr, Mn, Co, Cu, Sn, Ag, As, Ni, Zn and Fe) in the deep site bed sediment and crystalline oxyhydroxide concentrations are correlated with between 5-9 (Cr, Mn, Co, Cu, Sn, Ag, As, Ni and Fe) metals in one compartment at either site, and carbonate fraction concentrations were correlated with up to three metals (including Cr, Mn, Ag, As, Zn, Fe depending on the compartment), although these relationships were negative in shallow site bed sediment (See Table 3.2.1).

There are however, some metals, particularly Se and Cd associated with some fractions within compartments that show patterns that do not demonstrate a relationship to the fraction content of the bed sediment or SPM, and are perhaps controlled by extenuating factors such as variability in physico-chemical factors or anthropogenic influences.

Table 3.2.1: Summary of metals that show significant correlations between metal concentration and the concentration of the fraction in which they are incorporated. Only metals that show significant relationships are listed ($r^2 > 0.50$, $p < 0.05$).

	Shallow Bed	**Deep Bed**	**Shallow SPM**	**Deep SPM**
Carbonate		Cr r^2= -0.62 As r^2= -0.72 Fe r^2= -0.80	Mn r^2= 0.56 Ag r^2= 0.56	Cr r^2= 0.55 Zn r^2= 0.78
Amorphous Oxyhydroxide	Cr r^2= 0.92 Mn r^2= 0.75 Co r^2= 0.85 Cu r^2= 0.78 Ag r^2= 0.78 As r^2= 0.75 Ni r^2= 0.96 Fe r^2= 0.99	Cr r^2= 0.77 Mn r^2= 0.81 Co r^2= 0.98 Cu r^2= 0.93 Sn r^2= 0.56 Ag r^2= 0.60 As r^2= 0.77 Ni r^2= 0.72 Zn r^2= 0.80 Fe r^2= 0.97		Mn r^2= 0.67 Ni r^2= 0.88 Fe r^2= 0.98
Crystalline Oxyhydroxide	Cr r^2= 0.60 Mn r^2= 0.95 Co r^2= 0.61 Cu r^2= 0.50 As r^2= 0.63 Ni r^2= 0.87 Zn r^2= 0.70 Fe r^2= 0.99	Cr r^2= 0.50 Mn r^2= 0.77 Co r^2= 0.68 Cu r^2= 0.51 As r^2= 0.63 Ni r^2= 0.68 Fe r^2=0.97	Cr r^2= 0.84 Mn r^2= 0.93 As r^2= 0.51 Ni r^2= 0.92 Fe r^2= 0.94	Cr r^2= 0.64 Mn r^2= 0.72 Co r^2= 0.51 Cu r^2= 0.64 Sn r^2= 0.95 Ag r^2= 0.53 As r^2= 0.62 Ni r^2= 0.81 Fe r^2= 0.92

3.3 Metal Partitioning

3.3.1 Solid-Aqueous Partitioning

The previous discussion has summarized observed site and/or temporal trends in dissolved and solid phase compartment concentrations for the suite of 12 metals analyzed. However, it is the behaviour of metal partitioning, or the relative distribution of elements between a solid compartment (e.g. bed and/or SPM) and the dissolved fraction, that is most commonly examined for identification of the processes and likely controlling factors that lead to observed metal distributions. This reflects both the dynamic exchange that can occur between sediment and dissolved compartments, i.e. sediment associated metals are not necessarily irreversibly held, as well as the importance of interfacial reactions between solid surfaces and aqueous solution in controlling metal dynamics between solid and dissolved compartments. All of these processes are affected by the nature and concentrations of solid fractions, the physicochemical conditions and the concentrations and nature of dissolved species (Warren and Haack, 2001 and references therein; Tessier et al., 1979). Partitioning is specifically used to quantify the distribution of metals between the solid (i.e. bed sediment or SPM) and the solution (i.e. dissolved component) phases through partitioning coefficients (K_D, which are also referred to as distribution coefficients in the literature) expressed as:

$$K_D = C_S/C_W \text{ (L kg}^{-1}\text{)},$$

where C_S is defined as the concentration of metal in the solid (in mol of metal per kg^{-1} of sediment) and C_W is the concentration of metal in the dissolved compartment (in mol of metal per L^{-1} of water). K_Ds can be further defined to reflect the partitioning to a particular solid fraction (i.e. oxyhydroxide, carbonate or organic matter associated), in this instance, C_S is described as mols of metal per kg^{-1} of the specific sediment fraction. K_Ds normalize the solid-compartment associated metal concentrations to the metal concentrations in the dissolved compartment, in theory, rendering values for the solid compartments independent of the concentration of the solid itself (Warren and Zimmerman, 1994; Cantrell et al., 2003). Normalized K_D values allow for comparison of metal dynamics between the dissolved and solid compartments between metals, sites, solid compartments (bed sediment, SPM) and fractions (Table 3.3.1).

3.3.2 Spatial and Elemental Partitioning

Total bulk sediment seasonal mean K_Ds in both solid compartments at both sites ranged from 10^3-10^5 for most metals, however, Se K_Ds indicated that there was 2 to 4 orders of magnitude less partitioning to the sediment than other metals (10 - 10^2 in both sites and compartments). Further, for any metal at a site, mean seasonal K_D values were of the same order in bed sediment and SPM (10^3L/kg: Cd and Zn at both sites; 10^4L/kg: Cr, Co, Cu, As, Ni and Fe at both sites, Sn and Ag the shallow site and Cd at the deep site; 10^5L/kg: Mn at both sites and Sn and Ag at the deep site; Table 3.3.1). These values are typical of other systems (Cd, Cu and Zn: Warren and Zimmerman, 1994; As, Cd, Cr, Cu, Ni, and Zn: Sauvé et al., 2000; Cd, Cr, Zn: Peng et al., 2003; Cd, Zn: Peng et al., 2005).

Ranges of fraction-specific K_D values for bed sediment were, generally, similar between the two sites for each fraction, however, the values ranged over 2 to 4 orders of magnitude for a given fraction: exchangeable range 10^0L/kg -10^3L/kg, carbonate range 10^1L/kg -10^5L/kg, amorphous oxyhydroxide range 10^4L/kg -10^6L/kg, crystalline oxyhydroxide range 10^4L/kg -10^6L/kg, organic matter range 10^1L/kg -10^4L/kg (Table 3.3.1). Comparison of Kd values indicate that, for most metals, the greatest affinity and associated metal per mass of solid fraction occurred in the amorphous and crystalline oxyhydroxides. There was greater than one order of magnitude, and up to three orders of magnitude, more Cr, Cu, Sn Ag and Fe associated with the oxyhydroxide fractions for a given weight of solid compared to the exchangeable, carbonate and organic matter fractions. Whereas Co, As, Ni, Zn and Cd partitioning to the carbonate fraction was more similar i.e. a difference of one order of magnitude or less, compared to the amorphous and crystalline oxyhydroxides, however, partitioning to oxyhydroxides remained greater in all instances. Furthermore, Mn had a greater affinity for the carbonate fraction than other metals and partitioning was similar to partitioning of Mn to the amorphous and crystalline oxyhydroxides (K_D~ $10^{5.9}$ – $10^{6.5}$ for carbonate, amorphous oxyhydroxide and crystalline oxyhydroxide in all compartments) and Se partitioning was particularly low in the oxyhydroxide fractions ranging from $10^{0.8}$ – $10^{2.6}$.

Mn (>10^5 for total K_D) and Zn (>10^4 for total K_D) in all compartments and Ni ($10^{4.8}$ for total K_D) in the shallow site bed sediment showed the greatest partitioning to the solid phase across fractions. Se was typically less associated with the solid fractions (<$10^{1.8}$ for total K_D), having a greater proportion of metal in the dissolved compartment compared to other metals, and Sn was consistently least associated with the organic fraction, often having solid associated concentrations below detection limits however, Sn showed relatively high partitioning to the crystalline oxyhydroxide fraction ($10^{5.9}$ – $10^{7.1}$ for total K_D; see Table 3.3.1).

Table 3.3.1: Partitioning of metals in different fractions in each compartment with Log K_D values in brackets. Metals are listed greatest to least partitioning from left to right; = ("equal") signs indicate that there less than one standard error difference in partitioning between metals.

Shallow Site Bed Sediment	**Exchangeable**	Mn(2.7) = Ni(2.4) > Cu(2.4) = As(2.1) = Zn(0.16) > Co(2.0) = Cr(1.9) > Cd(1.1) > Ag(0.68) > Fe(0.58) > Se(0.27) (no Sn)
	Carbonate	Zn(4.4) > Mn(6.0)> Ni(4.7)> Co(4.8)= As(4.5) > Cd(4.2)> Fe (3.8) = Cu(3.4) > Cr(3.1) > Ag(2.0) > Sn(1.8) > Se(1.6)
	Amorphous Oxyhydroxide	Zn(5.2) > Ni(6.0) > Mn(6.1) = Co(6.1) > As(5.6) = Cu(5.8) = Ag(5.7) = Fe(5.8)> Cd(5.0) > Cr(4.9) > Sn(2.6) > Se(1.1)
	Crystalline	Zn(4.8) = Ni(6.0) > Co(6.1) = Mn(5.8) = Cu(5.9) = As(5.6) = Sn(5.9) > Fe(5.8) > Ag(5.3) > Cr(5.3) > Cd(4.7) > Se(1.8)
	Organic Matter	Ni(4.8) = Zn(3.2) = Co(4.8) = Cu(4.8) > Mn(4.1) = As(3.8) > Cr(3.8) = Fe(3.7) = Cd(3.3) > Ag(2.3) > Se(2.2) (no Sn)
	Total	Zn(4.0) > Ni(4.8) = Mn(5.2) > Co(4.9) > As(4.4) = Cu(4.7) = Fe(4.6) = Sn(4.4) = Ag(4.5) > Cr(4.0) = Cd(3.8) > Se(1.4)
Deep Site Bed Sediment	**Exchangeable**	Mn(3.8) > Zn(1.0) = Cu(2.6) > As(2.2) = Ni(2.1) = Co(2.1) = Cr(2.0) > Cd(1.2) = Sn(1.2) > Fe(1.0) > Se(1.7) (no Ag)
	Carbonate	Zn(4.8) > Mn(6.0) > Co(4.7) = As(4.4) = Cd(4.5) = Ni(4.4) > Fe(4.2) > Cu(3.6) > Cr(3.5) > Sn(2.9) > Ag(2.1) > Se(2.1)
	Amorphous oxyhydroxide	Zn(5.4) > Mn(6.2) = Ag(6.2) > Cu(5.9) > Fe(5.8) = As(5.4) = Co(5.7) = Ni(5.3) = Cd(5.4) = Sn(5.3) = Cr(5.3) > Se(0.9)
	Crystalline	Zn(5.2) = Sn(6.8) > Mn(6.2) > Cu(5.7) = Ag(5.6) = Fe(5.8) = As(5.4) = Co(5.6) = Ni(5.3) = Cr(5.6) > Cd(4.8) > Se(.65)
	Organic Matter	Zn(3.7) > Cu(4.9) = Mn(4.6) = Co(4.7) = Ni(4.4) = Cr(4.4) > Fe(4.1) = As(3.8) = Ag(3.9) = Cd(3.5) > Se(2.3) (no Sn)
	Total	Zn(4.4) > Sn(5.6) = Mn(5.5) > Ag(5.0) > Fe(4.9) = Cu(4.9) = Co(4.9) = As(4.6) = Ni(4.5) = Cr(4.6) > Cd(4.3) > Se(1.6)
		More partitioning to solid → More partitioning to dissolved
Shallow Site SPM	**Exchangeable**	Mn(4.6) > Ni(3.1) = Zn(1.2) = As(3.0) > Co(2.9) > Cu(2.7) > Cr(1.9) > Cd(1.1) > Fe(1.0) = Ag(0.8) > Se(0.7) (no Sn)
	Carbonate	Zn(4.3) = Mn(6.1) > Ni(4.7) = As(4.8) > Co(4.8) > Cd(4.0) > Fe(3.9) > Cu(3.5) > Cr(3.2) > Ag(2.1) > Sn(2.0) > Se(1.7)
	Amorphous oxyhydroxide	Zn(5.1) > Ni(6.0) = Mn(6.1) = Co(6.0) > Fe(5.8) = Ag(5.6) = Cu(5.6) = As(5.4) > Cr(5.0) = Cd(4.7)> Sn(3.2) > Se(1.9)
	Crystalline	Zn(4.9) = Ni(6.0) = Sn(6.1) = Co(6.0) = Mn(5.9) > Fe(5.8) = Cu(5.7) = As(5.5) > Cr(5.4) = Ag(5.2) > Cd(4.5) > Se(2.6)
	Organic Matter	Zn(2.8) = Ni(4.2) = Cu(4.8) > Co(4.2) > As(3.7) = Mn(3.7) > Cr(3.5) > Fe(3.3) > Ag(2.2) = Cd(2.2) > Se(1.6) (no Sn)
	Total	Zn(3.9) = Ni(4.8) = Mn(5.3) > Co(4.8) > Cu(4.6) = Fe(4.6) = As(4.3) = Sn(4.5) = Ag(4.3) > Cr(4.0) > Cd(3.5) > Se(1.5)
Deep Site SPM	**Exchangeable**	Mn(4.8) > Zn(1.7) = As(3.2)= Co(3.3) = Ni(3.0) = Cu(3.1) > Cr(2.1) = Sn(1.7) > Cd(1.4) = Fe(1.3)> Ag(1.0) = Se(1.0)
	Carbonate	Zn(4.9) = Mn(6.5) > As(5.0) = Co(5.1) > Cd(4.7) = Ni(4.6) > Fe(4.2) = Sn(3.5) > Cu(3.6) > Cr(3.5) > Ag(2.2) = Se(2.3)
	Amorphous oxyhydroxide	Zn(5.4)> Mn(6.3) > Ag(6.1) > Cu(5.8) = Fe(5.8)= Co(5.7) = As(5.4) = Ni(5.4) = Cr(5.4) = Sn(5.3) = Cd(5.1) > Se(1.9)
	Crystalline	Zn(5.3)= Sn(7.1) > Mn(6.1) = Ag(6.0) > Cu(5.8) = Co(5.7) = Fe(5.8) = Ni(5.6) = Cr(5.7) = As(5.4) > Cd(4.8) > Se(2.2)
	Organic Matter	Zn(3.2) = Cu(5.0)> Co(4.2) = Ni(3.9)= Mn(4.0) = As(3.9) = Cr(3.9) = Ag(3.7) = Fe(3.7) > Cd(2.6)= Sn(1.8) = Se(1.9)
	Total	Zn(4.4) > Mn(5.7)= Sn(5.7) > Ag(5.0) = Cu(5.0) > Fe(4.8) = Co(4.8) = Ni(4.5) = As(4.5) > Cr(4.5)> Cd(4.2) > Se(1.8)

3.3.3 Temporal Variation in Partitioning

Coefficients of variation values ({standard deviation / mean}x100%) for partitioning of each metal as a function of sample time in all compartments and sites range from 10% - 320% (Figure 3.3.1 (a) – (f)). Generally, each metal followed a similar temporal pattern among all compartments and sites and fell into several ranges of variation: Cr, Co and Fe were <50%, Cu, Sn, Ag, As and Cd were generally between 50% and 100%, Mn was greater than 100%, and Zn varied the most with values consistently >150%. Ni showed variation that was site specific with shallow site compartments showing less variation (approx. 100%) than deep site compartments (>150%) and Se variation in amorphous and crystalline oxyhydroxides in all compartments and organic matter in SPM was >90% while variation in partitioning of Se for exchangeable, carbonate and totals in all compartments and organic matter in the bed sediment compartments was <50%.

Large variation in K_D values, such as that seen in Hamilton Harbour, suggests that partitioning for these metals is not at a stable equilibrium. Rather, K_D values indicate wide fluctuations in the relative proportions of most of the metals examined in solid and dissolved compartments over time (Figure 3.3.2). This result is particularly important as it shows that dissolved compartment metal concentrations are not a simple function of sediment associated metal concentrations, as is typically observed in less anthropogenically impacted systems (Sauve et al., 2000) and that associated biota in Hamilton Harbour are exposed to highly variable dissolved metal loads which may be more toxic than relatively static metal exposures. K_Ds are also widely used for their predictive capability commonly enabling the determination of likely total sediment or sediment fraction associated metal concentrations and/or likely dissolved concentrations from commonly measured parameters. Predictions can be made based on the assumption that the K_D value remains constant for a given system, thus, large variation in K_D values renders the predictive capability obsolete. Variation in partitioning reflects variation in physico-chemical and geochemical factors (Tessier et al., 1989; Warren and Zimmerman, 1993; Sauve et al., 2000; Unnikrishnan and Nair, 2004; Peng et al., 2005). Partitioning coefficients are assumed to be independent of the concentration of metal and fraction, however, the K_D values for Hamilton Harbour show substantive variability indicating that partitioning is highly dynamic within the system. Partitioning in Hamilton Harbour likely reflects the greater relative hydrodynamic variability and high point source discharges occurring in this system. However, in Hamilton Harbour and other multi-impacted systems, partitioning may be influenced by a greater array of factors in a dynamic interaction of physico-chemical factors, geochemistry and mechanical factors.

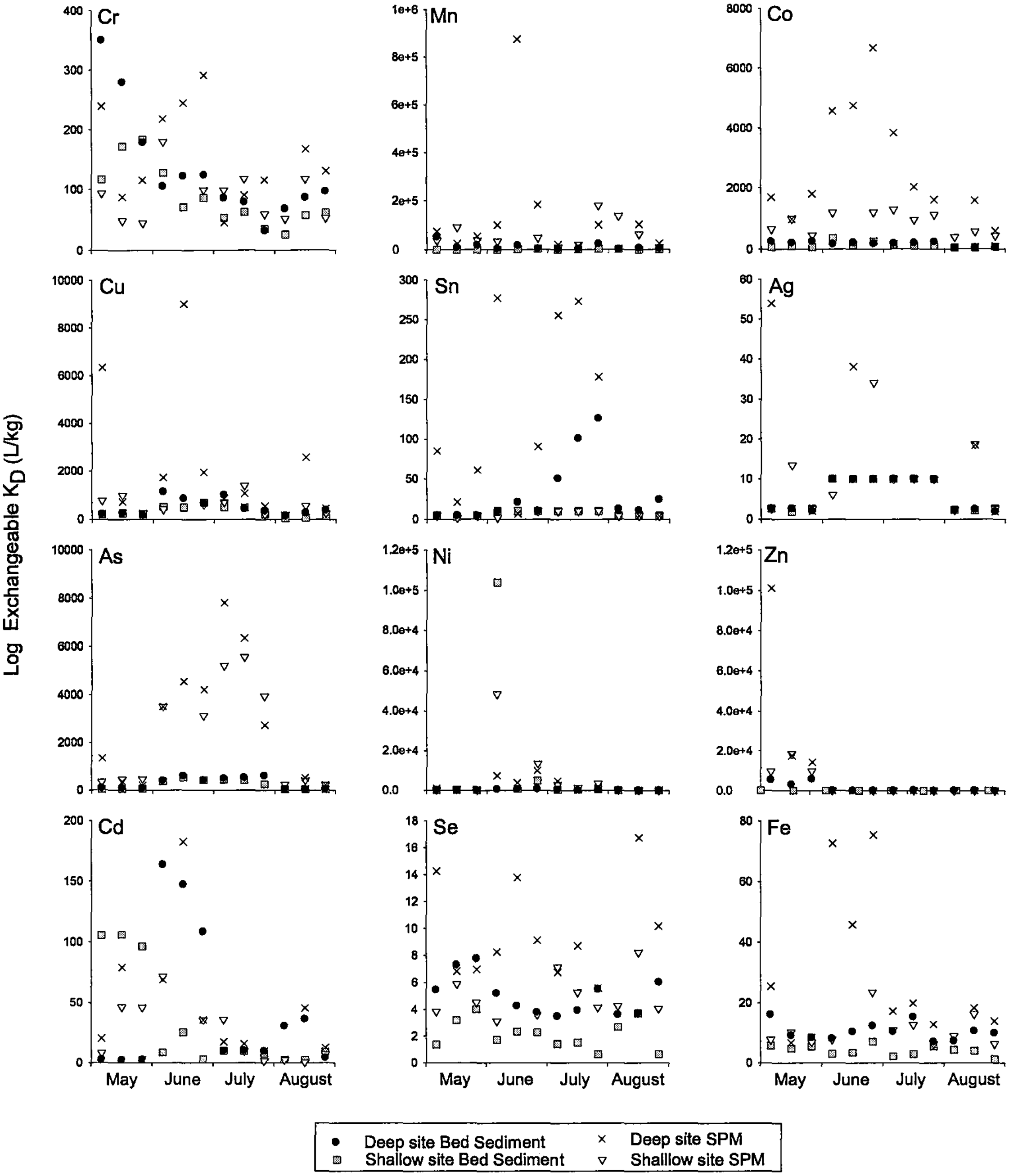

Figure 3.3.2 (a): K_D values for the exchangeable fraction from May to August.

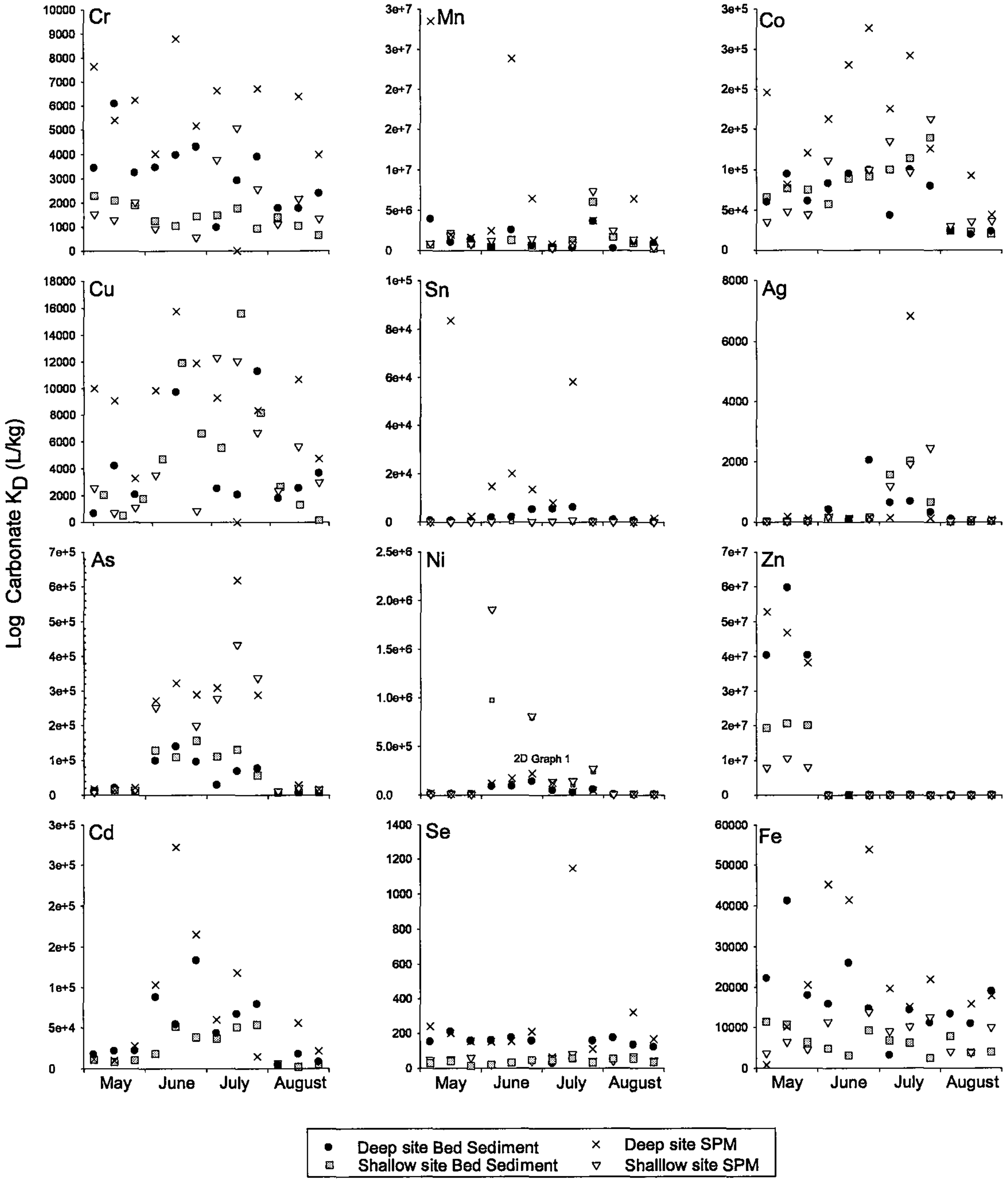

Figure 3.3.2 (b): K$_D$ values for the carbonate fraction from May to August.

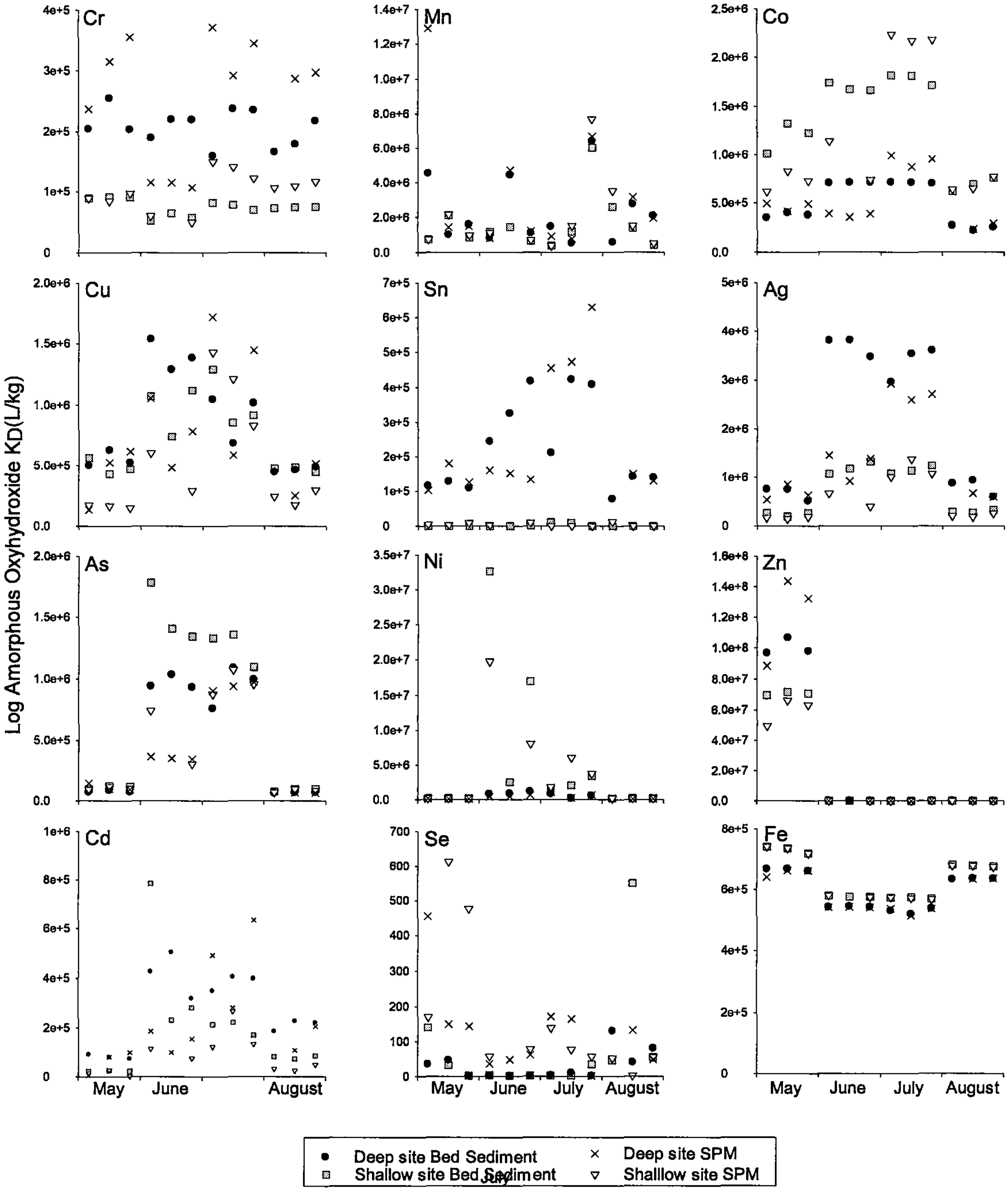

Figure 3.3.2 (c): K_D values for the amorphous oxyhydroxide fraction from May to August.

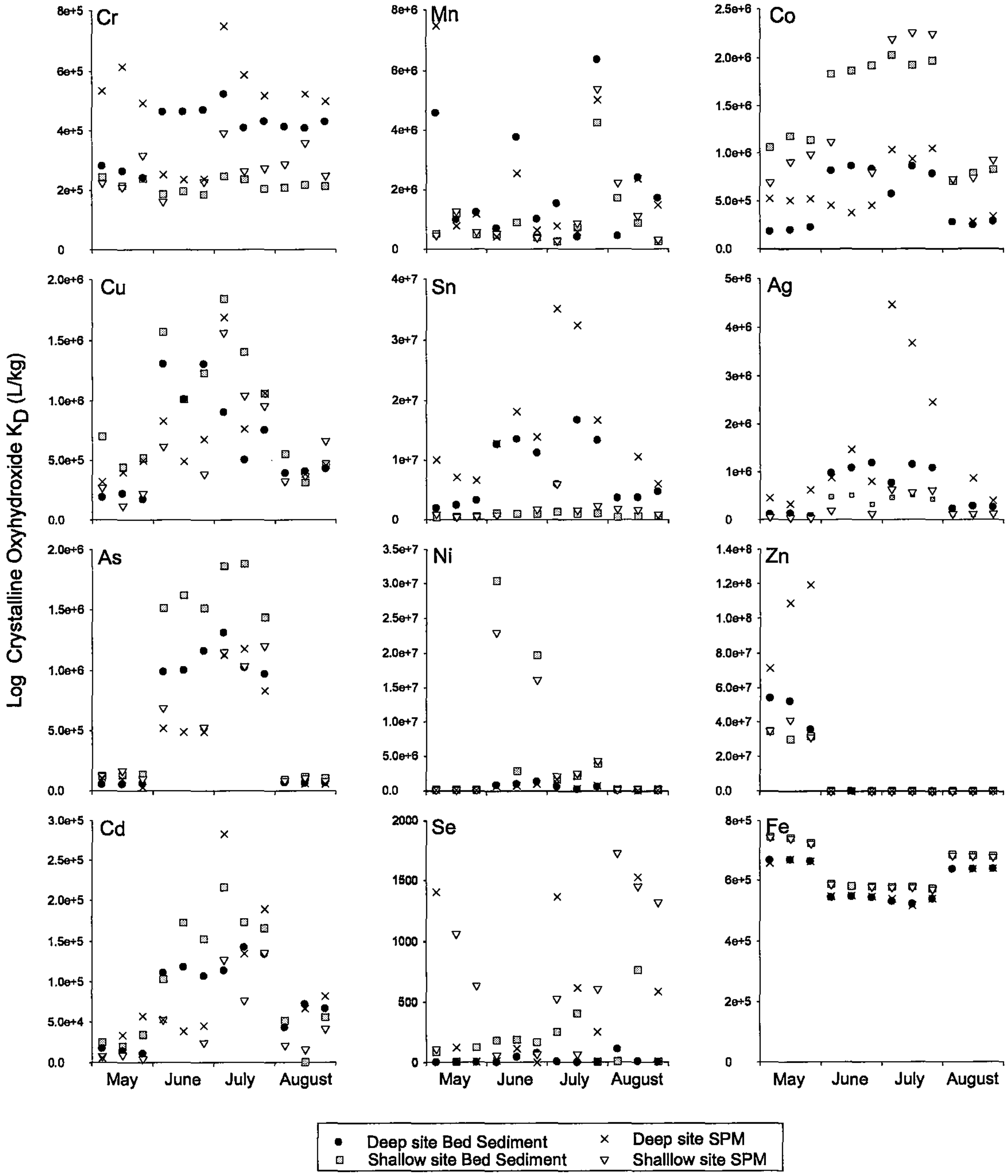

Figure 3.3.2 (d): K_D values for the crystalline oxyhydroxide fraction from May to August.

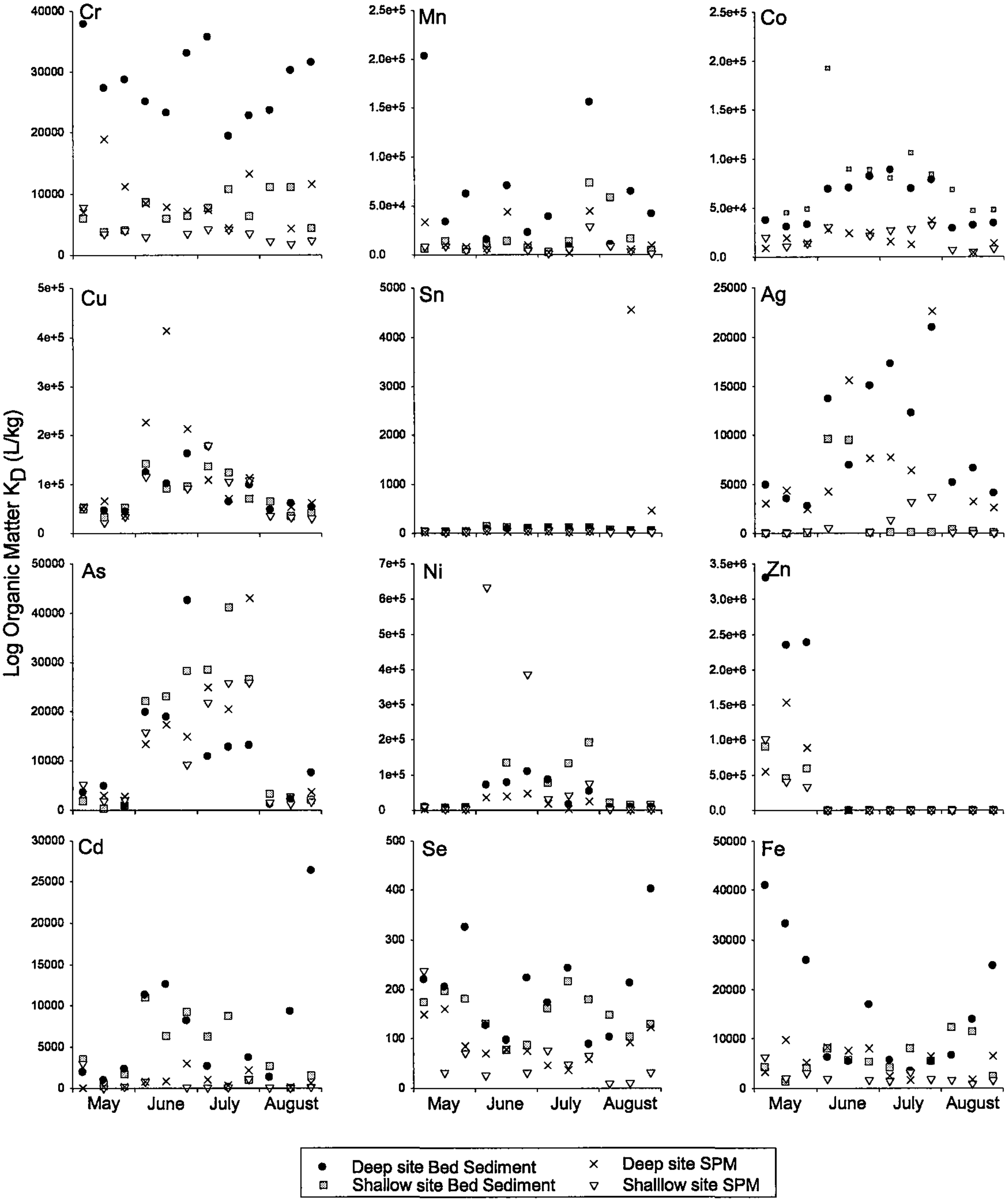

Figure 3.3.2 (e): K_D values for the organic matter fraction from May to August.

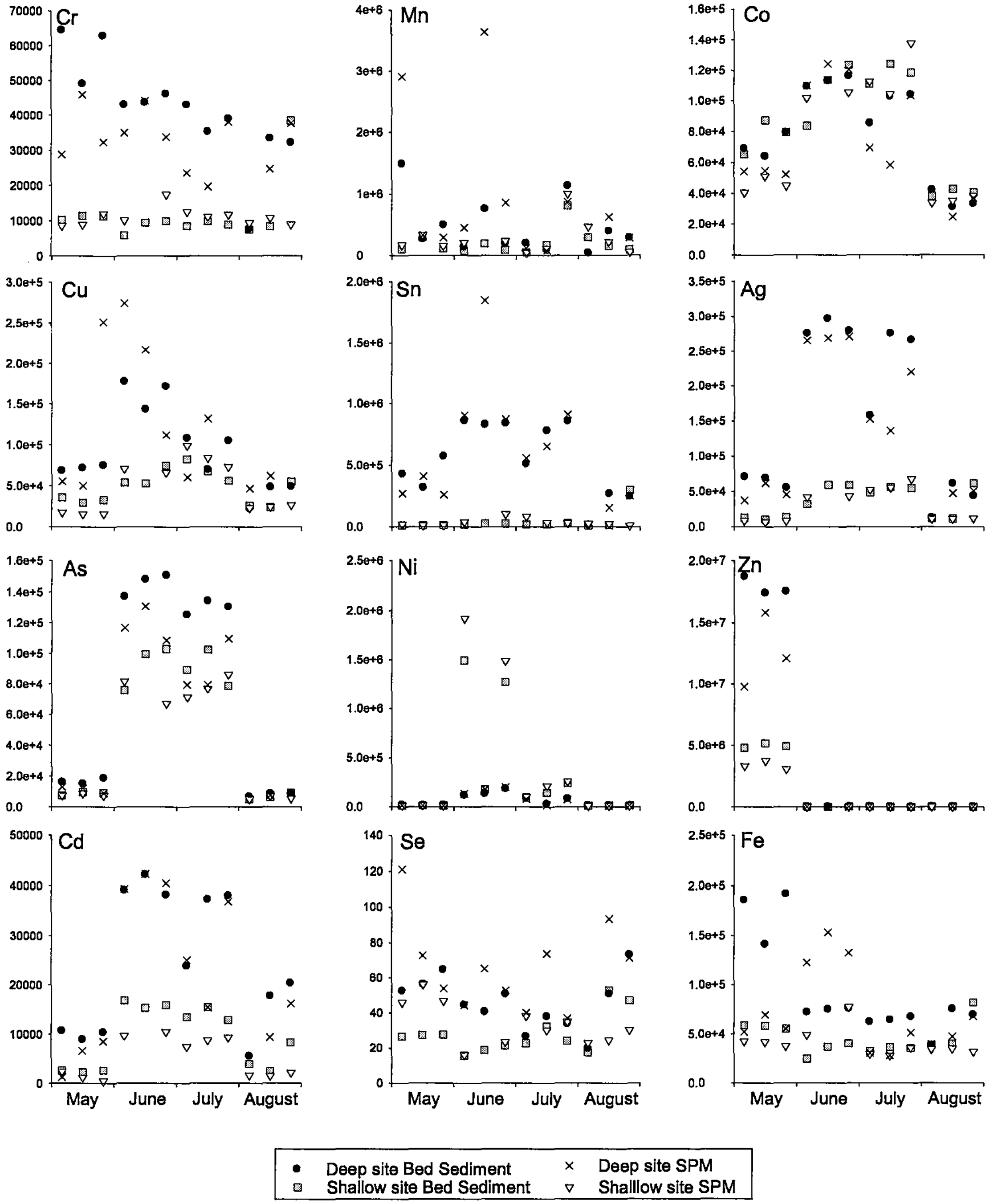

Figure 3.3.2 (f): Total K_D values from May to August.

3.4 Metal Behavior

As observed in Section 3.3, metal partitioning in Hamilton Harbour is highly spatially and temporally variable, indicating highly fluctuating distributions of all metals examined between sediment and solution phases. Several factors, including physico-chemical and geochemical conditions, sediment concentration and nature of components, and metal types and concentrations can influence metal partitioning between solid and dissolved compartments (see Chapter 1). Further, there may be a dynamic interplay among these factors temporally and/or spatially between sites and/or compartments, such that the relative influence of each of these potential controlling factors varies. Thus, to identify whether any factors were important in determining partitioning Harbour-wide, the pooled data for each metal (site and compartment) were used in multiple linear regression analysis (MLRA)..

Subsequently, MLRA analysis of the individual compartments was also evaluated to look for compartment or metal specific trends. Because many of the metals were significantly correlated with the concentration of the fraction with which they were associated, primarily the oxyhydroxide fractions (all metals, except Se showed a relationship with the associated fraction in at least one fraction in one compartment at one site; see Section 3.2.4.1 and Table 3.4.1 and 3.4.2 a-d, these relationships are denoted by an asterisk "*"), the concentration factor (C_F), defined as:

$$C_F = \frac{\text{[metal bound to sediment fraction] (in mol of metal /g of bulk sediment)}}{\text{[sediment fraction] (in g of fraction /g of bulk sediment)}} \quad ,$$

was used to evaluate potential controls on these particular metals and the dissolved concentration was included in the suite of independent variables.

The C_F normalizes the amount of metal bound to a fraction to the concentration of that fraction and thus changes in the C_F reflect differing relative scavenging per mass of sediment fraction. If the best predictor of the C_F was the dissolved concentration of that metal, the K_D was used as the dependent variable (removing the dissolved concentration and the concentration of the fraction from the suite of independent variables). Changes in environmental conditions, such as geochemical conditions, dissolved metal concentrations, solid compartment reactive fraction concentrations or SPM concentration (applicable to partitioning for the SPM fraction) will be reflected in the dependent variables (i.e. the metal concentration in a fraction, the C_F or the K_D values) only if they are affected by these physico-chemical variables. These parameters can affect metal behavior within the compartment by changing one or a combination of the following: the amount of sorbent in the sediment, the reactivity of that fraction or the amount of available metal.

The independent variables used in this analysis were a suite of water column physico-chemical parameters: temperature (Temp), pH, specific conductivity (SPC), oxidation-reduction potential (ORP), dissolved organic carbon concentration (DOC), per cent dissolved oxygen (DO%), SPM concentration (for SPM associated metals only), solid fraction concentrations (i.e. g carbonate /g solid, g amorphous oxyhydroxide / g solid, etc.), and dissolved metal concentrations. These parameters were chosen due to the influences that they are known, or expected, to have on formation and dissolution of important solid fractions, metal speciation, sorption and precipitation reactions and biotic activity (Strobel, 2005; Turner and Millward, 2002; Warren and Haack, 2001, Sauvé et al., 2000; Benoit and Rozan, 1995; Warren and Zimmerman, 1994; Rodda et al., 1993). The variable(s) that best predicted the metal concentration were reported if the following criteria were met: one single variable had $r^2>0.5$, $p<0.05$ or two variables had $r^2>0.8$, $p<0.05$.

3.4.1 "Harbour-wide" Metal Behavior

Analyses using pooled data indicated that the best predictor of Cr, Cu, As, Ni and Zn in the crystalline oxyhydroxide fraction, Cu and As in the organic matter fraction and As in the carbonate fraction was the concentration of that fraction (Table 3.4.1). All relationships were positive with the exception of the relationship of As with carbonate concentration. Positive relationships indicate that, an increase in the concentration of a particular fraction is associated with an increase in the concentration of metal associated with that fraction. Similar relationships between fraction concentrations and associated metal concentrations have been reported and attributed to availability of sorption sites (Singh et al., 2005; Haack and Warren, 2003).

MLRA using physico-chemical parameters and C_F values did not produce any significant relationships. The concentration of each fraction for pooled "Harbour-wide" data were also analyzed in the MLRA with the suite of physico-chemical variables to determine if there was a physico-chemical parameter that predicted the concentration of the fraction and, again, no significant relationships were identified. These results indicate that no single factor, or combination of factors, controls metal partitioning in a system-wide manner in Hamilton Harbour. Thus, site and compartment-based trends in metal behavior were investigated as discussed subsequently.

Table 3.4.1: Relationships between geochemical and physico-chemical parameters and the amalgamated metal concentration data from each fraction. Significant relationships were found between metal concentration and the concentration of the solid fraction that they are associated with, however there are no physico-chemical parameters that emerge as significant to explain these relationships.

	Exchangeable	**Carbonate**	**Amorphous Oxyhydroxide**	**Crystalline Oxyhydroxide**	**Organic Matter**
Cr				*	
Mn			**NA**	**NA**	
Co					
Cu				*	*
Sn					
Ag					
As		*(negative)		*	*
Ni				*	
Zn				*	
Cd					
Se					
Fe			**NA**	**NA**	

*Note: * indicates that there was a significant positive relationship between metal bound to a solid fraction and the concentration of that fraction, except As in the carbonate fraction where the As concentration in carbonate is inversely correlated with the concentration of carbonate – indicated as "negative".*

3.4.2 Fraction, Compartment and Metal Dependent Behavior

Some MLRA relationships that are compartment, site and metal dependent emerged (Tables 3.4.2 (a-d)). For both compartments at both sites, there are relationships between metal concentration in the carbonate, amorphous oxyhydroxide and crystalline oxyhydroxide fractions and the concentration of that fraction. These relationships are particularly common in, but not exclusive to, the amorphous and crystalline oxyhydroxides and occur with all metals except Se, in at least one compartment at one site in one fraction (discussed in chapter 3.2 section 3.2.4). Thus, an increase in the sediment concentration of the fraction will produce a proportional increase in the concentration of sorbed metal. Therefore, C_Fs were used to determine influences of the important environmental parameters chosen in this study on metal associations with fractions. These MLRAs produced a number of significant correlations (discussed subsequently), however it is important to note that, in many cases, the physico-chemical parameter that controls the sorptive capability of that fraction (i.e. produced from the MLRA with metal, C_F or K_D and chosen environmental parameters) for a particular metal, was either different than the physico-chemical parameter(s) that influence the concentration of the solid compartment fraction itself (i.e. temperature was significantly negatively correlated with the carbonate fraction in shallow site SPM, crystalline oxyhydroxide fraction in the deep site bed sediment and organic matter in the deep site bed sediment and positively correlated with organic matter in shallow site SPM while SPC was positively correlated with amorphous oxyhydroxide in deep bed sediment and crystalline oxyhydroxide in shallow SPM; see Table 3.4.3), in most fractions and compartments, or no significant relationship was observed between the C_F and the parameters used in this study. That is to say, the parameter that controls the concentration of the fraction does not necessarily control metal concentrations in that fraction simply by influencing the formation and/or dissolution of the fraction. These results suggest that a two-tiered process is involved in many of the metal sediment relationships observed: a physico-chemical influence on the fraction concentration and another, often different, physico-chemical factor that controls the metal sorption to that fraction. For example, temperature is a common predictor of metal behaviour, defined by the C_F, in the amorphous and crystalline oxyhydroxides in bed sediments at the shallow site for the metals Cr, Co, Cu, Ag and Ni (discussed subsequently). However, there is no significant relationship between temperature and the concentration of the amorphous oxyhydroxides. With this in mind, the predominant trends in MLRAs will be discussed.

3.4.2.1 Temperature

The parameter that was identified most often in the MLRA for bed sediment compartments was temperature, and temperature was the most common predictor of metal trends in amorphous and crystalline oxyhydroxides and organic matter at both sites in bed sediment. Temperature affects many factors that affect metal behavior such as reaction kinetics as well as microbial activity and thus, redox conditions and oxygen concentrations. Further, temperature increases through the summer season and can coincide with seasonally-related climatic patterns, such as an increase in daylight and ultraviolet light and precipitation events. To attempt to identify possible mechanisms underlying the observed temperature – solid metal concentration relationships, results were further evaluated on a compartment, fraction and metal basis.

3.4.2.1.1 Bed Sediment Amorphous and Crystalline Oxyhydroxides

There are significant relationships between temperature and the C_Fs of Co and Ag at both sites, Cd at the shallow site and Ni and Zn at the deep site in the amorphous oxyhydroxide fraction as well as Co, Cu and Ni at both sites, and Cr and As at the deep site in the crystalline oxyhydroxide fraction (Figure 3.4.2 (a) and (b)). The C_F was used to determine all of these relationships and shows that, for most metals, there is an increase in affinity for these metals in both of the oxyhydroxide fractions with an increase in temperature, with the exception of Co in both oxyhydroxides at the shallow site and in the amorphous oxyhydroxide at the deep site as well as Cu in crystalline oxyhydroxides at the shallow site. An increase in metal affinity for oxyhydroxides with temperature is congruent with the finding that reactivity of oxyhydroxides increases with temperature (Johnson, 1990; Angove et al., 1999; Rodda et al., 1996 and Rodda et al., 1993; Warren and Zimmerman, 1993; Gammons et al., 2005). In addition, increases in pH caused by biological activity, which is also positively correlated with temperature, may cause an increased reactivity in oxyhydroxide fractions (Staunton, 2004; Warren and Haack, 2001; Stumm, 1992). To explain the observed results, different scenarios must be proposed that are site specific: 1) at the shallow site photosynthetic layers on the sediment surface my cause microscale changes in pH, increasing pH with an increase in photosynthetic activity as temperatures increase and surface biofilm formation is established (Wetzel, 1983) 2) at the deep site where light does not penetrate to the bed sediment surface, microscale increases in pH may be caused by the reduction of sulfate, producing sulfides and consuming protons, in lower sediment layers by the equation:

$$SO_4^{2-} + 10H^+ \leftrightarrow H_2S + 4H_20$$

thus, increasing the reactivity of the oxyhydroxides at the surface. These two scenarios reflect different biological processes which can lead to increased pH and associated increased metal sorption.

At the deep site, an observed decrease in bed sediment crystalline oxyhydroxide with an increase in temperature occurred (Table 3.4.3). This result may reflect increased reductive dissolution of this phase, occurring concomitant with the increase in reactivity of the crystalline oxyhydroxides in this suite of metals discussed above. This scenario is further corroborated by the significant relationship between water temperature increases with decreasing oxidation-reduction potential (r^2= -0.659, p=0.02) indicating more reducing conditions with warmer waters that may cause the dissolution of the oxyhydroxide fraction.

In contrast to the suite of metals showing an increase, Co in both oxyhydroxides at the shallow site and in the amorphous oxyhydroxide at the deep site as well as Cu in crystalline oxyhydroxides at the shallow site are negatively correlated with temperature.

The negative correlation Co in the amorphous oxyhydroxide at both sites and in crystalline oxyhydroxide at the shallow site with temperature is an example of element specific behaviour. In the literature, it has been reported that Co behavior in the oxyhydroxide fraction is often associated with the behavior of Mn oxyhydroxides rather than Fe oxyhydroxides (Hamilton-Taylor et al., 2005; Taillefert et al., 2002; Kay et al., 2001; Leinemann et al., 1997). The observed results in Co behaviour may be explained by these literature observations. It should be noted that in this study Fe and Mn concentrations are, themselves, highly correlated within both the amorphous and crystalline oxyhydroxide fractions and thus, it is was not possible to distinguish between their relative roles in metal sorption in this fraction. However, the Mn concentration in the amorphous oxyhydroxide fraction at both sites in the bed sediment compartment is negatively correlated with temperature, although, the relationship at the shallow site was not significant at the $p<0.05$ level ($r^2=-0.49$, $p<0.11$ at shallow site; $r^2=-0.87$, $p<0.001$) These results suggest that increasing water temperatures increase microbial decomposition rates and reductive dissolution of Mn oxyhydroxides would occur before Fe oxyhydroxides due to their higher redox potential (Fe_3O_4, $pe^0 = 16.6$ and MnO_2, $pe^0 = 20.8$). The reductive dissolution of Mn oxyhydroxides would thus, specifically liberate any Co associated with them. The results are consistent with this proposed scenario however, it is not possible, based on the study dataset, to definitively conclude this process is occurring.

3.4.2.1.2 Organic Matter

Manganese concentrations in the organic matter fraction in shallow site bed sediment are positively correlated with temperature. This observed result may reflect a two step process: 1) increasing reductive dissolution of Mn oxyhydroxides by microbial activity with increasing temperature ($r^2=0.89$, $p<0.05$), leads to 2) increased Mn^{2+} in solution which then sorbs to the organic matter.

Conversely, Mn associated with organic matter in deep site bed sediment show a negative correlation with temperature which may reflect increasing decomposition with temperature at this site. Mn is not significantly correlated with the concentration of organic matter, however, there is a positive relationship between these two variables ($r^2=0.55$, $p=0.06$) that may influence the concentration of Mn in this fraction; furthermore, the organic matter is negatively correlated with temperature also indicative of decomposition processes.

3.4.2.2 Specific Conductivity (SPC)

There is a trend of increasing concentrations of Cr, Co, As, Ni, Zn and Cd in the carbonate fraction of bed sediments at the deep site with increasing SPC values in the overlying water column (sediment water interface). There is no evident mechanism by which increasing SPC (which indicates greater ionic strength of a solution) should lead to increased metal uptake specifically in carbonates. Further, metal concentrations associated with carbonate fractions were independent of carbonate mass within the sediment pool. However, it may be that increasing ionic strength shifts metals from the exchangeable to the next most labile fraction, the carbonates. This occurs because ionic strength affects the exchangeable fraction by decreasing the size of the charge differential zone that surrounds the particle thereby, decreasing the concentration of metals ions in the exchangeable fraction (Lützenkirchen, 1997; Puls et al., 1991). The desorbed exchangeable metals could then become incorporated into the carbonate fraction. Thus, a decrease in exchangeable metals with an increase in carbonate associated metals would be expected. However, this relationship is not seen. Furthermore, regression analysis of Cr, Mn, Co, As and Ni show significant positive correlations between metal in the carbonate fraction and metal in the exchangeable (Mn r^2=0.98, Co r^2=0.91, As r^2=0.59, Ni r^2=0.66, $p<0.05$, Cr was not significant) and amorphous fractions (Cr r^2=0.88, Mn r^2=0.86, Co r^2=0.91, As r^2=0.80, Ni r^2=0.61, $p<0.05$), contrary to the expected trend. Given this relationship, it may be possible that an increase in ionic strength could cause an increase in ion competition with other fractions, possibly leading to a "spilling over" of metals from this fraction to the other fractions, in this case the carbonate fraction, with an increase in SPC however, this relationship is not seen in the dataset.

3.4.2.3 SPM Concentration

There is a negative correlation between SPM concentration and the concentration of Cr, Ag, Zn and Cd sorbed to the amorphous oxyhydroxides in the shallow site SPM. It is possible that high SPM events are linked to a change in SPM quality i.e. grain size or composition. Higher SPM concentrations are observed at the shallow site (10mg/L – 35mg/L, See Section 3.1.1), compared to the deep site and likely reflect inputs associated with material from Grindstone Creek and the surrounding watershed. If there are amorphous oxyhydroxide inputs associated with this source, these new inputs of amorphous oxyhydroxide may be causing a dilution effect, where this new source of amorphous oxyhydroxide during the higher SPM events is competing for metals, thus, diluting the metals associated with this fraction. There may also be less reactive amorphous oxyhydroxides possibly due to occlusion of sites on the amorphous oxyhydroxides by other minerals or organic matter, or a decrease in the surface area exposed to the dissolved compartment by the input of larger amorphous oxyhydroxide particles during high SPM concentration events affecting the ability of these minerals to incorporate metals. This study did not include an investigation into SPM characteristics from this location i.e. grain size or structure of particles, so these hypotheses cannot be confirmed.

3.4.2.4 Other Significant Relationships

A number of significant relationships emerged between some metal concentrations in some fractions and variables that are difficult to mechanistically explain. These include: 1) pH is negatively correlated with the concentration of Mn, Ni and Zn sorbed to the carbonate fraction in deep site bed SPM 2) exchangeable Cr, Mn and Co in the deep site bed sediment are negatively correlated with temperature. 3) Cu and Cd in organic matter in shallow site bed sediment are negatively correlated with temperature.

Most of the relationships identified in this analysis do not extend outside of the compartment and are not consistent for all metals. There is some evidence of a shift in physico-chemical processes between compartments at the same site i.e. variables that appear to control some metals in the bed sediment do not appear as important variables in the SPM compartments.

In Hamilton Harbour there are no trends that can be applied across the whole system that will accurately describe metal behaviour. Instead, we see a spectrum of behaviour that appears to encompass specific geochemical niches within the Harbour. Hamilton Harbour is a complex system which displays a dynamic interplay of metal behavior and physico-chemical processes over a short time and spatial scale. These shifts in behavior reflect the turbulent and dynamic nature of the system caused by anthropogenic influences and unique hydrodynamic processes that occur in Hamilton Harbour.

Table 3.4.2(a): Results of Regression analysis of metal parameters vs. physico-chemical parameters for the shallow site bed sediment. The Dependent variable used was based on the analysis of metal sorbed to a fraction. If this regression analysis showed a strong positive relationship between the metal in a fraction and the concentration of that fraction in the sediment (r^2>0.50, p<0.05) then the C_F was used (denoted by *) as the dependent variable and if the metal analysis was strongly correlated with fraction concentration and dissolved concentration (r^2>0.5, p<0.05) or the C_F analysis was strongly correlated with dissolved (r^2>0.5, p<0.05) then the K_D value was used as the dependent variable (denoted by **). Fe and Mn concentrations are used in the calculation of the mass of the amorphous and crystalline oxyhydroxide fractions; therefore, the analysis of these metals in these fractions is not applicable (NA).

	Exchangeable	Carbonate	Amorphous Oxyhydroxide	Crystalline Oxyhydroxide	Organic Matter
Cr	**SPC r^2= -0.050,p=0.01		*	*	
Mn	pH r^2= -0.049,p=0.02		NA	NA	Temp r^2= +0.510,p=0.01
Co		Temp r^2= -0.492,p=0.02	*Temp r^2=-0.695, p=0.001	* Temp r^2=-0.547, p=0.01	
Cu			*	*Temp r^2=-0.706, p=0.01	Temp r^2= -0.758, p<0.001
Sn					
Ag			*Temp r^2=+0.751,p<0.001		
As			*	*	
Ni			*	* Temp r^2=+0.645, p=0.003	
Zn				*	
Cd	Temp r^2= -0.571,p=0.01		Temp r^2=+0.510, p=0.01		
Se		SPC r^2= -0.535,p=0.01			
Fe	SPC r^2=+0.494,p=0.02		NA	NA	

Table 3.4.2(b): Results of Regression analysis of metal parameters vs. physico-chemical parameters for the deep site bed sediment. Please see Table 3.4.2 (a) for explanation.

	Exchangeable	Carbonate	Amorphous Oxyhydroxide	Crystalline Oxyhydroxide	Organic Matter
Cr	**Temp** r^2= -0.689, <0.001	*** SPC** r^2= +0.549, p=0.01	*	**** Temp** r^2=+0.689, p<0.001	
Mn	**Temp** r^2= -0.901, <0.001	**Temp** r^2= -0.870, <0.001	**NA**	**NA**	**Temp** r^2= -0.651, p=0.002
Co	**Temp** r^2= -0.848, <0.001	**SPC** r^2= +0.785, <0.001	*** Temp** r^2= -0.710, p<0.001	*** Temp** r^2=+0.771, p<0.001	
Cu			*	*** Temp** r^2=+0.825, p<0.001	
Sn	**pH** r^2= +0.704, <0.001		*		
Ag			*** Temp** r^2= +0.751, p<0.001		
As		*** SPC** r^2=+0.510, p=0.01	*	*** Temp** r^2=+0.573, p=0.004	
Ni	**SPC** r^2=+0.649, =0.002	**SPC** r^2=+0.524, p=0.01	*** Temp** r^2= +0.729, p<0.001	*** Temp** r^2=+0.793, p<0.001	
Zn		**SPC** r^2=+0.878, <0.001	*** Temp** r^2= +0.792, p<0.001		
Cd		**SPC** r^2=+0.580, =0.004			
Se					
Fe		*	**NA**	**NA**	

Table 3.4.2(c): Results of Regression analysis of metal parameters vs. physico-chemical parameters for the shallow site SPM. Please see Table 3.4.2 (a) for explanation.

	Exchangeable	**Carbonate**	**Amorphous Oxyhydroxide**	**Crystalline Oxyhydroxide**	**Organic Matter**
Cr			**SPM Conc.** r^2= -0.493, p=0.02	*	
Mn	**pH & DOC** r^2=-+0.895, p=0.001 & <0.001	*	**NA**	**NA**	
Co	**DOC** r^2=+0.546, p=0.02				
Cu					**SPM Conc.** r^2= -0.628, p=0.006
Sn					
Ag	**Temp & DOC** r^2=++0.751, p=0.009&0.006	*	**SPM Conc.** r^2= -0.700, p=0.003		
As				*	
Ni				*	
Zn			**SPM Conc.** r^2= -0.554, p=0.014		
Cd	**SPM Conc.** r^2=+0.684, p=0.003		**SPM Conc.** r^2= -0.678, p=0.003		
Se			**Temp & DOC** r^2=0.827, p<0.001 & 0.008		
Fe			**NA**	**NA**	

Table 3.4.2(d): Results of Regression analysis of metal parameters vs. physico-chemical parameters for the deep site SPM. Please see Table 3.4.2 (a) for explanation.

	Exchangeable	**Carbonate**	**Amorphous Oxyhydroxide**	**Crystalline Oxyhydroxide**	**Organic Matter**
Cr		*		*	
Mn	**DO%** r^2= -0.508, p=0.01	**pH** r^2= -0.523, p=0.01	**NA**	**NA**	
Co		**Temp** r^2= -0.773, p=0.01		***DO%** r^2=0.50, p=0.02	
Cu				*	
Sn	**DOC** r^2= -0.552, p=0.01			*	**DOC** r^2=+0.784, p<0.001
Ag				*	**pH** r^2=+0.738, p<0.001
As				*	
Ni	**pH** r^2= -0.610, p=0.005	**pH** r^2= -0.690, p=0.002	*	*	
Zn		***pH** r^2= -0.623, p=0.004			
Cd					
Se					
Fe		**SPM Conc.** r^2=+0.503, p=0.02	**NA**	**NA**	

Table 3.4.3: Relationships between physico-chemical parameter(s) and fraction concentrations in each compartment, at each site.

	Shallow Bed	**Deep Bed**	**Shallow SPM**	**Deep SPM**
Carbonate			**Temp** r^2= -0.551, p=0.01	
Amorphous Oxyhydroxide		**SPC** r^2= +0.516, p=0.01		
Crystalline Oxyhydroxide		**Temp** r^2= -0.842, $p<0.001$	**SPC** r^2= +0.500, p=0.004	
Organic Matter		**Temp** r^2= -0.642, p=0.002	**Temp** r^2= +0.852, $p<0.001$	

Chapter 4: Conclusions

The results of this thesis demonstrate that metal concentrations in Hamilton Harbour are high, often exceeding guidelines in bed sediment, SPM and dissolved compartments. Metal concentrations in all compartments are also temporally dynamic, particularly in the dissolved compartment where 8 of 12 metals showed a 2.5-fold to 15-fold difference in concentration. Dissolved Zn and Cd concentrations ranged from below detection limits to above the Ontario Provincial Water Quality Guidelines, having implications for management decisions, particularly those that are based on a small number of samples.

The most important sedimentary fractions for metal incorporation in bed sediment and SPM were the oxyhydroxides. The amorphous and crystalline oxyhydroxides accounted for 58% – 90% of total metal concentrations for 10 of the 12 metals. However, the oxyhydroxides themselves accounted for a maximum of 23% of the total sediment mass.

The amorphous and crystalline oxyhydroxide concentration was often found to be linked to the concentration of a number of metals associated with these fractions. This result indicates that the formation and dissolution of the oxyhydroxide fractions will have an impact on metal uptake in this system. Further, the formation of amorphous oxyhydroxides is largely a microbially mediated process and, therefore, microbial processes are likely to be important in metal dynamics in Hamilton Harbour.

Partitioning between sedimentary compartments and the dissolved compartment reflect fluctuating metal concentrations resulting in non-equilibrium partitioning conditions, and consequently extremely variable partitioning. Further, element specific patterns in partitioning over time indicate that classic geochemical controls such as pH, temperature, conductivity, ORP, DOC, per cent dissolved oxygen, SPM concentration (for SPM associated metals only) solid fraction concentrations are not sufficient to explain the observed behaviour. This result indicates that other factors such as hydrodynamic variability (which results in movement and resuspension of sediment as a result of shipping traffic, channelized flow and water currents) as well as point and non-point source discharges are likely important in Hamilton Harbour and must be considered in future research.

In Hamilton Harbour and other highly anthropogenically affected systems, predicting the behaviour of metal contaminants is of key importance to management and remediation efforts. The results of this thesis indicate that in this system in addition to classical physico-chemical factors, an assessment of microbial processes, hydrodynamic impact and point and non-point source contributions are required to develop accurate models of metal dynamics in sedimentry and dissolved compartments.

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