ASHLAND

Assessment of Total and Dissolved Metal Concentrations in Groundwater-Surface Water Systems

Former Ciba-Geigy Site
Glens Falls, NY

Prepared for:
Ashland Inc.

Prepared by:
EHS Support
consider it done

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ACRONYMS

µm	micrometer
Ashland	Ashland Inc.
Cr^{6+}	chromate ion
EHS Support	EHS Support LLC
ft amsl	feet above mean sea level
GE	General Electric
GW/SW	groundwater/surface water
GWES	groundwater extraction system
M^{z+}	metal ions
NYSDEC	New York State Department of Environment and Conservation
PCBs	polychlorinated biphenyls .
RL	Reporting Limit
SSS	side sonar scan
TOC	total organic carbon
USEPA	United States Environmental Protection Agency
USGS	U.S. Geological Survey

1.0 INTRODUCTION

A review of the fate and transport of metals has been undertaken for historical direct discharges (via outfalls) and potential groundwater discharges from the former Hercules/Ciba-Geigy manufacturing plant near Glens Falls, NY (the Site) to the Hudson River (the River). This review was completed by EHS Support LLC (EHS Support) on behalf of Ashland Inc. (Ashland) and BASF (which respectively acquired Hercules and Ciba-Geigy, the Site permittees). This report was prepared to support assessment of data gaps noted in comments from the New York State Department of Environmental Conservation (NYSDEC) issued November 4, 2014 regarding the Supplemental RFI Report for Off-site Sediments (dated September 2014).

Based on a comprehensive assessment of Site historical operations and soil and groundwater conditions, the dominant mechanisms of metals discharge to the Hudson River from the Site was associated with direct discharges to the river during historical operations (EHS Support, 2015a). However, to ensure this assessment is complete, a discussion of groundwater-surface water interactions that can occur between Site groundwater and the river is also provided.

The Site is located just upstream of the section of the Upper Hudson River designated as the PCB Superfund Site. Extensive sediment studies and sediments removal actions have been competed by General Electric (GE) in response to historic PCB releases to the River. Historical data collected by GE provides an extensive data set of sediment quality and physical characteristics. The river sediment data includes side scan sonar (SSS), sediment coring and physical and chemical analysis of sediment samples. The SSS data extends along the entire length between mile marker 160 to 194.5 and provides a reliable data set that describes sediment physical characteristics, which has been validated by USEPA. In addition, select sediment samples were analyzed by GE for metals. (EHS Support 2015d). This data has been utilized to assess the fate and transport and likely distribution of metals in sediment.

The evaluation presented herein utilizes information from other assessments previously completed by EHS Support including an assessment of the hydrogeochemistry of metals in Site groundwater (EHS Support, 2014 and 2015a); and a review of available hydrology and geomorphology data for the river (EHS Support, 2015d).

1.1 Objectives

The objective of this document is to provide an overview of the fate and transport of chemicals in groundwater, the groundwater/surface water (GW/SW) interface, and in fluvial surface water of the Hudson River. For this assessment the theoretical mechanisms of fate and transport processes of both metals (i.e., barium, cadmium, chromium (trivalent and hexavalent), copper, lead, mercury and vanadium) are evaluated and comparison made to the known behavior of polychlorinated biphenyls (PCBs) in sediment.

In addition to the fate and transport assessment, this document discusses three important topics of interest in consideration of the fate and transport of metals in groundwater and surface water:

1. The aggregation and agglomeration of metal-containing colloids and their filtering (or entrapment) in materials within groundwater fracture zones and sediment within the banks and base of the fluvial system;
2. The key attenuation mechanisms that occur in the GW/SW interface and within the hyporheic zone; and
3. The attenuation and fate and transport processes for metals within the fluvial system.

1.2 Groundwater Discharge to the Hudson River – Groundwater-Surface Water Interactions

As described in the *Site Conceptualization and Groundwater Corrective Measures Effectiveness Evaluation Report* (EHS Support, 2015a), historically groundwater from the Site discharged directly into the Hudson River from the overburden and bedrock (shallow and intermediate zone) geology or via overburden groundwater seeps to the Hudson River. A groundwater extraction system has been in operation onsite since 2003, which captures groundwater from both the overburden and bedrock systems.

The GW/SW interface (or the hyporheic zone) refers to the exchange of water between a surface water feature (e.g. a river) and sub-surface water (groundwater). This interface is often characterized by temperature and chemical gradients that influence the behavior of chemicals and biota at and within the interface. The rate and magnitude of reactions taking place within the interface vary greatly and are controlled by surface water-groundwater head distributions, riverbed structure and composition, and ambient chemical and biological conditions (Hancock, 2002). The extent and magnitude of the interface varies spatially due to differences in river bed geology, i.e. it is expected to increase in size within finer grained sediments and decrease where bedrock is in direct contact with the surface water in the river.

Figure 1 provides a simple visual aid to assist in understanding the conceptualization of the historical groundwater-surface water interaction processes at the Site. The conceptualization as it would pertain to the Site is viewed as historical due to several factors. These include:

- The extensive remedial measures conducted across the site and within the river as part of the corrective measures program.
- The groundwater extraction system (GWES) continues to influence local groundwater hydraulic gradients within the overburden and bedrock, with the removal of groundwater and associated dissolved metal contaminants.

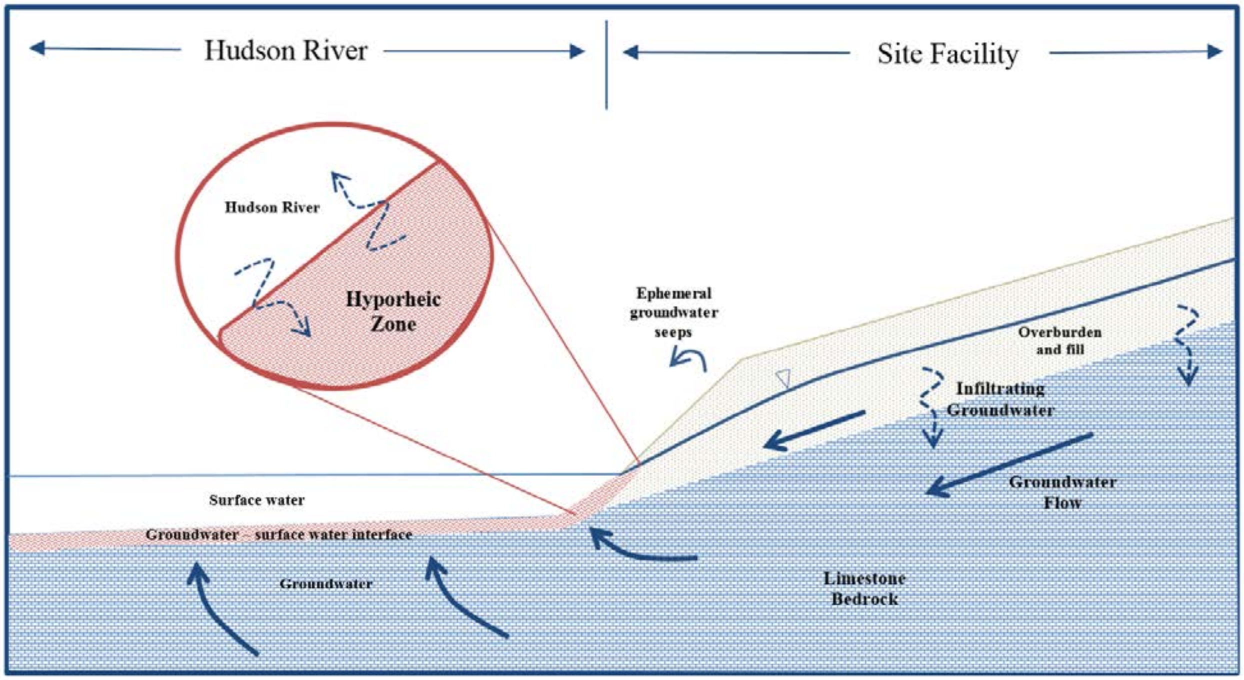


Figure 1 – Conceptual Model of Groundwater – Surface Water interaction

The U.S. Geological Survey (USGS) advocates a clear understanding of the linkages between groundwater and surface water and the contributions of groundwater mass flux that could potentially affect aquatic environments (USGS, 1998).

The following discussion aims to provide an overview of the expected processes in groundwater and surface water that attenuate or enhance the mobility of selected inorganic metal species (e.g., barium, cadmium, chromium (including anionic chromate ion, CrO_4^{2-}), copper, lead, and mercury), and organics (e.g., PCBs).

Historical processes that occurred onsite produced inorganic pigments in the form of insoluble precipitated metals (individual and combinations of metals). The main characteristic of the majority of the inorganic pigments was their stability, thus it can be reasonably assumed that the transport of metals within groundwater is likely to be in forms they were produced (e.g., chrome yellow is a combination of lead chromate co-precipitated with lead sulfate, and cadmium yellow is mainly a cadmium sulfide). All of these metal salt compounds have a low solubility in water, and would be carried as suspended particle if transported in water. Depending on the ambient groundwater or surface water chemistry (temperature, pH, redox) and the affinity and concentration of available ligands (e.g., carbonate, phosphate and sulfates), the form or phase of metal may change from the phase in which it was initially released. Although the metal salts are initially stable, the bonding forces that hold them together (ionic) are weak electrostatic forces of attraction and over time these bonds can be broken. This produces a free metal ion, which is able to form bonds with other ligands or can be attracted to colloids or mineral surfaces. Other processes (physical and geochemical), discussed in the following sections, further influence the mobility of metals.

1.2.1 Overburden discharge

Groundwater flow from the overburden is anticipated to discharge to the Hudson River. Discharge will be confined mainly to below the river stage; however, by-pass flow within the overburden may result in localized riverbank seeps above the river surface level. By-pass flow refers to ephemeral saturated flow within the vadose zone, which can occur during high intensity rainfall events. The seeps are likely to be representative of higher permeability conduits within the overburden that facilitate the transport of groundwater. Historically, these were associated with pipes/utility conduits that intersected the riverbank, and groundwater lateral flow above lower permeability materials (e.g., clay layers) resulting in seeps at the riverbank above the river stage. It is not known whether changes in river stage throughout the year have an influence on groundwater levels within the overburden though riverbank seeps have been reported historically. Assessment of historical sources of seeps is complicated by the historical presence of underground piping and facilities (e.g., sumps, unlined stormwater culverts, etc.) that may have contributed to seeps. Historical analysis of seep water samples from select locations along the riverbank reported concentrations of metals above groundwater and surface water screening criteria (EHS Support, 2015a). Due to the corrective measures implemented at the site (e.g., capping and groundwater extraction), current concentrations of metals within overburden groundwater are presumed to not be indicative of the majority of overburden flux that may have historically discharged to the Hudson River below the river surface level. The engineered caps (which changed infiltration rates) and groundwater extraction system were installed in 2003, and the groundwater extraction system has been in operation since that time with the aim of mitigating metal contaminant flux to the river. Extracted groundwater is reported (April 2014 sampling event analytical results) to have detectable levels of metals, which is reducing the overall flux of metals within overburden and bedrock groundwater.

Infiltration of overburden groundwater vertically into the limestone bedrock is expected to be low based on geochemical comparisons between overburden groundwater and underlying bedrock groundwater (EHS Support, 2014). The upper surface of the bedrock may have had some degree of fracture clogging by finer particle fractions of the overburden and fill material. This assumption is also supported by the need for periodic redevelopment of extraction wells within the groundwater extraction system. The bedrock fracture clogging infers that suspended material is transported into bedrock and, as flow pathways become significantly narrower, suspended material is filtered out. This physical mechanism and its implications are discussed in more detail within **Section 1.2.3**.

1.2.2 Bedrock discharge

The riverbed of the Hudson River is limestone bedrock and is probably representative of the shallow bedrock beneath the Site. Site bedrock extraction well discharge evaluations (Antea, 2014) revealed the shallow and intermediate bedrock horizons onsite show hydraulic connection with the river. Physical and geochemical (and some biologically influenced) processes within the bedrock groundwater zone are similar to the processes described in the **Section 1.2**.

As surface water flows over a river bed, the amount of groundwater-surface water interface exchange varies depending on river discharge. Volumetric river discharge and the height (stage) of the river do vary significantly due to the influence of precipitation and snow melt in upstream areas. As river stage and surface water flow discharge increase, groundwater discharge into the river is impeded and eventually it is limited to a very small zone at the interface of the river bed. Under high stage and flow conditions, surface water can penetrate into the river bed sediments (or bedrock) (Cardenas and Wilson, 2007). On the basis of these processes (and demonstrated through tracer tests) groundwater can spend a longer duration in the GW/SW interface than in the open channel (Jones and Holmes, 1996).

Groundwater gauging data from 2013 for wells adjacent to the river indicate that potential discharge of groundwater to the river from shallow and intermediate bedrock (based on head differences only) decreases between December and March and remains relatively constant between March and June (refer to **Table 1**). Between June and December groundwater levels increase first in shallow bedrock and then in intermediate bedrock. The average river level measured adjacent to the Site (SG-9) is 210 feet above mean sea level (ft amsl); for bedrock groundwater to discharge to the river, groundwater levels on Site would need to exceed the river level elevation (refer to **Table 1**). Ultimately the ability of groundwater to discharge to the river is controlled by the GWES, hydraulic gradient between the river and the groundwater and the structure and fabric of the rock. Further discussion of local groundwater hydraulic behaviour and the influence of the GWES on the local groundwater flow regime is presented within EHS Support 2015a. The presence of a surface water signature in pumping wells indicates there is hydraulic communication between the shallow bedrock and the river (EHS Support 2015a).

Table 1 – Gauged groundwater levels 2013 (ft amsl)

Well ID	Horizon	March 2013	June 2013	Sept 2013	Dec 2013
MW-26	Overburden	231.85	233.29	231.48	231.45
MW-25S	Shallow	204.82	203.50	212.95	213.97
MW-25D	Intermediate	205.82	204.70	203.77	211.74
AW-C2	Deep	189.04	191.86	191.20	191.43

These observations, in conjunction with literature data, suggest that groundwater discharge to the river adjacent to the Site (and in the absence of groundwater extraction influence) are variable throughout the year.

1.2.3 *Physical Attenuation Mechanisms*

The physical properties of an aquifer that can potentially control the migration of colloids and complexes in groundwater primarily include the variation in pore throat size in intergranular aquifers and fracture size and connectivity in dual porosity aquifers.

Variations in pore throat size can act as a filtering mechanism if the pore throat diameter is less than the diameter of a colloidal species. A colloid is described as an aquatic suspended particle of a specific size range. Colloids range in size from 1 micrometer (um) to 10^{-3} um while pore throat sizes vary between rock types and within the same rock type by several orders of magnitude (10^{1} to 10^{-3} um). As illustrated in **Figure 2**, pore throats are expected to increase in size from clays and shales through to sandstones.

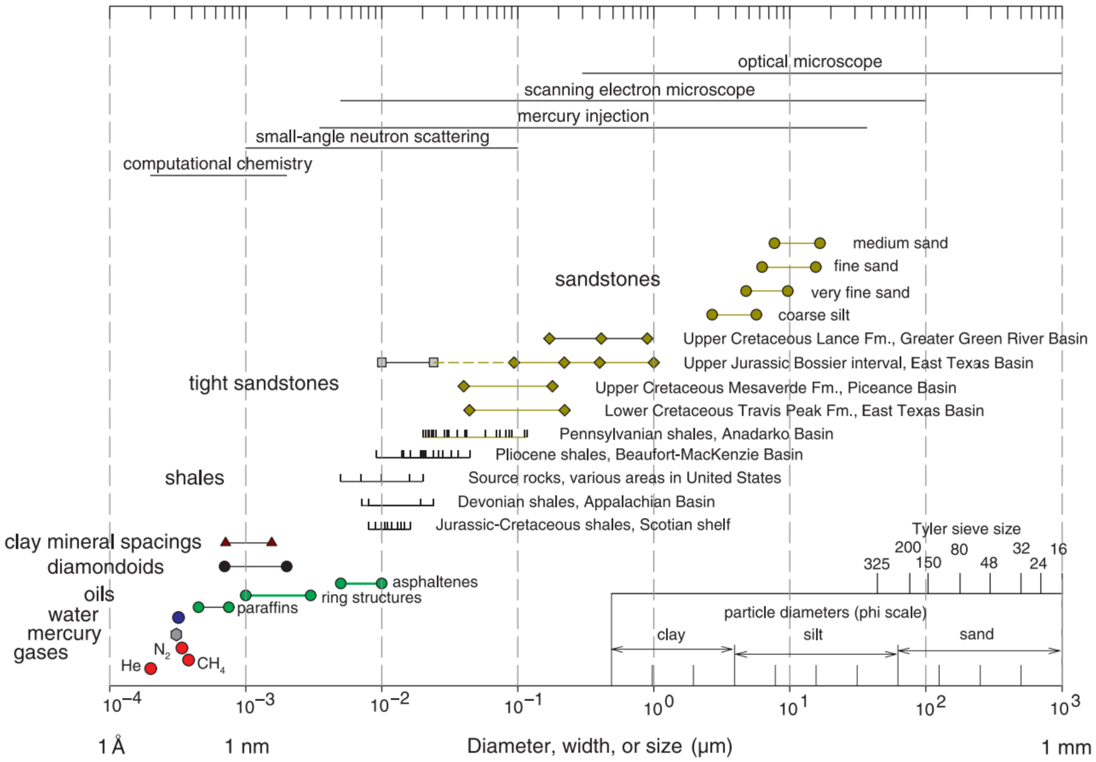


Figure 2 – Sizes of molecules and pore throats in siliciclastic rocks on a logarithmic scale covering seven orders of magnitude. The symbols show pore-throat sizes for sandstones and shale lithologies and clay mineral spacings (Nelson, 1990)

The metal salts, as mentioned earlier, generally have a low solubility when initially released into groundwater. This is ultimately controlled by the pH and redox conditions and the ligand (associated anion with the metal), for example carbonate, sulfate or hydroxide. Over time the bonds between the metal and ligand can be broken and metals can become associated with colloidal particles also present in groundwater. The accumulation, aggregation and agglomeration of colloids in groundwater results in a physical change in size and density of the colloid, and likely are the result of electrostatic attraction between the colloid masses. The aggregation of colloids is primarily a kinetic phenomenon and colloid stability is characterised by the rate of aggregation or the frequency at which colloids collide and attach to each other (Stumm and Morgan, 1996). This aggregation process therefore increases with time. A portion of these colloids will be either filtered by fines within infilled fractures or sediments that are present on the banks and base of the fluvial system or filtered by overburden deposits that naturally overly the bedrock. In addition, there is potential for electrostatic attraction between the colloids and minerals within the rock or existing infilled materials within the fracture zone.

At the Site, the processes of filtering and electrostatic attraction are likely to be significant in the attenuation of metals especially given the geochemical properties of the aquifer, which are conducive to the precipitation of metals and/or their incorporation into calcite deposits. However, as noted within the geochemical modelling (EHS Support 2014), the operation of the groundwater extraction system and the resulting influx of surface water may be causing dissolution of calcite and enhancing secondary porosity. Where fractures are of relatively wider aperture and free of material/filling, the migration of metal constituents in colloids may only be retarded by sediments present within the stream base and banks.

1.2.4 Geochemical Attenuation Mechanisms

The geochemical processes within the GW/SW interface can influence the precipitation of minerals and sorption of metals. These processes can be enhanced by the exchange of surface water and groundwater within the interface which promotes precipitation by influx of oxidizing surface water. The density of reactive sites per volume of GW/SW interface water is increased via contact of dissolved metals with potential reaction or sorption sites of precipitating mineral phases, e.g. manganese oxide (Fuller and Harvey, 2000). **Figure 3** presents the range of processes that affect metal behaviour in aqueous environments.

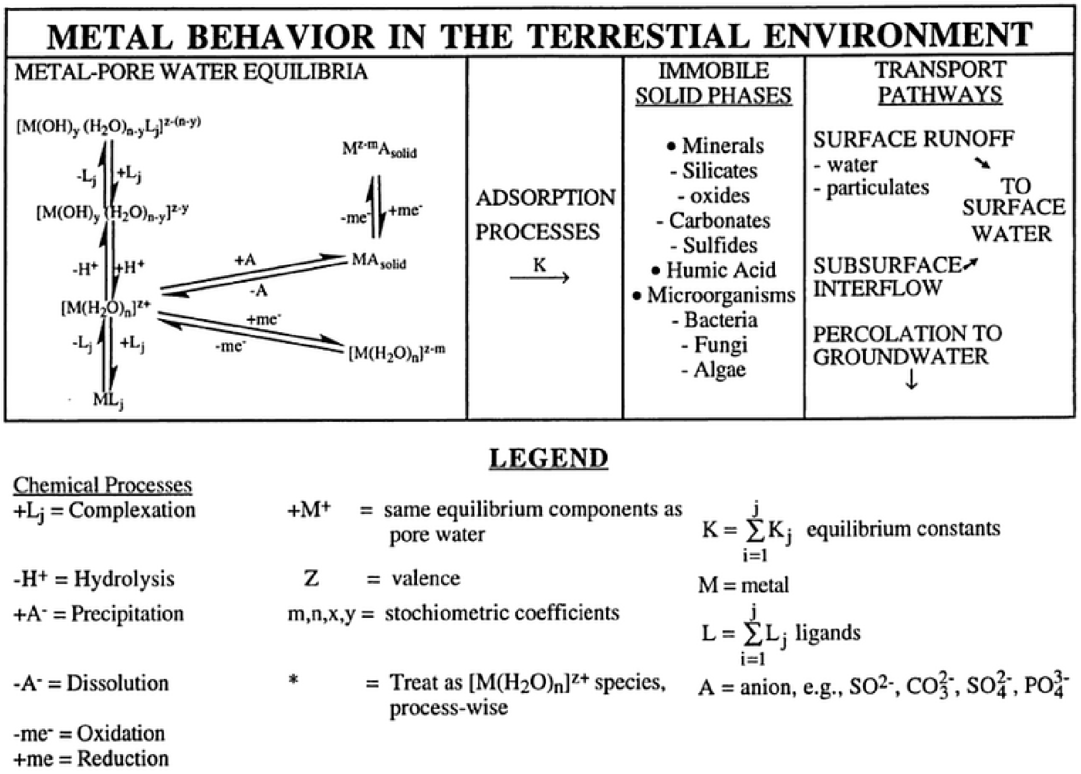


Figure 3 – Summary of fate and transport processes affecting metal concentration in the sub-surface (Allen, 1995)

There are several processes within the sediment sub-surface that can lead to the immobilisation of metals:

- Redox reactions
- Sorption:

  - Surface complexation
  - Cation exchange
- Precipitation/dissolution, and
- Interaction with fauna and flora

Sorption is a term used to capture a variety of different mechanisms that serve to attenuate metals. In all mechanisms the metal is associated with a surface (mineral or colloid) but the forces of attraction that hold the metal to a surface vary in magnitude. Electrostatic forces, e.g. ionic bonding, is one of the weakest bonds between a metal and surface. Covalent bonding forces are much stronger. Surface complexation of metals to a surface include both ionic and covalent bonding. Cation exchange involves ionic bonding but an ion is physically and preferentially exchanged between the surface and the metal species.

Given that the processes listed above are also important in terms of the fate and transport of metals within the fluvial system these physical and chemical reactions within sediment are described in detail in Section 1.2. It is noted that assessment of the influence of fauna and flora on metals concentrations is outside the scope of this evaluation and not discussed herein.

1.3 Fate and Transport in Sediment within the Fluvial System

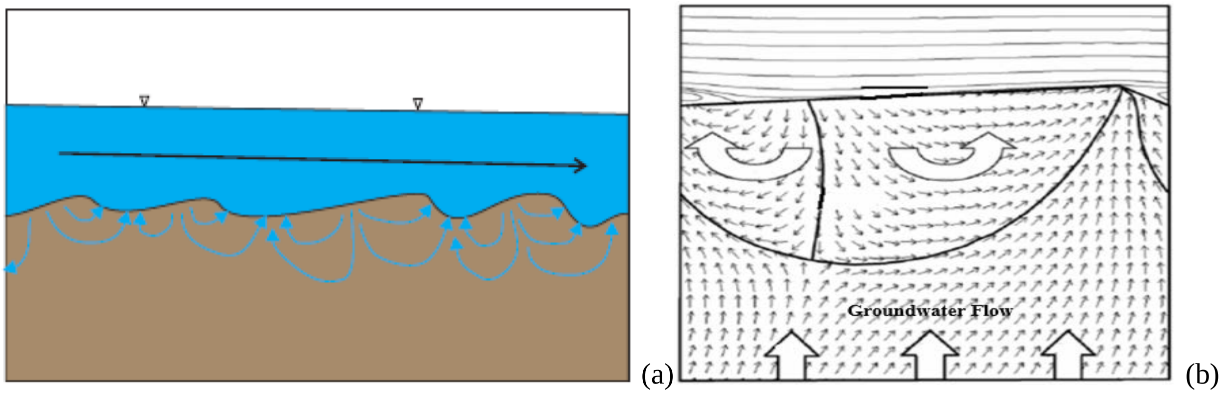
The potential for mobility of metals within sediment is primarily associated with physical sediment transport within the fluvial system and colloidal mobility of organo-metallic complexes. However, in the context of flowing fluvial systems, physical transport of sediment due to storm events or mechanical disturbance of sediment (for example, navigational dredging) are dominant.

High organic carbon materials tend to exhibit lower particle density and size (excluding detritus) and as a result their presence is generally greatest in low energy deposition areas. Similarly silts and clays which are characterised by large surface area and sorption potential are also preferentially deposited in low energy settings. As a consequence, areas with low water velocities are characterized by sediments with higher content of organic carbon, silts and clays. Given the affinity of metals for silts and clays, metal concentrations also tend to elevated in low water velocity environments. Organic matter, which is usually deposited in association with finer grained sediments such as silts and clays, provides a key means of immobilizing metal ions. This organic matter in these deposits is not usually a contributor to dissolved organic carbon in the water column, however, it provides a long term sink for metals in sediments providing the sediment is not disturbed. Potential movement of metal ions is further decreased as reducing conditions are created as organic matter is buried within the sediments and metal ions are more likely to precipitate out as insoluble mineral phases under these more reducing conditions.

The fate and transport behaviour of key metals of interest (associated with historical Site operations and/or identified as elevated in the Hudson River) has been further evaluated: barium, cadmium, chromium (trivalent and hexavalent), copper, lead, mercury and vanadium. For the purposes of this evaluation, the metals are assumed to be present as metal ions (M^{z+}) and subsequent reactions with ligands and sorption are discussed. As described below, sorption of metals occurs through a combination of surface complexation and cation exchange with organic carbon, silts, and clays all playing an important role in this process. Similarly for organic compounds, sorption to organic carbon in sediment influences the attenuation of PCBs (due to their high K_{oc}, a function of the partitioning behaviour of an organic compound between organic carbon and water). A detailed discussion of geochemical reactions in the GW/SW interface and sediments follows.

1.3.1 Physical Flow Behaviour in Sediment

As well as the expected exchange of flow between groundwater and surface water flow in the river, irregularities in the river bed induce circulation of river water through the river bed (**Figure 4**).



(a) GW/SW interface flow due to gradients in dynamic head formed when water flow encounters irregular river bed (Environment Agency, 2009)
(b) Numerical model results from a turbulent surface water/laminar groundwater model (Cardenas and Wilson, 2007)

Figure 4 – Interactions between river flow and sediment flux

In conjunction with head induced flows of groundwater into surface water, sedimentation and colmation can act to retard flow into or out of river systems by decreasing riverbed permeabilities. Deposition and the accumulation of fine grained sediment at the upper surface of the river bed is typically discussed as being limited to low velocity sections of the river. However, colmation can occur in high flowing sections of the river and lead to significant reductions in riverbed permeability.

Colmation is the process of the deposition and movement of fine-grained sediments and organic material into the interstices of gravel beds in streambeds, normally as a result of filtering of sediment-containing down-welling stream water by the porous sediments of the streambed and sedimentation (Brunke and Gonser 1997). In some situations, it can form a layer of low permeability sediment, known as colmatage, which can blind (clog pore spaces) the riverbed sediments (Petts 1988, Schalchli 1992). This can have implications for the transfer of dissolved oxygen within the GW/SW interface and the creation of anoxic environments. Colmation has been observed to be most common in rivers subject to excessive soil erosion (as a result of poor land management practices) in the surrounding catchment. It occurs especially under low surface flow conditions and when there is a net discharge of surface water from the river to groundwater (i.e., a losing stream). As these catchments are frequently affected by other human work and activities that lead to pollution, the colmatage can have beneficial effects as a barrier to pollution across the groundwater–surface water interface (Younger *et al.* 1993, Brunke and Gonser 1997). It should, however, be noted that colmation will vary significantly with river flow conditions and in response to influent and effluent flow direction and is likely to be a temporally influenced effect.

The effect of colmation results in classic fining and coarsening upward sequences within fluvial sediments. Migrating channel deposits result in the upward fining sequences, whereas coarsening upward sequences are created during high energy events or sediments deposited during river regression. The attenuation potential of the river sediments is enhanced at the interface between the moderately stable base of the riverbed (bedrock) and the overlying unconsolidated sediment material. Suspended colloidal material within the river water column that can settle out under low flow conditions can potentially infiltrate coarser sediments on the riverbed (colmation). Organic or metal species associated with the colloids are also entrained within these coarser grained materials. Subsequent scouring within the river during higher energy conditions can re-mobilise colloidally attenuated contaminants over time. As mentioned previously colmatage can bind the river bed and act as a barrier or attenuating filter for contaminants within groundwater that may be discharged to the river system.

1.3.2 Geochemical Reactions in Sediment

1.3.2.1 Reduction and oxidation (redox) Reactions

Generally, metals within fluvial system sediments form stable complexes with available ligands (water/hydrolysis, phosphate, carbonate, and sulfate). The solubility limit of complexes (hydroxides and oxides) varies with pH. Changes in pH can occur within the GW/SW interface as surface water and groundwater mix. As demonstrated in **Figures 5** and **6**, predominance diagrams (using field measurements on water samples from the Hudson River yielding average Eh ~250 mV and pH of 7.45, and assumed 2×10^{-4} moles bicarbonate) indicate that cadmium, copper, trivalent chromium and lead will either hydrolyze or form carbonate complexes and precipitate (dependent on the metal and ligand concentration). Both hexavalent chromium and vanadium form anionic complexes and are not expected to precipitate unless they are reduced (e.g., Cr^{6+} to Cr^{3+}) or they reach saturation (vanadium oxides). Barium and methyl mercury (if present) are also expected to be mobile over the redox and pH ranges expected in the Hudson River.

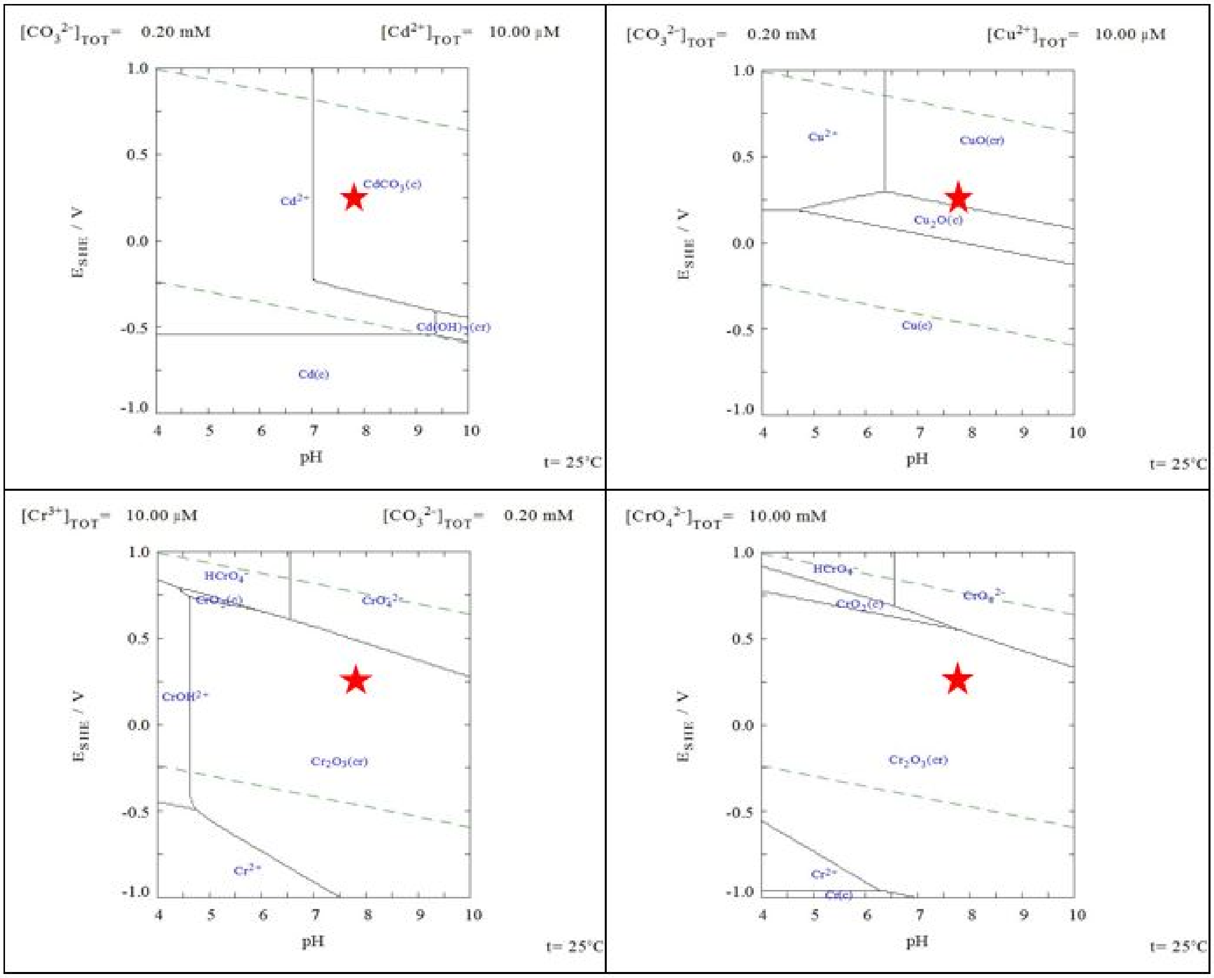


Figure 5 – Predominance diagrams for cadmium, copper and trivalent chromium in the presence of $2x10^{-4}$ moles alkalinity as bicarbonate (hexavalent chromium is anionic so carbonate is not an active ligand) – cadmium, copper, trivalent and hexavalent chromium metal species at nominal concentration of $1x10^{-5}$ moles (red star is representative of field measured Eh and pH)

Of note is the behavior of chromate, which is predicted to reduce to trivalent chromium under ambient environmental conditions (oxidizing, circum-neutral pH). Although chromium oxide (a Cr(III) species) is the stable phase at the field redox and pH measured in the river, chromate [a Cr(VI) species] is always the dominant species in solutions which are mildly oxidizing and alkaline. Numerous publications refer to the unexpected recalcitrance of the reduction of hexavalent chromium in the presence of redox sensitive mineral phases, such as iron (oxy)hydroxides (Dresel et al, 2008), however, oxidizing aqueous conditions appear to inhibit the reaction. This leads to the interpretation that the redox driven conversion of Cr^{6+} to Cr^{3+} is decoupled from other redox reactions in the chromium system such that Cr^{6+} remains in solution and is not reduced to Cr^{3+}. More likely, the conversion is kinetically influenced and without a catalyst proceeds at a very slow rate. Microbiological organisms can act as biotic catalysts; however, the phase diagrams do not capture the potential for biological transformations.

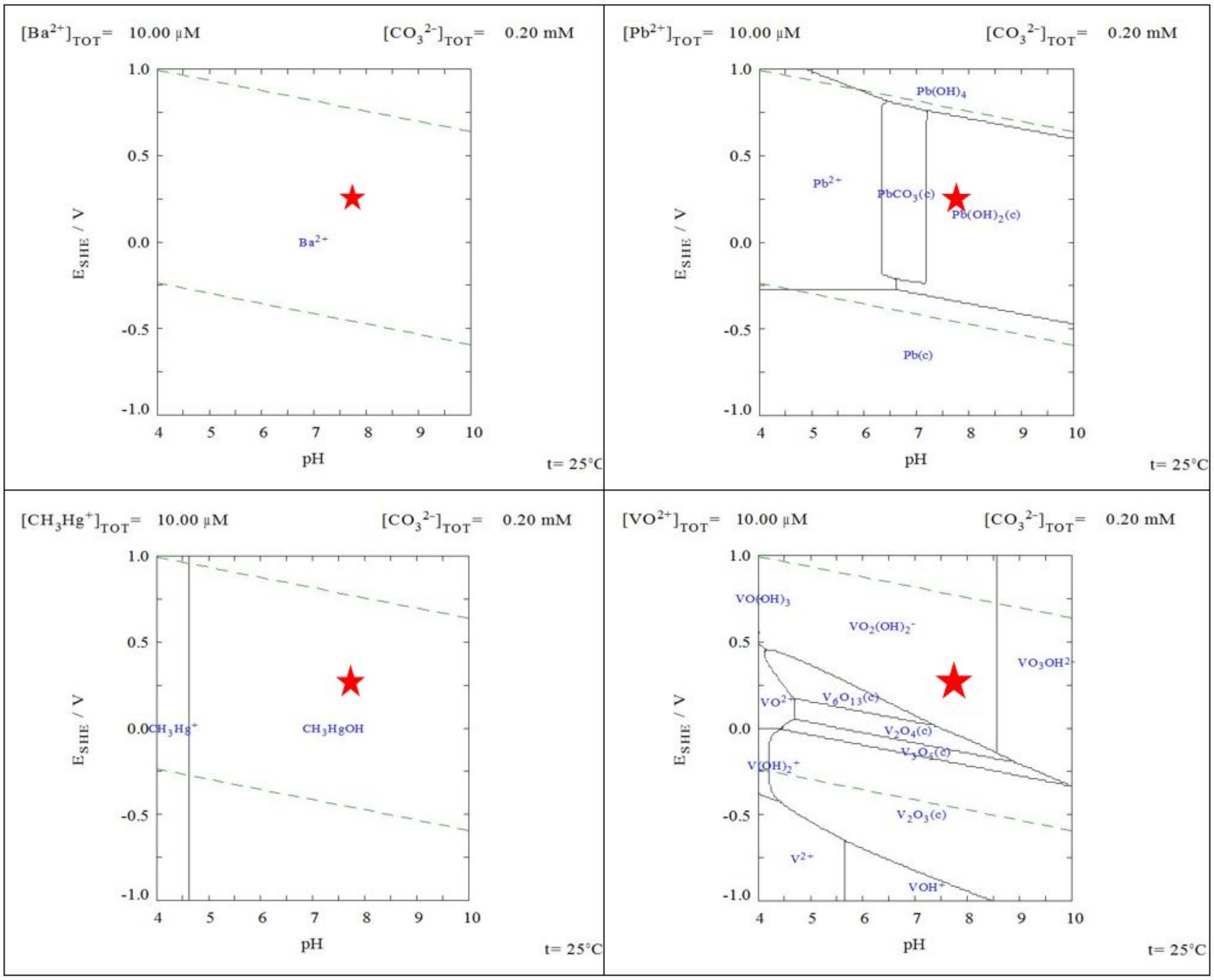


Figure 6 – Predominance diagrams for barium, lead, methyl mercury and vanadium in the presence of 2x10^{-4} moles alkalinity as bicarbonate (barium, lead, mercury and vanadium metal species at nominal concentration of 1x10^{-5} moles; red star representative of field measured Eh and pH)

1.3.2.2 Sorption Reactions

Sorption describes a broad range of processes that immobilize metals in the formation or in sediments. These include mineral surface sorption, precipitation of minerals and cation exchange that, in combination with filtering (as described previously), all contribute to the immobilization of metals within groundwater and sediment within the fluvial system.

As noted above, sorption contributes to the immobilization of metals within sediment, with these attenuation reactions occurring on the surfaces of minerals and organic carbon within the sediment matrix. Sorption mechanisms include electrostatic attraction and covalent bonding (complexation) and ion exchange. For sorption reactions where complexation dominates, the differentiation between electrostatic attraction and covalent bonding is dependent on the sorbing surface and the ligand attached to the surface and often the type of bonding is not known unless atomic resolution studies are undertaken. For simplification, the following sorption discussions are split into complexation and ion exchange reactions.

Complexation

As observed in **Figure 7**, trace metals as cationic species are not expected to be mobile over the expected pH range in a limestone bedded river (pH 7.5 to 8, EHS Support, 2014). These sorption curves relate to the ionic species of the metal and in association with an iron (oxy)hydroxide. Other mineral phases which are important as sorbing surfaces are clays, and manganese and aluminium hydroxides. Data on the mineralogy of the sediment and the relevance of each process in sorption has not been completed for sediment samples collected within the Hudson River.

Cationic species of metal ions increase their sorption potential as pH increases. The sorption behaviour presented in **Figure 7** is for illustrative purposes only and is a simplification of the relationship of sorption between the metals presented and the specific sorption mechanisms, which are described in more detail below.

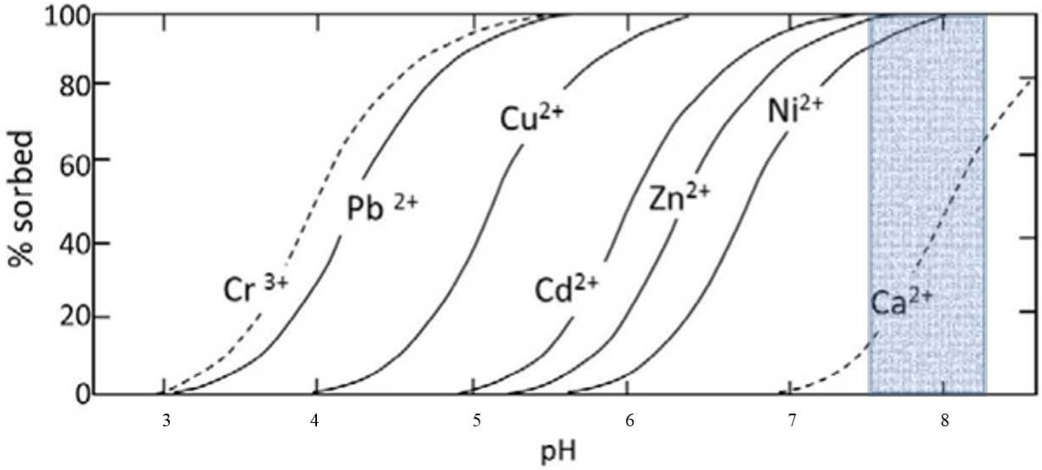


Figure 7 – Sorption of metals on the surface of ferrihydrite as a function of pH (Appelo and Postma, 2005) – shaded area represents the expected pH range of the Hudson River

The process of mineral surface sorption is a key process in the immobilisation of metals within an aquifer matrix and in sediments within the river. Mineral surface sorption can attract and fix metal ions through surface complexation or ionic exchange. This results in a selectivity sequence of metals based on the exchange isotherms of metals and a sorbing surface. This sequence is usually in the order:

$\mathrm{Ni} < \mathrm{Zn} \leq \mathrm{Co} < \mathrm{Cd} \approx \mathrm{Pb} \approx \mathrm{Cu}$ (Auboiroux et al, 1998)

soft cations ↔ hard cations

Where nickel is the least sorbed and copper is retained the most strongly. The metal cations towards the left of the sequence are more likely to form outer sphere complexes (electrostatic or ionic bonding), mainly due to the hydration of the ions. This is supported by their higher ionic potential in comparison to the other metal ions. The hard cations are more likely to form inner sphere (covalent bonds) complexes which are much stronger than electrostatic bonds. An inner sphere complex forms between the metal cation and a ligand on the sorbing surface and displaces the hydration waters surrounding the cation. With outer sphere complexes, at least one water molecule remains between the metal ion and the surface ligand. Dependent on the sorbing surface, lead and copper can be interchangeable as can zinc and cobalt. Copper and lead tend to form inner sphere complexes on both amorphous aluminium and iron oxides (McBride, 1982; Yamaguchi and Okazaki, 2002), whereas zinc forms outer sphere complexes on amorphous iron and aluminium oxides and inner sphere complexes on crystalline iron oxide (Trivedi et al, 2001).

Metal Cation	**Hard/Soft cations**	**Ionic Potential (nm^{-1})**	**Misono parameter (nm)**
Mercury (Hg$^{2+)}$	Hard	19.6	0.396
Lead (Pb$^{2+)}$		16.9	0.393
Cadmium (Cd$^{2+)}$	↕	21.1	0.303
Copper (Cu$^{2+)}$		27.4	0.284
Barium (Ba$^{2+)}$	Soft	14.8	0.260
Chromium (Cr$^{3+)}$		48.4	0.226
Vanadium (V$^{4+)}$		67.8	0.211

Table 2 – Atomic properties of selected metals (Sposito, 1986)

The tendency for a metal ion to form either electrostatic or covalent bonds was evaluated by Misono (Misono et al, 1967) and the Misono parameter provides a quantitative indication of the type of bond a metal ion will form. Hard cations have high electronegativity and low polarizability and soft cations have a high ionic potential and high polarizability.

As can be noted from **Table 2** the Misono softness parameter does not identify the sorption sequence that may potentially occur in the presence of all mineral surfaces. Chromium (trivalent only) and vanadium are observed to have Misono parameters <0.25 nanometers (nm), which indicates that the mobility of these metal ions is characterised by their solubility and not sorption, i.e., they will form insoluble complexes and precipitates instead of sorbing to mineral surfaces.

Barium, as presented in **Figure 6**, is predicted to be mobile in oxidizing and alkaline aqueous environments at low concentrations (10 micromolar, uM). This is in contrast to the other metal species discussed above. Barium is expected to have behaviour very similar to calcium (Figure 7) and will precipitate (concentrations > 1 millimolar, mM) as barium carbonate which is not very soluble.

The sorption behaviour of anionic metal complexes is expected to decrease with an increase in pH. **Figure 8** illustrates this for a ferrihydrite (iron (oxy) hydroxide) surface, however, this behaviour will be observed for the majority of mineral surfaces over this pH range. Therefore, under oxidizing conditions the chromate ion mobility (Cr^{6+}) is expected to increase with an increase in pH. If the chromate ion is associated with colloids, which subsequently agglomerate in the reducing zone of sediments, then there is a potential for reduction to the Cr^{3+} (trivalent) ion. The presence of microbes can also facilitate the reduction of hexavalent chromium to trivalent chromium. The trivalent chromium ion has limited mobility in groundwater and surface water systems, due to its low solubility.

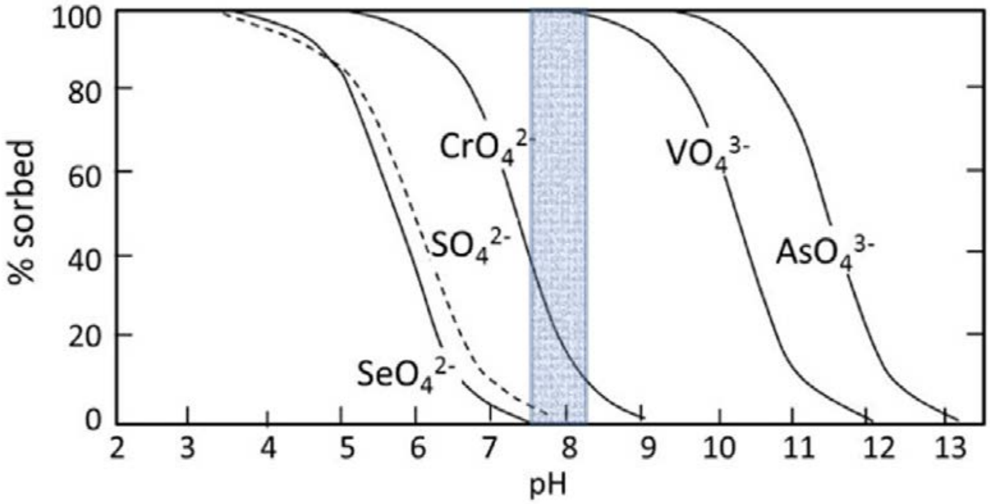


Figure 8 – Sorption of anionic metal complexes on the surface of ferrihydrite as a function of pH (Sigg et al, 2000) – shaded area represents the expected pH range of the Hudson River

Metal sorption can also occur onto organic matter. As noted by Johnson (1974) and described earlier in this document, nearly all the finer sediments in the low energy portions of fluvial systems comprise silt and/or clay, which are dominated by organic mineral aggregates where metals are selectively sorbed.

The sorptive enrichment of organic matter can provide a major sink for the removal of metal ions in water (Murphy and Zachara 1995). However, as observed in **Figure 7**, trace metals as cationic species are not expected to be mobile over the expected pH range in a limestone river (pH 7.5 to 8, EHS Support, 2014). These sorption curves relate to the ionic species of the metal and in association with an iron (oxy)hydroxide; data regarding the capacity of sorption surfaces within the study area were not available to review for this evaluation. The presence of organic matter can also reduce metal sorption to sediment surfaces by either competing more effectively for metal ions or being preferentially adsorbed onto sediment surfaces instead of the metal ions (Baham and Sposito, 1994, Davis, 1984, Elliott and Denneny, 1982, Kaizer and Zech, 1997, Spark et al., 1997 Xu et al., 1989). If organo-metallic complexes are formed (chelates) between organic matter and metal ions, metals can be transported in a dissolved organic carbon fraction with mobility defined by the dissolved fraction of organic carbon within surface water. The relative mobility of the organo-metallic complexes is defined by the ion speciation and varies between metal species. However other modes of attenuation can also occur with dissolved organic carbon utilized by aquatic plants and taken up by plant roots together with any sorbed metals.

The formation of organo-metallic complexes and/or the potential for surface sorption is influenced by not only dissolved organic matter concentrations but variations in temperature, redox conditions, ionic strength, pH and the concentrations of metal species. These geochemical influences in association with physical changes within the surface water system and groundwater hydraulics can produce large temporal variances in metal fluxes within the river.

Ion Exchange

Cation exchange capacity is the ability of a substrate (e.g., soil or sediment) to exchange cations with cations in water. Cation exchange is the mechanism where a cation is exchanged between a solution and a surface. Cation exchange capacity varies in relation to pH, exchangeable ion concentration and ionic strength of the aqueous environment. Cation exchange can provide a major sink for the attenuation of metal ions but is dependent on favourable ion exchange surfaces, which include clays and mineral growth phases such as iron and aluminium hydroxides and calcite. Information on the presence of these mineral phases within the river sediments was not available for review for this assessment.

1.3.2.3 Precipitation

Precipitation of trace metals can occur either as a solubility induced mineral phase precipitation or co-precipitation in association with another mineral phase. The former process is unlikely given the usually low concentrations of trace metals encountered within the environment, however, co-precipitation has been observed in iron (oxy)hydroxides (chromium and uranium) and calcium carbonates (strontium – calcium solid solution series). Co-precipitation can be abiotically or biotically influenced. In the former, species concentration, redox conditions and pH play an important role in metal species solubility. In the latter, biological organisms either play a direct or indirect role in the reduction of metal species which under specific redox and pH conditions have the potential to precipitate. Provided the pH and redox conditions remain conducive to precipitation, the mineral phase (precipitated metal species) continues to stabilise and age within the sediments. If redox and/or pH conditions change e.g., water becomes more acidic or oxidizing conditions increase, precipitated minerals could undergo dissolution and the metals associated with the mineral remobilise. The potential for calcite dissolution as a result of surface water ingress into groundwater at the Site (by the action of the groundwater extraction system)was identified and is discussed in the groundwater conceptualization report recently completed for the Site (EHS Support, 2014). This could lead to the remobilisation of co-precipitated metals in the calcite structure at the Site.

1.3.2.4 Summary of Geochemical Reactions in Sediment

In summary, under the oxidizing and moderately alkaline conditions encountered within Site groundwater and Hudson River water, the metal behaviour outlined in **Figure 9** is expected.

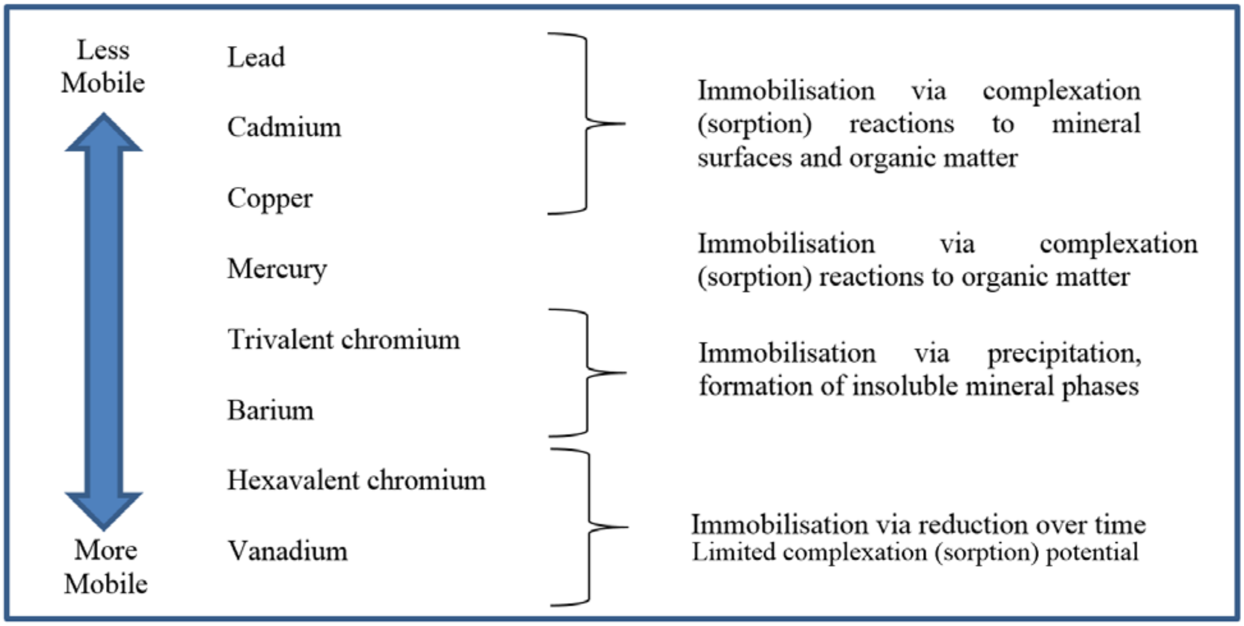


Figure 9 – Metal behaviour expected in fluvial sediments

These assumptions presented in **Figure 9** are based on mineral surfaces available for sorption to occur and concentrations of metals to allow saturation and precipitation to occur. The reduction reactions are also more strongly influenced by kinetic controls and may not occur within a similar time frame as other processes. **Figure 9** also assumes chemical equilibrium in the aqueous system once metal species have been immobilised, this is not always the case in environmental systems especially when viewed over different temporal scales. The evaluation has not accounted for the original concentrations of metals that may have been released as a result of Site industrial processes and the influence on chemistry, i.e. saturation and precipitation of mineral phases and exhaustion of cation exchange sites on mineral phases. This may not be an important consideration as historical sources of metals discharge ceased more than 25 years ago, and fine-grained sediments were preferentially dredged from the river adjacent and immediately downstream of the Site as part of the Site Corrective Measures for off-site sediments. Additionally, dredging of sediments downstream of the Site has been conducted over many years for navigational maintenance (pre- and post historical Site operations; EHS Support, 2015b), and further dredging in large areas of the river has been conducted between 2009 and 2015 as part of the PCB Superfund removal action (following the sediments characterization sampling completed by GE in 2002 through 2005).

2.0 EVALUATION OF THE CO-LOCATION OF ORGANICS AND INORGANICS

PCBs have also been identified as constituents of interest within the Hudson River. Similar to metals, organics such as PCBs will be preferentially associated with finer grained sediments and organic matter. Numerous studies (Ghosh et al, 2003; McLeod et al, 2004; Werner et al, 2005 and Zimmerman et al 2004) have shown the affinity of PCBs with organic matter. Carbonaceous material (activated carbon, charcoal and coke) have been used in remedial systems due to their high attenuating potential.

Organic matter has been demonstrated to have a greater sorption potential than clay minerals for non-polar compounds such as PCBs (Hassett et al, 1980; Means et al, 1980). The mechanism for sorption between organic molecules and clay minerals is different to that of metals and clay surfaces. Sorption can occur through hydrogen bonding from the hydroxyl surfaces of clays (gibbsite>kaolinite>montmorillonite) toward the oxygen atoms in the organic molecules. Hydration of the montmorillonite surface appears to decrease the sorption potential by hydrogen bonding. The sorption of PCBs on organics was further researched in Estes (1992), which focused on the relative distribution of PCBs in size and density fractions of three sediments collected from other river dredging activities (sediments sampled from Calumet River, IL, New York Harbor, NY and New Bedford Harbor, MA). PCBs were also found to sorb to clay minerals.

Consistent with the discussion above, the expectation is that finer grained sediments within the Hudson River will also have the highest percentages of organic carbon and due to both sorption onto organic matter and clay minerals, PCBs and metals will be co-located within fine-grained river sediments.

The following sections discuss the results of the GE sediment sampling and assesses the distribution of metals within sediment types to determine if metals exhibit a similar affinity to fine grained sediments as PCBs. This understanding of the behavior and distribution of metals is critical to the development of the planned sediment sampling programs and assessment activities, and assesses the distribution of metals within Sediment Types

2.1 Assessment of Hudson River physical and chemical data

With consideration of the fundamentals of inorganic and organic constituents fate and transport in sediment described above, an assessment of the GE sediment quality and physical characteristics data was conducted. These data were obtained directly from the Hudson River database maintained by USEPA. Sediments in the Hudson River were classified by GE into the following five sediment types using SSS data (validated by sediment probing, confirmatory grain-size (particle) analysis, and visual textural classifications of surficial sediments samples):

- Type 1 (clay, silt, fine sands): smooth, generally featureless bottom; principally composed of soft silty sediments;
- Type 2 (sands): smooth to mottled bottom; principally composed of semi-compact to compact sand deposits;
- Type 3 (coarse gravel and sand mixtures): irregular bottom; principally composed of compact gravel and cobble deposits intermixed with sand;
- Type 4 (mixed sediments): smooth and irregular bottom; a varying assemblage of sediments typically associated with Types I, II, and III; or
- Type 5 (rocky): extremely irregular bottom; principally composed of bedrock, cobbles, and/or boulders that are often overlain by a variable thickness of unconsolidated sediments.

As detailed in EHS Support 2015d, the PCB dredging and capping activities have been focused in sediments classified as Type 1 and Type 2 where PCBs were found to be preferentially distributed. It should be noted that given GE's focus on Type 1 and Type 2 sediments, the chemical data density for other sediment types

(Types 3, 4 and 5) in some cases is limited and insufficient to support comparative statistics. Additionally, for this evaluation samples with no SSS data (collected at river banks or near the edges of the river) or with no GIS information (x and y coordinates) were assigned as “Type 0”. Type 0 samples were not included in statistical analysis.

Statistical analysis of the available sediments data for this evaluation focused on simple analytical tools to evaluate data distributions and potential correlations for sediment types. Review of the data indicated that the majority of parameters exhibited non-parametric distributions, which could not be manipulated for general statistical analysis techniques (for example, assessment of variance). On this basis, the assessment was conducted using primarily scatter plots and box plots (provided in **Attachment A**) for assessment of data distribution by sediment type and for assessment of potential correlations. The hypothesis based on literature expectations was that the detection of metals and PCBs would increase with increasing percent (%) Clay, % Fines and/or total organic carbon (TOC), and metals are more likely to be associated with clays and silts (fines) than with sands and coarser grained sediments.

It is noted that a number of the assessments were affected by the nature of the data sets including:

- The large number of deep samples which may not have been affected by historical industrial operations;
- The attenuation in COPC concentrations along the length of the Hudson River which weakened the correlations; and
- The non-parametric nature of the data set.

2.1.1 Association of metals with Fines and Clay

The total concentration (milligram per kilogram; mg/kg) data for seven metals was compared against %fines and %clay (Attachment A **Figures A1** and **A2**, respectively) in samples collected from the Hudson River representing a range of sediment depths within the river (overall depth profile of 0 to 87 inches). The % fines measurement is understood to comprise both clay, silt and potentially fine sands. The number of samples where both a specific metal and %fines or %clay were measured in tandem was low, and in the case of copper, cadmium and vanadium there were no paired data results (refer to figures for sample numbers assessed). Both barium and mercury were observed to have a linear relationship with %fines and %clay, although the small dataset is likely to influence this outcome. Chromium and lead had a best fit for metal concentrations against both %fines and %clays using an exponential relationship, however, this is influenced by a potential outlier in each dataset and also the limited number of paired data results. A linear relationship is observed between %clay and %fines which is not unexpected since the fines measurement incorporates the clay fraction of particles size.

2.1.2 Association of metals with Total Organic Carbon

Total concentration (mg/kg) data for seven metals were compared against TOC concentrations (mg/kg) within samples from the Hudson River (**Figure A3 in Appendix A**). The samples are representative of a range of sediment depths within the river (overall depth profile of 0 to 87 inches). The number of samples where both a specific metal and TOC concentration were measured in tandem was low, and in the case of copper and vanadium there were no paired data results. Barium, chromium and cadmium were observed to have a linear relationship with TOC, although the small datasets likely influenced this outcome (refer to figures for sample numbers assessed). The cadmium dataset consisted of only 2 paired values and therefore even a linear trend is not a robust observation. Mercury had a best fit using an exponential relationship, however, this is influenced by a potential outlier in the dataset and also the limited number of paired data results.

2.1.3 Association of Total PCBs with Clay, Fines and Total Organic Carbon

The concentrations of total PCBs (over a range of sediment sample depths) was compared to the concentration of TOC and %clay and %fines (**Figure A4, Appendix A**). There does not appear to be a correlation between either %clay and total PCB concentration or %fines and total PCB concentration, even within defined depth ranges. Overall, TOC does not appear to be correlated with the distribution of total PCBs, however TOC concentrations do appear to decrease with depth, but this is based on a decreasing dataset, i.e. the number of samples decreases with depth. The assumption that TOC concentration affects total PCB concentration with depth cannot be made due to the decreasing amount of paired data results with depth.

2.1.4 Box and Whisker Plots of Metals Distributions in Various Sediments Types

Box and whisker plots of selected metals (barium, cadmium, chromium, lead, copper, vanadium and mercury) and TOC in association with the sediment Type classifications are presented in **Figure A5 (Appendix A)**. The plots represent the five number summary (extremes, lower and upper quartiles and median) of each dataset and identified possible outliers (open circles). Type 1 and 2 sediments correspond respectively to clay/silt/fine sands and sands. Sediment Types 2, 3 and 4 are increasing coarser gravel and sand mixtures with Type 5 comprising bedrock, cobbles and/or boulders. Type 0 samples (arbitrary name assigned to samples with no SSS data or no GIS location coordinates) are included in histograms of sample counts for each sediment Type, but are not included in the statistical analysis.

For ease of interpretation, the key features on the box and whisker plots comprise the following:

- The bold line in the box represents the median value
- The top and bottom of the box represents the first and third quartile values respectively
- The vertical line extending beyond the box represents 1.5 times the interquartile range (IQR) of the first and third quartile values (outlier boundaries)
- The dots outside of these features reflect potential data outliers (outside 1.5 times the IQR values)

The plots for lead, vanadium, copper, chromium and cadmium clearly show that higher concentrations of these metal species are more likely to be associated with Type 1 sediments (clay, silt and fine sands). Mercury shows a slight bias to Type 1 sediments but is also associated with the undefined, Type 0 sediments (likely fine-grained deposits on the edge of the river where no SSS data is available). Barium does not appear to show a trend with respect to sediment type (and particle size). There does not appear to be an outwardly clear trend for TOC in any sediment Type.

2.1.5 Wilcoxon rank sum test and Kruskal-Wallis Multiple comparison test

The differences in individual metal concentrations between each sediment types were evaluated using the Wilcoxon and Kruskal-Wallis statistical tests. The statistical evaluation for each metal, based on the metal concentration distributions in the individual sediment types are provided within Attachment B. The statistical evaluation of concentration distributions of the individual sediment Types show for three metals (barium, copper, and vanadium) no significant difference in their distributions between sediment Types 1, 2 and 4 (insufficient data were available for assessment of Types 3 and 5). Four metals (cadmium, chromium, lead, and mercury) had concentration distributions in Type 1 sediments that significantly differed from their distribution in Type 2 and Type 4 sediments, while their distribution in Type 2 and Type 4 sediments did not significantly differ. .

The statistical assessment is consistent with the data distributions represented in box plots with higher medians and interquartile ranges for cadmium, chromium, lead and mercury in Type 1 sediments relative to the other sediment types. This statistical finding and the distribution of the data (described above) indicates that cadmium, chromium, lead and mercury are preferentially distributed in fine grained Type 1 sediments.

3.0 SUMMARY AND CONCLUSIONS

In summary, published literature on laboratory and field studies indicate that a range of mechanisms exist for the immobilization of metals within groundwater, the GW/SW interface and within the fluvial system sediment. Consistent with the geochemical modelling conducted for Site groundwater (EHS Support 2014), sorption, precipitation and redox reactions are all critical components of understanding the fate and transport of metals. Identified key processes that limit the flux of specific metals from groundwater into surface water and immobilize these metals in groundwater and within sediment, include:

- The physical filtering of colloids can occur within the aquifer matrix and the sediments present on the banks and base of the river (pore throat < colloid size);
- The GW/SW interface can provide enhanced attenuation potential for the retardation of metals and PCBs mobility. These processes are similar to those found in groundwater but also include the retention or utilization of metals and organics by microbes, microfauna and vegetation. It should be noted that the extent and magnitude of the GW/SW interface will change in response to differences in river bed geology and the associated extent and magnitude of attenuation mechanisms;
- Aggregation and precipitation of mineral phases (refer to **Section 1.3.2.3**) within the surface water column is expected to further reduce the mobility of cadmium, copper, trivalent chromium and lead;

Considering the range of physical and geochemical processes the anticipated behaviour of constituents are summarized as follows:

- Barium, mercury, hexavalent chromium and vanadium are predicted to have a relatively higher mobility in oxidizing and moderately alkaline fluvial waters which are representative of groundwater and surface water chemistry within the Site vicinity;
- Hexavalent chromium and vanadium are predicted to have a low sorption potential in oxidizing and moderately alkaline fluvial waters which are representative of groundwater and surface water chemistry in the Site vicinity;
- PCBs exhibit a greater affinity to organic matter, however, will still sorb to a lower extent to clay mineral surfaces.
- Concentrations of metals in fluvial systems are positively biased to fine-grained sediments (clays and silts) and organic matter, with metals bound within organics and high cation exchange capacity silts and clays.
- Fine-grained sediments and organic matter are expected to be co-located within low energy environments which enables sedimentation of clay and silts and preserves organic matter within the matrix.

The comparison of metal concentrations with box and whisker plots indicate cadmium, chromium, lead, and mercury concentrations are all positively skewed to the finer grained Type 1 sediments. This finding is consistent with the theoretical principles of metals fate and transport described herein. Other metal constituents (for example barium, copper, vanadium) did not show these significant relationships, but this is likely affected by the relatively low data density for these constituents and potentially an absence of major anthropogenic sources relative to those for the other metals.

The outcome of the scatter plot comparisons of metal distribution in association with percentages of clay, fines and TOC media (**Figures A1** to **A4, Appendix A**) indicates overlapping data distributions in data sets exhibiting large variances.. Advanced statistical analysis using non-parametric statistical methods indicate that the cadmium, chromium, lead, and mercury exhibit significantly different distributions in fine grained Type 1 sediments relative to other sediment types. This finding is consistent with the data distributions represented in box plots and indicate that cadmium, chromium, lead and mercury are preferentially distributed in fine grained Type 1 sediments.

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ATTACHMENT A

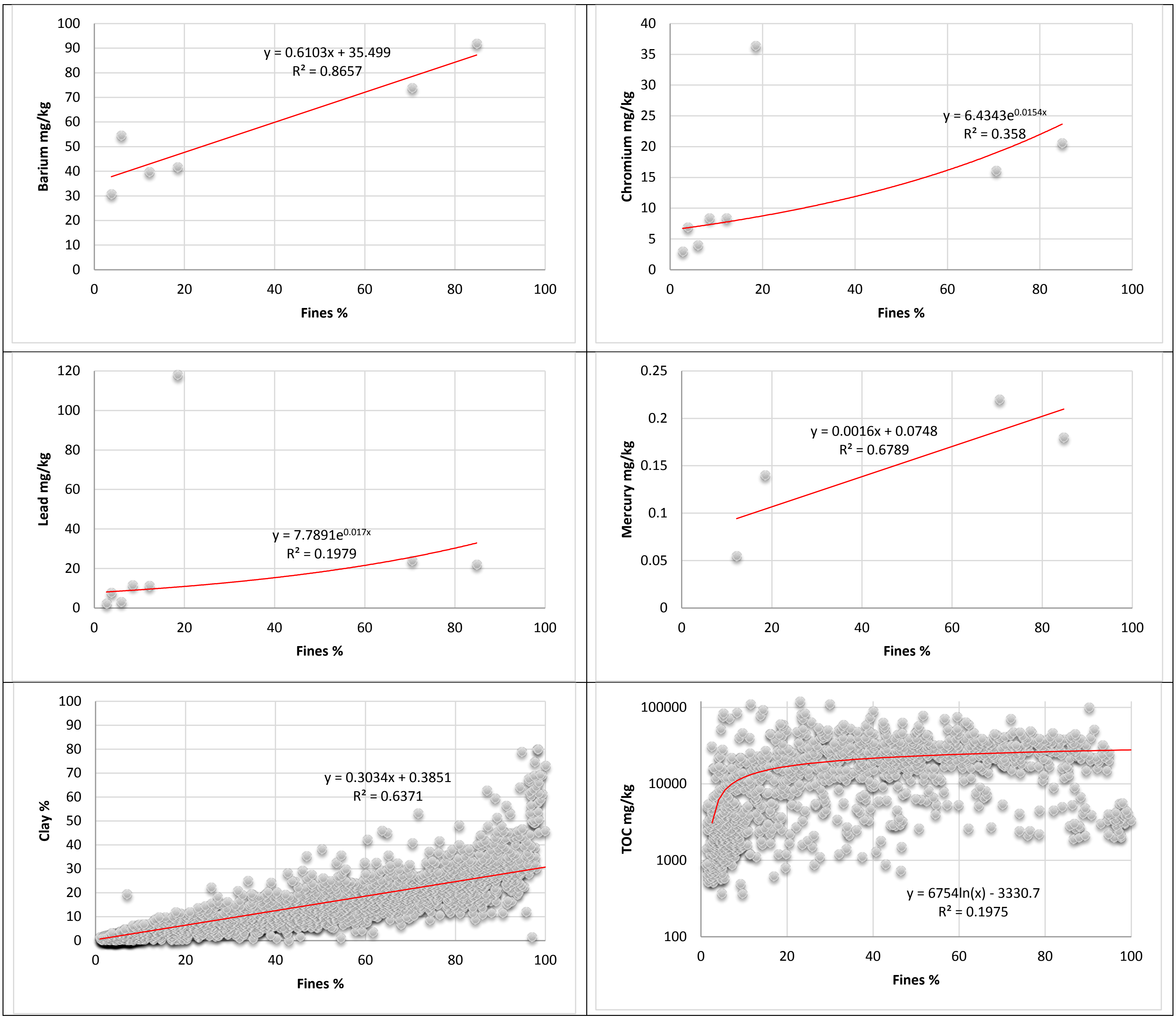

Figure A1 – Plots of Fines against barium (6 samples), chromium (8 samples), lead (8 samples), mercury (4 samples), clay and TOC (no paired data values for Fines and copper, cadmium or vanadium)

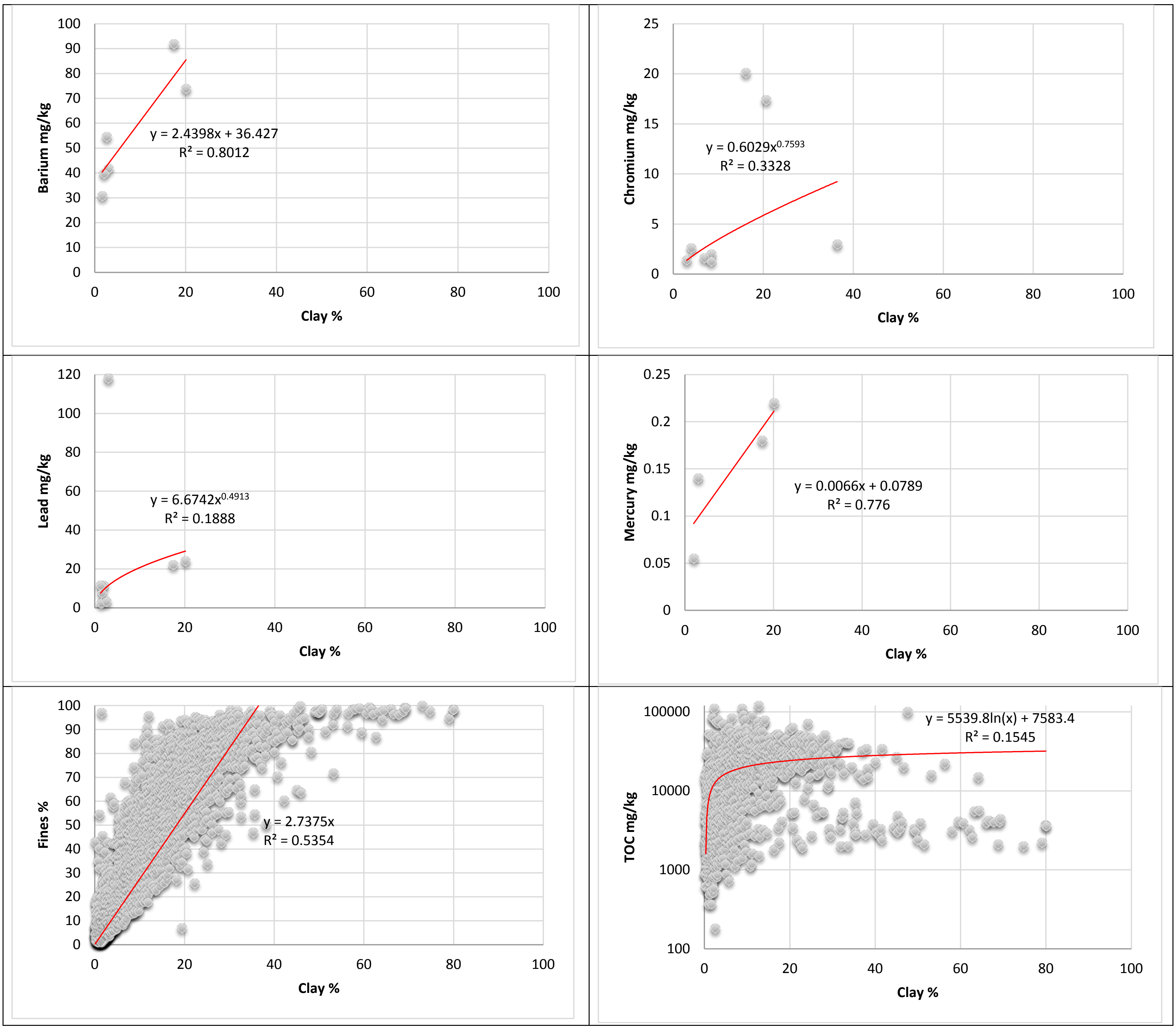

Figure A2 – Plots of Clay against barium (6 samples), chromium (8 samples), lead (8 samples), mercury (4 samples), clay and TOC (no paired data values for Clay and cadmium, copper or vanadium)[1]

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[1] Fines % vs Clay % intercept set to zero due to variable dependence, i.e. zero fines % is equal to zero clay %

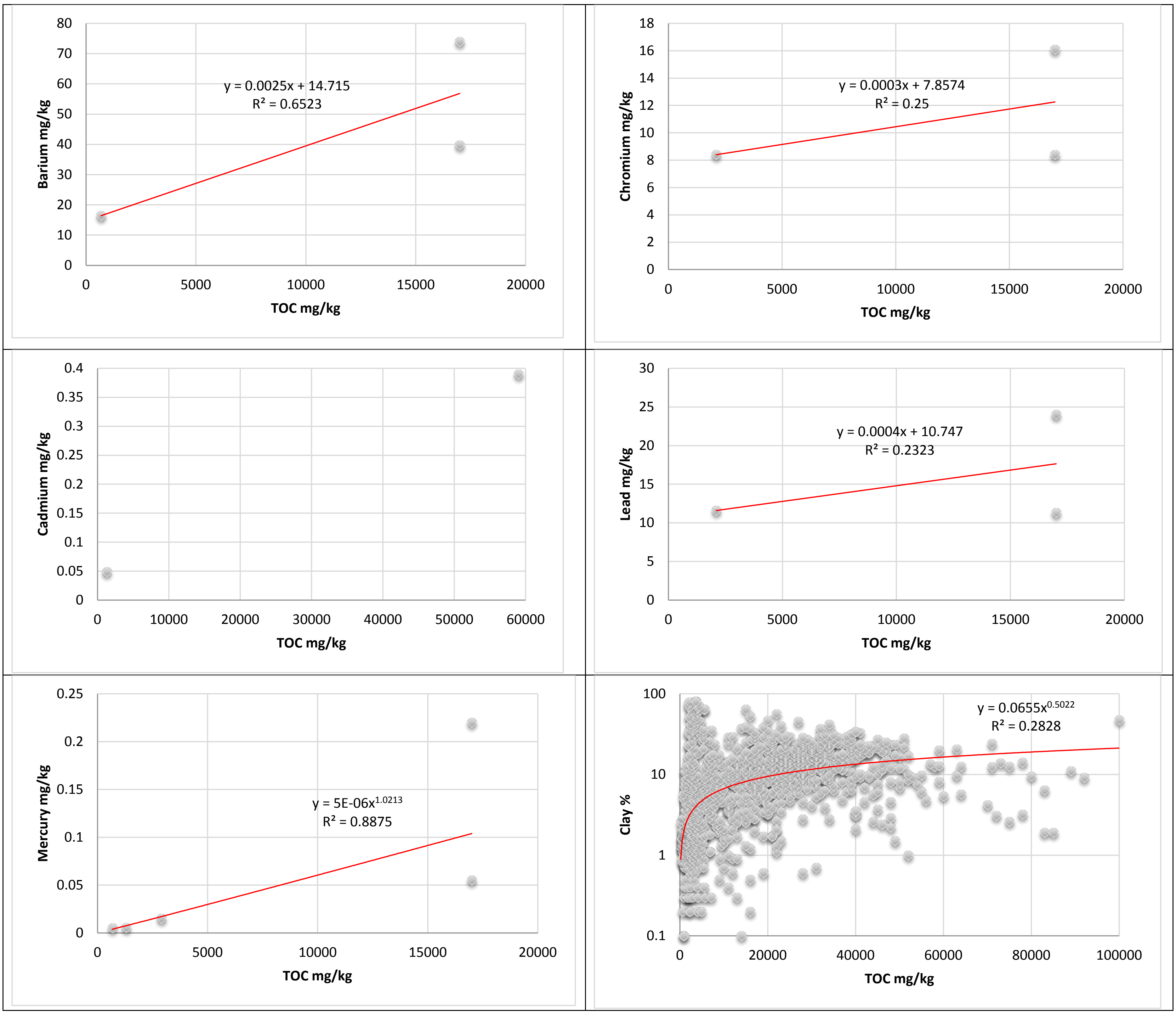

Figure A3 – Plots of TOC against barium (3 samples), chromium (3 samples), cadmium (2 samples), lead (3 samples), mercury (5 samples), clay and Clay (no paired data values for Clay and copper or vanadium)

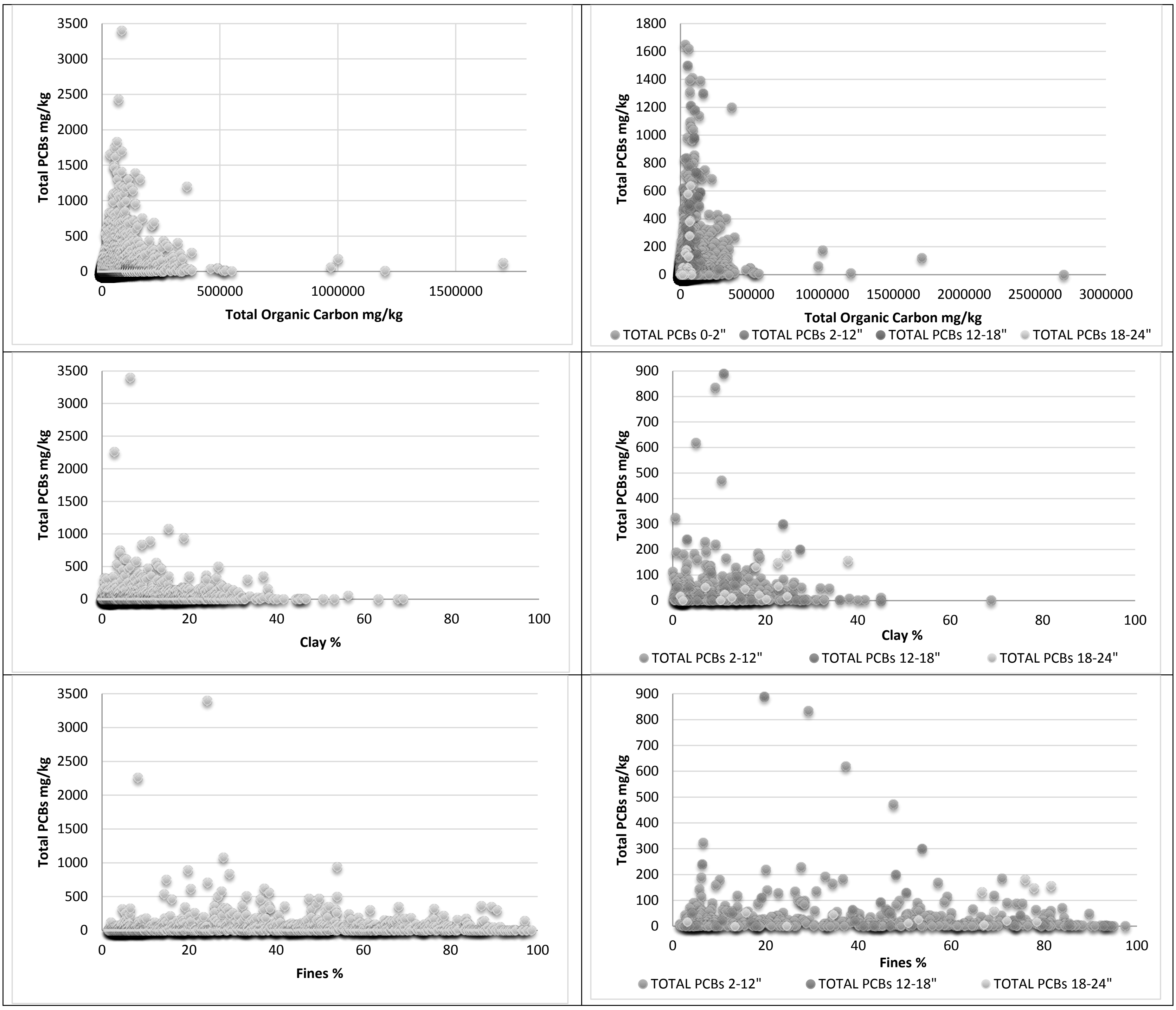

Figure A4 – Plots of TOC, Clay and fines against Total PCBs (all data and all depths in left column, all data in depth ranges in right column)

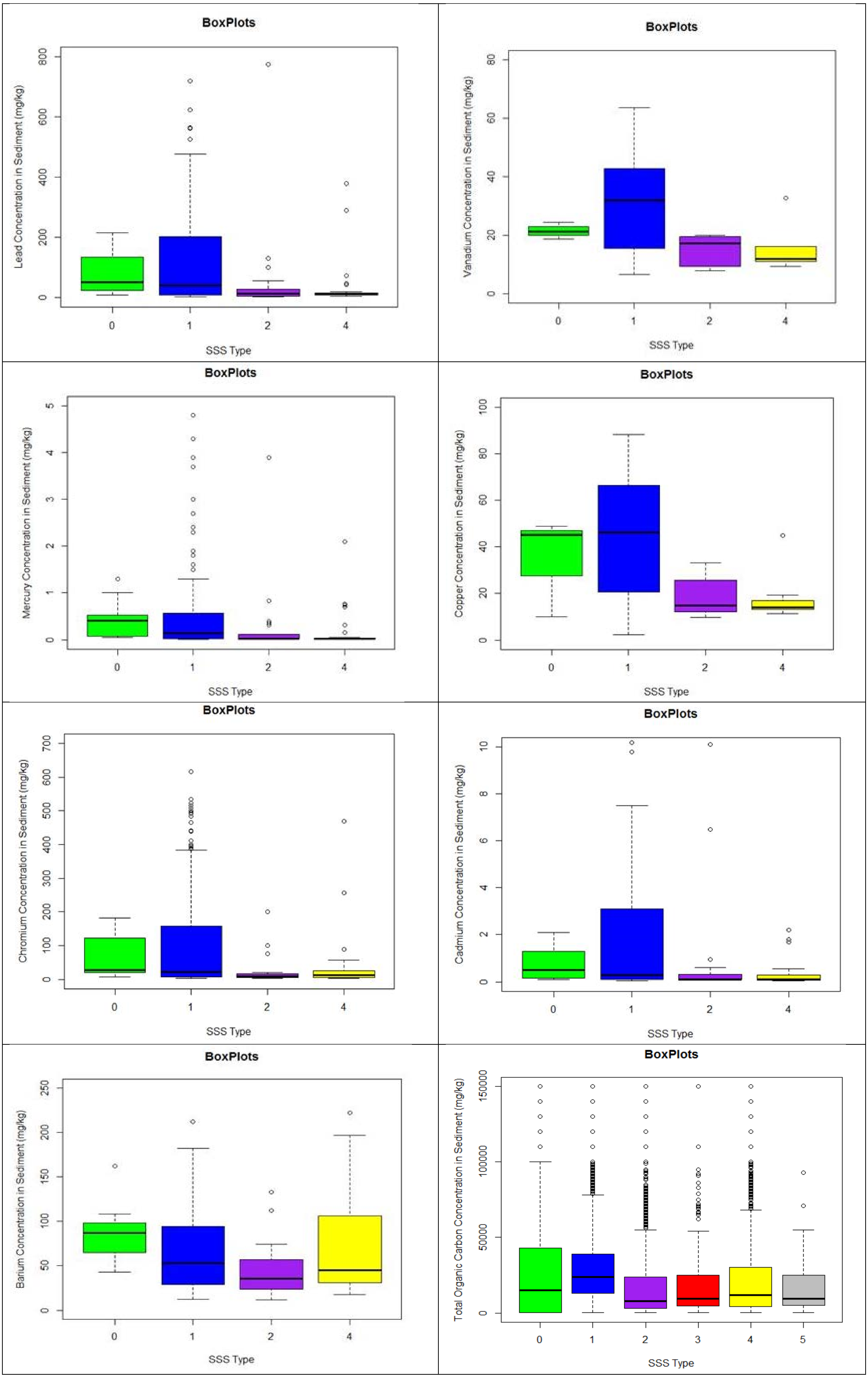

Figure A5 – Box and Whisker Plots for lead, vanadium, mercury, copper, chromium, cadmium, barium and Total Organic Carbon in association with SSS types 0, 1, 2, 3 4 and 5 (TOC only)

Figure A5 - Box and Whisper Plots
Sample Counts for various sediment types

Sediment Type	0	1	2	3	4	5
Barium	19	209	30	0	39	0
Cadmium	19	209	30	0	39	0
Chromium	19	209	30	0	39	0
Copper	3	48	5	0	7	0
Lead	19	209	30	0	39	0
Mercury	19	209	30	0	39	0
TOC	1165	5447	1711	294	2509	56
Vanadium	3	48	5	0	7	0

ATTACHMENT B

Wilcoxon rank sum test and Kruskal-Wallis Multiple comparison test

A statistical evaluation was performed to compare the differences in individual metal concentrations between each sediment Type. With some of the individual sample populations not being either normally distributed (Gaussian) or log-normally distributed, non-parametric testing was used to determine if the means and variances for the metal concentrations within each individual sediment Type (SSS Type) were statistically different based on Wilcoxon Signed Rank Test and Kruskal Wallis One-Way Analysis of Variance Test, respectively. These tests assign a “rank” instead of using the actual concentration; therefore, all non-detections regardless of the analysis Reporting Limit (RL) were assigned the same “rank.” With multiple comparisons being calculated between the individual sediment Type metal concentrations, a Bonferroni Correction was used to maintain the type I error at an alpha=0.05 (95% confidence limit). Both tests assume that the different sediment Types have the same distribution type. As noted in Section 2.1.4, the group of samples with metal concentrations available but no SSS sediment Type assigned were assigned the arbitrary Type “0”. Samples for which no SSS data were available were not included in statistical calculations. The metal concentrations in the Type 0 sediments are included for reference in histogram and box and whisper plots for each metal.

Both statistical test methods are considered appropriate for skewed data sets or categorized data. The Wilcoxon Signed Rank test is used when comparing two related samples, matched samples, or repeated measurements on a single sample to assess whether their population mean ranks differ (i.e., it is a paired difference test). The Kruskal–Wallis one-way analysis of variance tests whether samples originate from the same distribution, and is conducted by comparing two or more samples that are independent, and that may have different sample sizes. When rejecting the null hypothesis of the Kruskal-Wallis test, then at least one sample stochastically dominates at least one other sample.

In the assessment presented below both test methods have been employed with the Kruskal-Wallis one-way analysis including the hypothesis findings in the tables for each metal evaluated. The statistical assessments presented below show statistical differences that had a type I error of 0.05 or a $p < 0.05$ for the individual metal distributions for each sediment Type.

Overall, the statistical evaluation of concentration distributions of the individual sediment Types show for three metals (barium, copper, and vanadium) no significant difference in their distributions between sediment Types 1, 2 and 4 (insufficient data were available for assessment of Types 3 and 5). Four metals (cadmium, chromium, lead, and mercury) had concentration distributions in Type 1 sediments that significantly differed from their distribution in Type 2 and Type 4 sediments, while their distribution in Type 2 and Type 4 sediments did not significantly differ. The statistical evaluation for each metal, based on the metal concentration distributions in the individual sediment Types are detailed below.

Barium

Barium concentrations were associated with samples from three sediment Types (Type 1, 2, and 4). The number of samples from each Type and the number of Type 0 samples (no SSS data available) are provided in histogram form on **Figure B-1**.

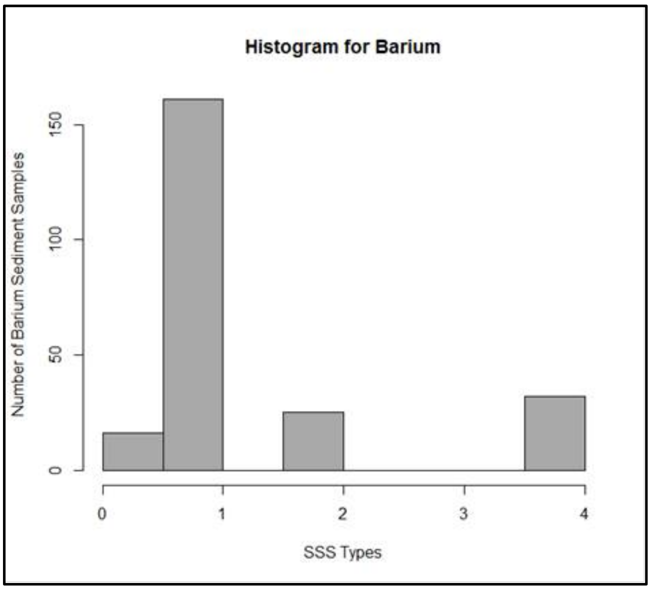

Figure B1 – Histogram for the Number of Barium Samples for Each SSS Type

Based on the results of the Wilcoxon Signed Rank Test provided in **Table B-1**, barium concentrations in sediment Types 1, 2, and 4 were not significantly different with a 95% confidence level ($p<0.05$) based on analysis of their mean ranks.

Table B1 – Pairwise Comparison of the Probabilities Using Wilcoxon Rank Sum Test for Barium (Bolded values represents the two groups are not significantly different)

Sediment Type	1	2
2	**0.13**	---
4	**1.0**	**0.33**

The Kruskal-Wallis Test results in **Table B-2** confirms the Wilcoxon Rank Sum Test that there is no significant difference at a 95% confidence interval ($p>0.05$) between the mean ranks of the sediment Type distributions.

Table B2 – Results of the Kruskal Wallis Tests for Barium

Sediment Type Comparisons	Observed Difference	Critical Difference	Difference
1-2	27.133292	32.46039	False
1-4	2.336083	29.22610	False
2-4	29.509375	40.30627	False

In summary, there is no significant difference in the barium concentrations between sediment Types 1, 2, and 4. The similarities are reflected in the box and whisker plot provided in **Figure A5** (**Attachment A**) with Types 1, 2, and 4 having similar population means on a log-scale with values of 1.71(+/-0.29), 1.58(+/-0.25), 1.78(+/-0.34), respectively.

Cadmium

Cadmium concentrations were associated with samples collected from three sediment Types (Types 1, 2, and 4). The number of cadmium samples from each Type and the number of Type 0 samples (no SSS Type assigned) are provided in histogram form on **Figure B-2**.

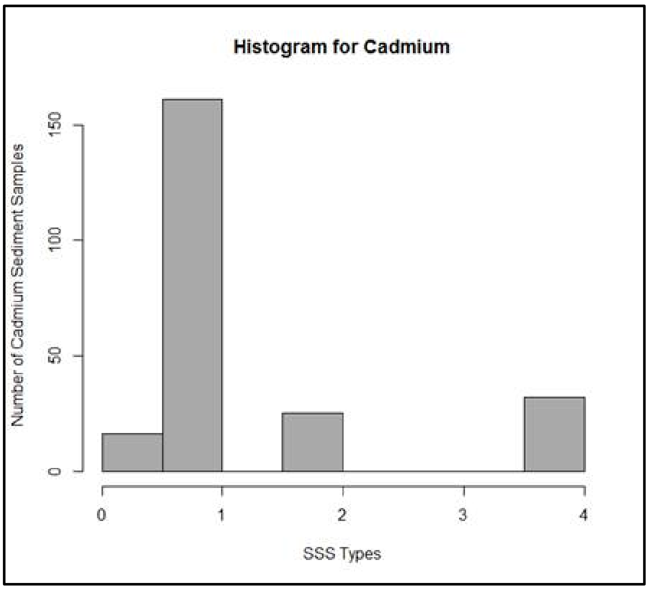

Figure B2 – Histogram for the Number of Cadmium Samples for Each SSS Type

Based on the results of the Wilcoxon Signed Rank Test provided in **Table B-3**, cadmium concentrations distributions for Type 1 sediments were significantly different with a 95% confidence level ($p<0.05$) based on the analysis of their mean ranks than cadmium concentrations distributions for the Type 2 and Type 4 sediments. The cadmium concentrations distributions in Type 2 and Type 4 sediments were not statistically different.

Table B3 – Pairwise Comparison of the Probabilities Using Wilcoxon Rank Sum Test for Cadmium (Bolded values represents the two groups are not significantly different)

Sediment Type	1	2
2	0.0109	---
4	0.0012	**1.0**

The Kruskal-Wallis Test results in **Table B-4** confirm the Wilcoxon Rank Sum Test results and show there is a significant difference at a 95% confidence interval ($p>0.05$) between the mean ranks of the Type 1 sediments cadmium distributions and the mean ranks of the Type 2 and Type 4 sediments cadmium distributions. The Kruskal-Wallis test results also show there is no significant difference between the cadmium concentrations distributions between the Type 2 and the Type 4 sediments.

Table B4 – Results of the Kruskal Wallis Tests for Cadmium

Sediment Type Comparisons	Observed Difference	Critical Difference	Difference
1-2	38.44671	32.46039	True
1-4	43.03921	29.22610	True
2-4	4.59250	40.30627	False

In summary, there is a significant difference in cadmium concentrations distribution for Type 1 sediments compared to the concentration distributions for Type 2 and Type 4 sediments. There is no significant difference in cadmium concentrations distributions between the Type 2 and Type 4 sediments. These differences are reflected in the box and whisker plots provided in **Figure A5** with the cadmium concentrations being much higher in the Type 1 sediments, having a population mean on a log-scale of -0.245 and a standard deviation on a log-scale of 0.827, while the Type 2 and Type 4 sediments concentrations had population means on a log-scale of -0.709 (+/-0.577) and -0.754 (+/-0.592), respectively.

Chromium

Chromium concentrations were associated with samples collected from sediment Types 1, 2, and 4. The number of chromium samples from each sediment Type and the number of Type 0 samples (no assigned SSS Type) are provided in histogram form on **Figure B-**3.

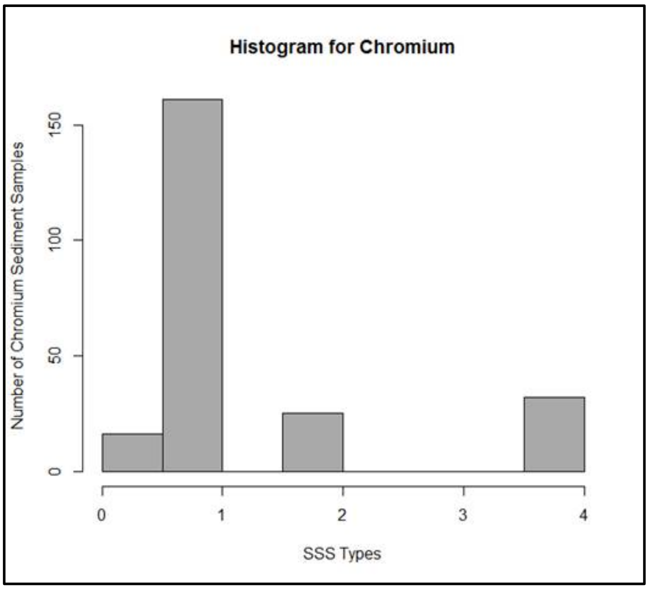

Figure B3 – Histogram for the Number of Chromium Samples for Each SSS Type

Based on the results of the Wilcoxon Signed Rank Test in **Table B-5**, the chromium concentrations distribution in Type 1 sediments was significantly different with a 95% confidence level ($p<0.05$) based on analysis of their mean ranks than the distribution in the Type 2 sediments. The Type 1 distribution was not significantly different from that in the Type 4 sediments, and there was no significant difference in the chromium concentration distributions in the Type 2 and Type 4 sediments.

Table B5 – Pairwise Comparison of the Probabilities Using Wilcoxon Rank Sum Test for Chromium (Bolded values represents the two groups are not significantly different)

Sediment Type	1	2
2	0.005	---
4	**0.059**	**0.791**

The Kruskal-Wallis Test results in **Table B-6** confirms the Wilcoxon Rank Sum Test and shows there is a significant difference at a 95% confidence interval ($p>0.05$) between the mean ranks of the chromium distributions in the Type 1 and Type 2 sediments. The results also show there is no significant difference between the distributions for the Type 4 sediments compared to the Type 1 and Type 2 sediments.

Table B6 – Results of the Kruskal Wallis Tests for Chromium

Sediment Type Comparison	Observed Difference	Critical Difference	Difference
1-2	43.41764	32.46039	True
1-4	27.92139	29.22610	False
2-4	15.49625	40.30627	False

In summary, there is a significant difference in chromium concentrations distribution for the Type 1 and Type 2 sediments, while there is no significant difference in chromium concentrations distributions between Type 4 sediment compared to the Type 1 or the Type 2 sediments. These differences are reflected in the box and whisker plots provided in **Figure A5**. The chromium concentrations for the

Type 4 sediments have a population mean on a log-scale of 1.141 and a standard deviation on a log-scale of 0.497, which is between the Type 1 and Type 2 sediments chromium concentrations with population means on a log-scale of 1.484 (+/-0.727) and 1.007 (+/- 0.497), respectively.

Copper

Copper concentrations were associated with samples collected from three sediment types (Types 1, 2, and 4). The number of copper samples from each sediment Type and the number of Type 0 (no SSS Type assigned) are provided in histogram form on **Figure B-4**.

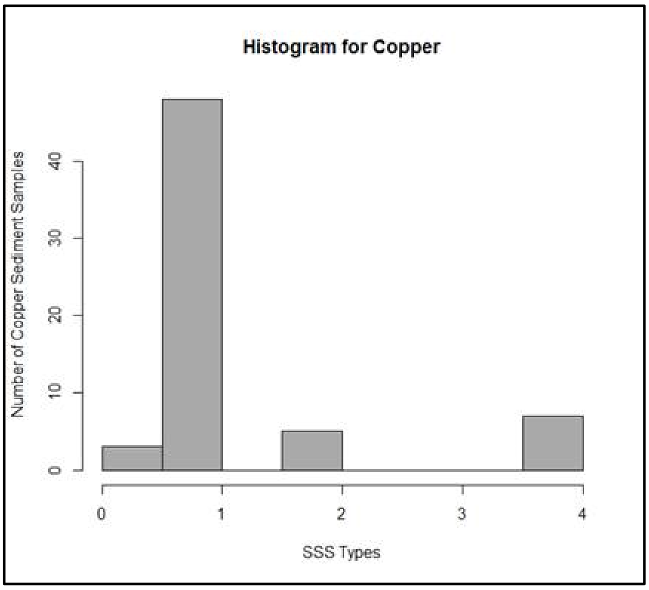

Figure B4 – Histogram for the Number of Copper Samples for Each SSS Type

The Wilcoxon Signed Rank Test results in **Table B-7** show there is no significant difference at a 95% confidence interval (p>0.05) between the copper concentrations distributions in sediment Types 1, 2 or 4.

Table B7 – Pairwise Comparison of the Probabilities Using Wilcoxon Rank Sum Test for Copper (Bolded values represents the two groups are not significantly different)

Sediment Type	1	2
2	**0.120**	---
4	**0.067**	**1.0**

The Kruskal-Wallis Test results in **Table B-8**, confirms the Wilcoxon Rank Sum Test that there is no significant difference at a 95% confidence interval (p>0.05) between the mean ranks of the copper distributions in the sediment Types 1, 2 and 4.

Table B8 – Results of the Kruskal Wallis Tests for Copper

Sediment Type Comparison	Observed Difference	Critical Difference	Difference
1-2	16.8125000	19.64729	False
1-4	16.3839286	16.91539	False
2-4	0.4285714	24.48088	False

In summary, there is no significant difference in the copper concentrations in sediments Types 1, 2, and 4. These similarities are reflected in the box and whisker plot provided in **Figure A5** with Type 1, Type 2, and Type 4 sediments having similar population means on a log-scale of 1.53(+/-0.38), 1.23(+/-0.22), 1.22(+/-0.20), respectively.

Mercury

Mercury concentrations were associated with samples collected from three sediment types (Types 1, 2, and 4). The number of mercury samples from each sediment Type and the number of Type 0 samples (no SSS Type assigned) are provided in histogram form on **Figure B-5**.

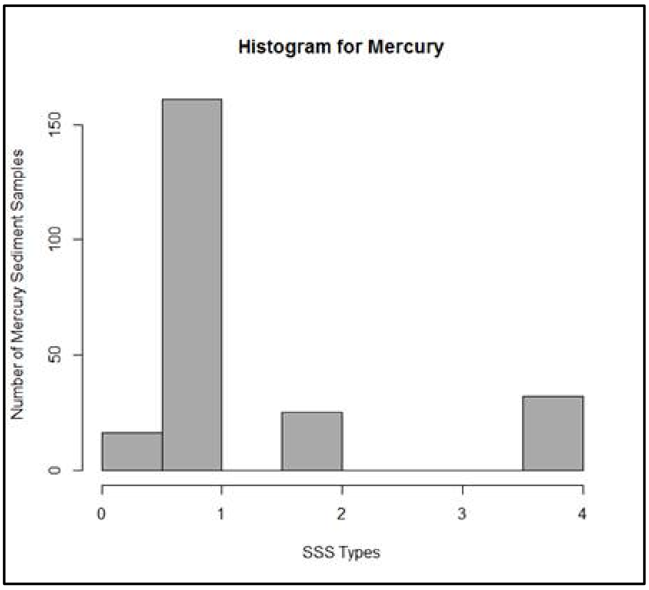

Figure B5 – Histogram for the Number of Mercury Samples for Each SSS Type

Based on the results of the Wilcoxon Signed Rank Test in **Table B-9**, mercury concentrations distributions for Type 1 sediments were significantly different with a 95% confidence level (p<0.05) based on the analysis of their mean ranks than mercury concentrations distributions in the Type 2 and Type 4 sediments. The Type 2 and Type 4 sediments distributions were not significantly different.

Table B9 – Pairwise Comparison of the Probabilities Using Wilcoxon Rank Sum Test for Mercury (Bolded values represents the two groups are not significantly different)

Sediment Type	1	2
2	0.02	---
4	0.01	**1.0**

The Kruskal-Wallis Test results in Table **B-10**, confirm the Wilcoxon Rank Sum Test and show there is significant difference at a 95% confidence interval (p>0.05) between the mean ranks of the mercury concentration distributions in Type 1 sediments compared to that for Type 2 and Type 4 sediments. The Kruskal-Wallis test results show there is no significant difference between the mercury concentration distributions for the Type 2 and Type 4 sediments.

Table B10 – Results of the Kruskal Wallis Tests for Mercury

	Observed Difference	Critical Difference	Difference
1-2	36.90857	32.46039	True
1-4	35.39732	29.22610	True
2-4	1.51125	40.30627	False

In summary, there is a significant difference in mercury concentrations distribution for Type 1 sediments compared to Type 2 and Type 4 sediments, while distributions in the Type 2 and Type 4 sediments did not differ significantly. These differences are reflected in the box and whisker plots provided in **Figure A5** with the mercury concentrations being much higher in the Type 1 sediments, having a population mean on a log-scale of -0.828 and a standard deviation on a log of 0.754, while the

Type 2 and Type 4 sediments had population means on a log-scale of -1.24 (+/-0.643) and -1.25(+/-0.679), respectively.

Lead

Lead concentrations were associated with samples from three sediment types (Types 1, 2, and 4). The number of lead samples from each sediment Type and the number of Type 0 samples (no assigned SSS Type) are provided in histogram form on **Figure B-6**.

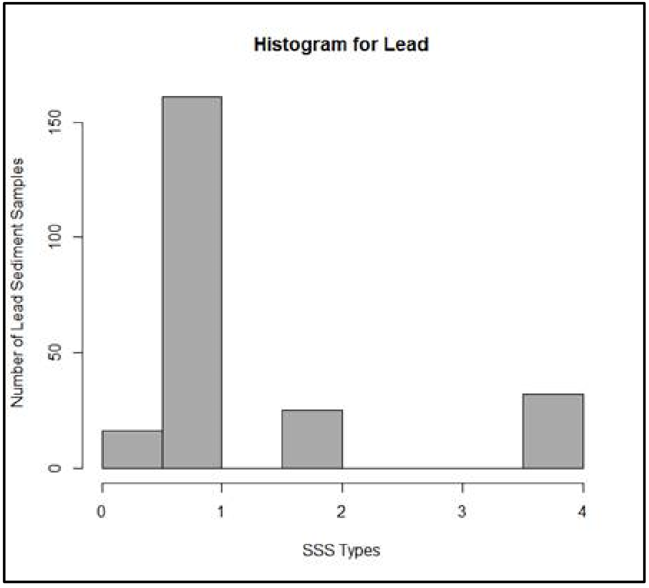

Figure B6 – Histogram for the Number of Lead Samples for Each SSS Type

Based on the results of the Wilcoxon Signed Rank Test in **Table B-11**, lead concentrations distribution in Type 1 sediments was significantly different with a 95% confidence level ($p<0.05$) than the distribution in Type 2 and Type 4 sediments. Lead concentration distribution between Type 2 and Type 4 sediments were not significantly different.

Table B11 – Pairwise Comparison of the Probabilities Using Wilcoxon Rank Sum Test for Lead (Bolded values represents the two groups are not significantly different)

Sediment Type	1	2
2	0.0134	---
4	0.0088	**1.0**

The Kruskal-Wallis test results in **Table B-12** show that there is a significant difference with a 95% confidence interval ($p>0.05$) between the mean ranks of the distribution for lead in the Type 1 sediments and the Type 2 and Type 4 sediments. There is no significant differences in the mean ranks distributions for the Type 2 and Type 4 sediments.

Table B12 – Results of the Kruskal Wallis Tests for Lead

Sediment Type Comparison	Observed Difference	Critical Difference	Difference
1-2	38.200870	32.46039	True
1-4	36.651495	29.22610	True
2-4	1.549375	40.30627	False

In summary, there is a significant difference in lead concentrations distribution for Type 1 sediments compared to the distribution in Type 2 and Type 4 sediments, while there is no significant difference in lead concentration distributions between the Type 2 and Type 4 sediments. This difference is reflected in the box and whisker plots provided in **Figure A5** with the lead concentrations being higher in the

Type 1 sediments, having a population mean on a log-scale of 1.58 and a standard deviation on a log-scale of 0.78 while the Type 2 and Type 4 sediments had population means on a log-scale of 1.09 (+/-0.65) and 1.10 (+/- 0.47), respectively.

Vanadium

Vanadium concentrations were associated with samples from three sediment types (Types 1, 2, and 4). The number of lead samples from each sediment Type and the number of Type 0 samples (no SSS Type assigned) are provided in histogram form on **Figure B-7**.

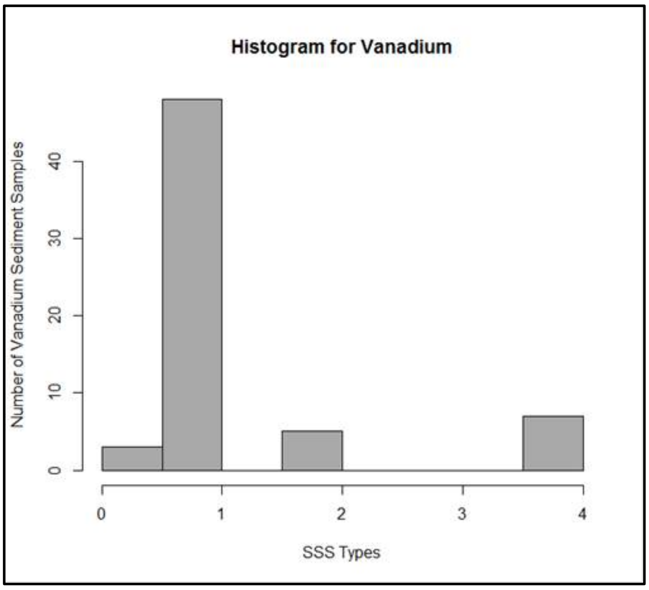

Figure B7 – Histogram for the Number of Vanadium Samples for Each SSS Type

Based on the results of the Wilcoxon Signed Rank Test provided in **Table B-13**, vanadium concentrations in the sediment Types 1, 2 and 3 were not significantly different with a 95% confidence level (p<0.05) based on the analysis of their mean ranks.

Table B13 – Pairwise Comparison of the Probabilities Using Wilcoxon Rank Sum Test for Vanadium (Bolded values represents the two groups are not significantly different)

Sediment Type	1	2
2	**0.160**	---
4	**0.065**	**1.000**

The Kruskal-Wallis Test results in **Table B-14** confirm the Wilcoxon Rank Sum Test that there is no significant difference at a 95% confidence interval (p>0.05) between the mean ranks of vanadium concentrations sediments Types 1, 2 and 4.

Table B14 – Results of the Kruskal Wallis Tests for Vanadium

Sediment Type Comparison	Observed Difference	Critical Difference	Difference
1-2	15.9395833	19.64729	False
1-4	16.3824405	16.91539	False
2-4	0.4428571	24.48088	False

In summary, there is no significant difference in the vanadium concentration distributions between the three sediment Types 1, 2, and 4. These similarities are reflected in the box and whisker plot provided in **Figure A5** with Type 1, Type 2, and Type 4 sediments having similar population means on a log-scale, with values of 1.41(+/-0.27), 1.14(+/-0.19), 1.15(+/-0.18), respectively.

Summary

A statistical evaluation of concentrations relative to sediment types was undertaken using the Wilcoxon Sign Rank and Kruskal Wallis Tests. Both test methods are non-parametric tests used to assess the potential differences in populations relative to an independent variable. Barium, copper, and vanadium showed no significant difference in their distributions between sediment Types 1, 2 and 4 (insufficient data were available for assessment of Types 3 and 5).

Four metals (cadmium, chromium, lead, and mercury) had concentration distributions in Type 1 sediments that significantly differed from their distribution in Type 2 and Type 4 sediments, while their distribution in Type 2 and Type 4 sediments did not significantly differ. The differences in these metal concentrations between sediment types reflects higher concentrations within Type 1 sediments. This finding is consistent with the observations from analysis of the box plots. Median values for these four metals were higher and the interquartile range larger in Type 1 sediments ls than other sediment types. This statistical finding and the distribution of the data indicates that cadmium, chromium, lead and mercury are preferentially distributed in fine grained Type 1 sediments.