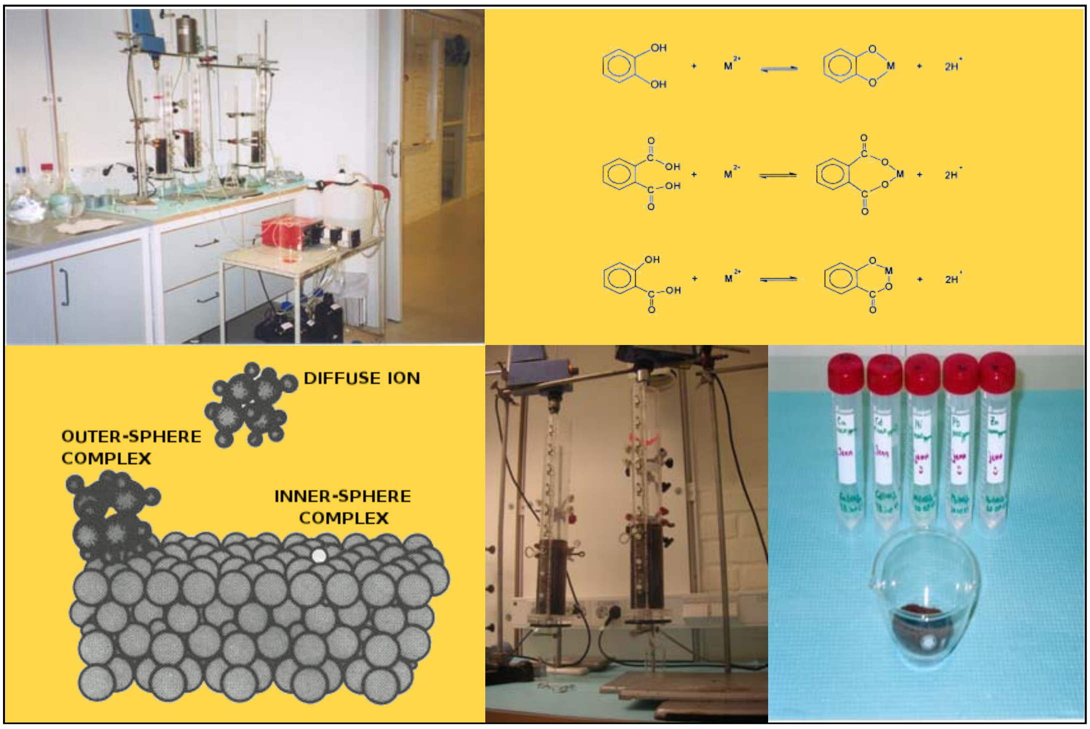

Competitive Adsorption and Displacement Behaviour of Heavy Metals on Peat

Master of Science Thesis in Applied Environmental Measurement Techniques

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Department of Civil and Environmental Engineering
Division of Water Environment Technology
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Cover photos (clockwise, from upper-left):
Experimental set-up for metal displacement experiments on peat; mechanisms of metal complexation on humic substances (Dupuy and Douay, 2001); metal-nitrate solutions and ground dry peat; modified column set-up for metal adsorption experiments on peat; types of complexes formed on surfaces and in aqueous solution (Sposito, 1989).

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ABSTRACT

Adsorption is recognized as an effective process of metal ion removal from contaminated water. Peat is a material that has been investigated as a metal adsorbent because of its advantages in terms of both adsorption efficiency and economic viability. The organic components of peat, particularly the humic substances, are mainly responsible in providing negatively-charged adsorption sites on which metals bind through several mechanisms. Metal adsorption on peat is thought to occur through a combination of physical adsorption, ion-exchange, and complexation. The selective adsorption of metals is influenced by factors such as pH, metal speciation, ionic strength, and properties that are inherent to the target metal.

The long-term viability of peat as an adsorbent requires that the material should be able to bind and adsorb metals for long periods of time. The possibility of displacement of an adsorbed toxic heavy metal upon additional loadings of other metals is therefore a concern that needs to be examined. Only few studies have been done about displacement on peat. Thus, there is a need for the development of a method to analyse the dynamics of competitive adsorption and displacement.

In this study, the displacement of Cd and Pb from peat due to competition with Cu, Ni, and Zn ions was investigated. The occurrence and extent of displacement was shown to be closely related to pH, as this influences the metal species present in solution as well as the corresponding ionic charges. The preference of peat adsorption for one metal over another was also dependent on the solution pH level. Properties such as electron configuration and ionic size also contribute to the effectiveness of a metal in competitive adsorption. Cadmium was shown to be more easily displaced than Pb, as higher aqueous concentrations of Cd were measured in the presence of competing metal ions. The binding of Pb ions to peat was found to be effective at pH < 7. Among the competitor ions, Ni was found to be most effective at pH 4, Cu was the most effective at pH 5.6, and Zn at pH 7.

The displacement of Cd and Pb from the peat surface is a function of the following factors: a) the pH-dependent speciation of Cd or Pb; b) the pH-dependent speciation of the competing metals; and, c) the type and strength of complexation of Cd or Pb compared to that of the competing metal. The results obtained from the experiments were consistent with predicted and observed behaviour in related studies.

The competitive adsorption and displacement of heavy metals on peat are processes that have yet to be fully understood. Improvements in the experimental set-up are necessary in order to more closely approximate the actual distribution of metal species on the adsorbent and in solution. The precision of the analytical method also needs to be tested in order to detect areas of further development.

Keywords: Competitive adsorption, displacement, peat, heavy metals, humic substances, pH-dependent speciation, method development

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Jenny Perez Holmberg

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Chapter 1: Introduction

Widespread industrialisation has resulted in the release of numerous harmful substances. Heavy metals, although mostly found in nature, are artificially discharged at much higher concentrations, a significant amount of which accumulate in both soil and water systems. Metal cations in their soluble form pose a great threat, as these are easily transported and taken up by living ecosystems. The removal of heavy metals from industrial wastewater is thus very important.

Adsorption is recognized as an effective process of metal ion removal from aqueous solutions. A number of materials have been studied in the past in terms of efficiency for metallic adsorption as well as economic viability. One of these is peat, a natural material found in abundance and possessing favourable adsorptive characteristics.

Peat is a complex material that has several organic components, such as lignin, cellulose and humic acids, which have specific influences on the adsorption of metals. The heterogeneity of its surface and pore structure provide numerous adsorption sites which may also act selectively in terms of affinity for certain metals. These features and the multi-component character of contaminated waters, make the adsorption and removal of metals a complex and competitive process.

This project attempts to understand the physical and chemical processes involved in the adsorption of heavy metals on peat, with emphasis on the competition and displacement behaviour of Cd, Pb, Cu, Ni, and Zn.

1.1. Objectives of the study

The main objectives of the study are:

1. To understand the competition and displacement behaviour between heavy metals on adsorption sites on peat
2. To develop a method for the analysis of displacement involving binary metal/peat solutions

This pilot study is a part of a larger-scale research on adsorption materials used as potential in-situ remediation alternatives for contaminated areas (Kalmykova et al., 2006a). The methods applied and the results obtained from the experiments can be used in further methodology development, as displacement behaviour between metals is a significant aspect of adsorption dynamics that needs to be understood. The information obtained can also be used in future studies involving tertiary and other multi-component aqueous metal solutions.

1.2. Background of the study

Peat moss is a complex organic material, which is derived from the partially decomposed residue of sphagnum moss, sedges and other plants in the water-logged environment of marshes, bogs, and swamps. The precise composition of the peat formed depends on such factors as the nature of the vegetation, the regional climate, the acidity of the water, and the degree of metamorphosis. Peat is mostly composed of lignin and hemicellulose, which partly break down to humic substances. These substances bear polar functional groups, such as alcohols, aldehydes, ketones, carboxylic acids, phenolic hydroxides, and ethers that can be involved in chemical bonding. The polar characteristics of peat make the specific adsorption potential for dissolved solids, such as metals and polar organic molecules, quite high. This has lead to the examination of the potential of peat as an agent for the purification of wastewaters contaminated with dissolved metals (Chaney and Hundemann, 1979; Spedding, 1988; Brown, P.A. *et al.*, 2000; Chauvet, 2003).

In industrial applications, precipitation has been the most common technology for metal removal. However, precipitation can only reduce the dissolved metal concentration to the solubility product constant. Not only is this insufficient to meet stringent standards for the removal of toxic metals, the necessary "polishing" stages entails additional expenses to the already large costs of contaminated sludge management (Patterson, 1989; Brown, P.A. *et al.*, 2000). Guideline values that set the limit for heavy metals in Swedish waters can require levels that are < 5 µg/L (Sedin, 2002). Treatment of metallic wastewater should thus be efficient enough to address removal at low concentration conditions. The common methods for the removal of metals at lower concentrations, such as electrolyte extraction, reverse osmosis and cementation, are often economically unfavourable and/or technically complicated. The costs are prohibitive for wide-scale remediation of contaminated areas (Brown, P.A. *et al.*, 2000). If Sweden is to be at the forefront of contaminated land rehabilitation, technically-sound but cost-effective approaches need to be explored and utilised. Adsorption and/or ion-exchange onto low-cost media such as peat now offer an attractive, inexpensive option for the removal of colloidal and dissolved metals. Prepared sphagnum peat moss is less than 10% of the cost of active carbons and molecular sieves (Ho, Y.S. and McKay, G., 1999).

The use of natural and rest-product materials as filters for metallic wastewater has been investigated in earlier thesis projects at Chalmers. Part of these involved the analysis of peat in batch experiments using single-metal solutions and column experiments using heterogeneous multi-component leachate from an industrial landfill (Chauvet, 2003; Kalmykova, 2004). The efficient performance of peat as an adsorbent was demonstrated in these experiments. However, the efficiency of peat as a long-term option for the treatment of metallic wastewater needs to be proven. This means not only analysing for metal adsorption properties, but also studying the possible desorption or displacement of metals in the presence of competing ions. Desorption and displacement of metals is a particularly important process for soils that are already contaminated. To predict the fate and mobility of contaminants in such soils and to develop sound and cost-effective remediation strategies, information on desorption is required. If this process is extremely slow or if little to no desorption occurs, there is less threat to ground water. In contrast, if the process occurs easily, it brings possible contamination of water supplies (Sparks, 1995). With this in mind, this project tests the ability of peat to maintain already adsorbed metals despite additional metal loads.

1.3. Scope and Limitations

The experiments focused mainly on the competitive adsorption among Cd, Pb, Cu, Ni, and Zn. Displacement behaviour was studied using binary solutions, with Cd and Pb as the targets of displacement. The experimental methodology was designed for the purpose of determining whether or not Cd or Pb that is adsorbed on peat can be displaced back into aqueous solution by progressive additions of a competing metal ion. The working hypothesis is: a metal that is more favourably adsorbed will displace Cd or Pb from peat in concentrations that are proportional to the amount of metal added to solution.

An analysis of competitive and displacement dynamics necessarily involves adsorption thermodynamics. Although some aspects are highlighted in the analysis, the thermodynamics of the interactions is not discussed in full detail. Langmuir or Freundlich adsorption isotherms were not empirically determined for the systems in this study. Instead, such information was referred from previous studies in literature.

It is also emphasized that the study was an initial attempt in understanding the mechanisms involved in the displacement of metals and that methodology development is one of the main objectives. This is a small-scale pilot study that can serve as the basis for more detailed investigations on metal displacement from peat. The results obtained from the study are indicative of adsorption trends, but these only form only a partial picture and may not be sufficient to establish a valid model for the displacement of metals from peat.

Chapter 2: Review of Related Literature

2.1 Studies on metal adsorption by peat

Studies on peat as an adsorbent material date back to the 1970s. However, rising costs of wastewater treatment have encouraged more investigations on the adsorption capacity of peat for heavy metals and other unwanted substances.

The potential of peat as an agent for wastewater purification was studied in 1974 by Lalancette and a follow up study in 1976 showed that dry peat can adsorb most metals efficiently up to 4% of its weight (Lalancette, 1974; Coupal and Lalancette, 1976). The ability of peat components to capture heavy metals was further explored in a number of studies, some of which, along with the findings relevant to metal adsorption, appear in **Table 1**.

Field testing was also conducted on the use of peat for the treatment of wastewater. The natural ability of peat bogs to retain heavy metals was studied in the early 1980s, when marshland was used to treat sewage as well as mining stockpile leachate. In these studies, it was found that the removal of trace metals from solution can cover a range of 30 - 100%, with > 30% removal of Ni and > 99% removal of Cu (Eger *et al.*, 1980; Pakarinen *et al.*, 1981; Glooschenko and Copobianco, 1982). A full scale treatment plant using beds of un-drained and treated peat was tested as a low-cost treatment option for landfill leachate (Heavey, 2003).

Several species in aqueous solution can influence metal adsorption by peat. In a mixture of metals, the total adsorption of metals is observed to increase, but individual species adsorption is reduced through metal interaction and competition for adsorption sites (Hanzlik et al., 2004). The uptake of a particular ion may be less than if it was present alone, but the total adsorption capacity of peat increased (Brown, 1993). The presence of Na^+ ions was found to reduce the sorption of other metals. The reduction of adsorption when monovalent ions are present indicates a buffering action of sorption sites (Dissanayake and Weerasooriya, 1981). The difference in effects of Ca found within the peat structure vs. Ca in solution on total sorption has been illustrated in a number of studies (Wolf *et al.*, 1977; Brown, P.A. *et al.*, 2000). It was found an increase in the concentration of Ca in peat enhanced the sorption of certain heavy metals, such as Pb, Cd, Cu, and Zn, but increasing the Ca concentration in aqueous solution reduced sorption.

Table 1: Overview of selected studies on metal adsorption by peat (adapted from Kalmykova)

Author/year	Metals removed	Working concentrations	Equilibrium time used[1]	Experimental conditions/ Relevant findings
(Ho et al., 1995)	Ni	10 – 200 mg/L	4 hours	• H^+ released when Ni is adsorbed, release is proportional to the Ni concentration. • Equilibrium time was dependent on initial concentration.
(Crist et al., 1996)	Ca, Zn	0.1 M	30 minutes	• Overall displacement as a 3-fold mechanism characterised by a fast first step. The slower succeeding steps implied a slow ion transport within the solid phase.
(Gardea-Torresdey, 1996)	Cu	0.5 g peat/100 mL metal solution	1 hour	• Some of the humic acids were found to be soluble at pH > 4. • Humic acid has the highest sorption capacity among peat humic substances.
(McKay and Porter, 1997)	Cu, Cd, Zn		24 hr contact time (equilibrium at 6 hrs)	• The presence of humic acids was considered to be primarily responsible for metal ion adsorption onto peat.
(Ho, Y. S. and McKay, G., 1999)	Pb	200 – 500 mg/L	4 hours	• The rate of Pb uptake increased rapidly with temperature. • Agitation of the mixture only has a small influence on the equilibrium time. Sorption increased slightly with agitation speed.
(Twardowska and Kyziol, 2003)	Cu, Cd, Zn	1 – 7500 mg/L	12 hours	• The presence of complexing anions and contact mode affect sorption capacity and binding strength of peat.
(De la Rosa *et al.*, 2003)	Cd, Cu, Pb, Ni, Cr	Multi-metal, 100 – 400 µg/L	1 hour	• No difference in sorption at pH 5 – 6 • Oxidation state of Cr was found to influence the sorption of other metals. • Different functional groups may be responsible for binding at low and high concentrations.
(Hanzlik et al., 2004)	Ag, Cd, Cu	25, 50, 2000 mg/L	60 hr contact time (max. removal in 1st 5 hours)	• Single, binary and tertiary metal mixtures were used. • In a mixture, the total adsorption of metals increased, but individual species adsorption was reduced.

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[1] Equilibrium time is the time at which no change has been observed in the concentration of the solute on the solid surface or in the bulk solution. Some authors used a contact time longer than the equilibrium time for the system.

Most adsorption studies on peat assume ion exchange as the main mechanism of metal ion adsorption and focus on humic and fulvic acid components as main adsorption agents. The majority utilise measurements of metal concentration in the aqueous phase. Direct analyses of metals attached on the adsorbent are quite rare. An example is a study that attempted to understand the kinetics of cation displacement by direct measurements of species that were sorbed on the solid phase (Crist *et al.*, 1996). It was discovered that the overall displacement process is a 3-fold mechanism. First is a very fast step characterised by a high rate constant, followed by two processes that involve slow ion transport within the solid phase

The mechanism of metal binding on peat is an area of great debate. Ion exchange, complexation and surface adsorption are the most prevalent theories in metal ion adsorption. The heterogeneity of peat in terms of different locations of origin and degrees of decomposition, in addition to differences in experimental methodology, makes comparison of study results difficult (Brown, P.A. *et al.*, 2000).

2.2 Preferential adsorption – predicted trends and observed results

Several authors have proposed different criteria for the preferential adsorption of metal ions on peat. The affinity of metals for organic adsorbents has been hypothesized as a function of properties such as ionic size, electronegativity and standard reduction potential, among others. These have been used to predict adsorption behaviour and to explain observed results in experimental trials. Depending on whether the adsorption occurs by electrostatic surface interactions (i.e., positive ions adsorbed physically on peat without bond formation), ion exchange, or chelate formation, a corresponding set of properties can explain the relative order of metal adsorption and give an indication of which ion will be more successful or will likely be displaced in the presence of competitors. In most systems, metals can attach to peat through a combination of processes. Thus, a several factors may be used to explain competitive adsorption behaviour.

Listed in **Table 2** are trends in metal adsorption (an expanded version is found in **Appendix B**) for the metals selected for this study (Cd, Cu, Ni, Pb, and Zn). These trends are based both on behaviour predicted by ionic properties and observations made in experimental results. A combination of properties may account for the success of a particular metal ion in competitive adsorption, and the trends in this section will be compared later on with the experimental results in the displacement experiments.

Table 2: Metal adsorption trends predicted in literature and/or observed in experiments

Property	Trends	Rationale	Authors cited
A. Properties related to electrostatic interactions (physical adsorption and/or ionic bonding)			
Charge and hydrated radius, hydrated ion size	$Pb^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+}$	Ions with the higher charge and the smaller hydrated radius have higher affinity; greater polarization facilitates electrostatic ion exchange.	(Helfferich, 1962; Sparks, 1995; Xiao and Thomas, 2004)
Ionic Potential (Charge-to-radius ratio)	Ni > Cu > Zn > Cd > Pb	Effect on ionic bonding - the strongest bond should be formed by the metal with the greatest charge-to-radius ratio. Removal of metals from solution is sequential according to the ionic potential.	(Ong and Swanson, 1966; McBride, 1994)
B. Properties related to covalent bonding, complexation and redox			
Electronegativity (Pauling)	Cu > Ni > Pb > Cd > Zn	The more electronegative metals should form the strongest covalent bonds with O atoms on any particular mineral surface.	(McBride, 1994; McKay and Porter, 1997; Brown, T.L. *et al.*, 2000)
Standard reduction potential	Cu > Pb > Ni > Cd > Zn	The trend corresponds closely with electronegativity in explaining the relative complexing strength of Cu compared to those of Cd and Zn.	(McKay and Porter, 1997; Brown, T.L. *et al.*, 2000)
Irving-Williams order of complexing strength (metal ion radius & electron configuration)	Cu > Ni, Zn	Divalent metals of smaller radius generally from the stronger complex with organic ligands. But for transition metals, it is a factor of both radius and electron configuration.	(Sposito, 1989; McBride, 1994)
Intrinsic binding constants	$Cu^{2+} > Pb^{2+} > Ni^{2+} \sim Zn^{2+} > Cd^{2+}$	Related to pH metallic speciation, the numbers are a good indicator of the relative extent of complexing to be expected between the individual metals and natural dissolved organic matter. Also accounts for electrostatic attraction/repulsion, and takes account of non-specific binding due to counterion accumulation.	(Tipping and Hurley, 1992; Drever, 1997)

C. Other trends observed in experimental results		
Metal ion-exchange	Pb > Cu > Zn	(Chen et al., 1990)
Sorption of metals	$Pb^{2+} > Cu^{2+} > Zn^{2+}$	(Pakarinen et al., 1981)
Affinity for peat	$Cu^{2+} > Zn^{2+} > Ni^{2+}$	(Maslennikov and Kiselva, 1989; Chistova *et al.*, 1990)
Adsorption efficiency	Cu > Pb > Zn	(Kalmykova et al., 2006a)
Sorption capacity	Pb > Cu > Ni > Cd > Zn	(Kalmykova et al., 2006b)

Based on the information presented in **Table 2**, Cu and Pb are expected to be the more successful metals in terms of competitive adsorption. Cadmium, Nickel and Zinc are in variable ranking, depending on the property that is relevant. The trends are helpful in understanding the behaviour of these metals in multi-element solutions. However, the information shown above is an aggregate of data obtained from different types of adsorbent at varied pH and ionic concentrations. Experimental testing has to be done in order to check the performance of the metals in the specific conditions outlined in this study.

Unfortunately, no consistent rule of metal selectivity for organic matter can be given, as selectivity depends on a number of factors beyond the properties of the metals themselves, including: a) the chemical characteristics of the organic ligands, such as the type of functional group involved in binding; b) the pH at which adsorption is measured; and, c) the ionic strength of the solution in which adsorption is measured, as this determines the intensity of competition by other cations for the complexing sites (McBride, 1994).

Chapter 3: Theoretical Concepts

3.1 Adsorption processes on peat

3.1.1 Fundamentals of adsorption

Adsorption is defined as the increase in concentration of a particular component at the surface or interface between two phases (Faust and Aly, 1998). In this case, the interaction of H^+ and metal ions between the solid peat and the surrounding aqueous solution is the main focus.

Adsorption processes may be classified as physical or chemical. The nature of the forces that attract ions or molecules to the solid surface determines the characteristics of the binding and gives rise to the classification. Physical adsorption (or physisorption) does not involve the sharing or transfer of electrons and is essentially reversible. It has a low degree of specificity; thus, adsorbed molecules are free to cover the entire surface of the adsorbent. A physisorbed molecule keeps its identity and upon desorption returns to the fluid phase in its original form. Chemisorption, on the other hand, involves chemical bonding and is essentially irreversible. Chemisorbed species are fixed at specific sites and are linked to reactive parts of the adsorbent surface, confining the adsorption to a monolayer. The extent of chemical adsorption is dependent on the reactivity of the adsorbent and adsorptive (Faust and Aly, 1987; Faust and Aly, 1998; Rouquerol *et al.*, 1999). Many cases are actually an intermediate of physical and chemical adsorption, with both pore structure and reactive functional groups contributing to metal removal. Such is the case with peat (Chauvet, 2003).

The removal of ions from aqueous solutions involves concentration of the solute on the solid surface. As the adsorption proceeds, solutes are simultaneously adsorbed and desorbed. Eventually the rates of adsorption and desorption will attain an equilibrium state, called the adsorption equilibrium. At equilibrium, no change can be observed in the concentration of the solute on the solid surface or in the bulk solution. The position of equilibrium is characteristic of the entire system and is dependent on the solute, adsorbent, solvent, temperature and pH, among others (Faust and Aly, 1987).

3.1.2 The role of humic substances in proton and metal adsorption

The influence of the chemical composition of natural organic matter on the binding of heavy metals has yet to be fully explored. However, humic substances are considered to be main adsorption agent in peat. Humic substances are extremely complex, and polydisperse[2] mixtures of natural organic compounds formed during the microbial decomposition of plant and animal debris in terrestrial and aquatic environments (Kretzschmar and Christl, 2001). Almost 50% of peat consists of humic substances (Chauvet, 2003). Depending on the source materials, degree of decomposition and environmental conditions, humic substances of different overall composition are found. Humic substances consist of a chemically heterogeneous mixture of compounds, and cannot be regarded as single chemical entities characterised by unique, chemically defined molecular structures (Senesi and Loffredo, 1999). The heterogeneity of humic substances results in wide distributions of binding affinities for each ion. Despite the contribution of some chemical models to the understanding of proton and metal cation binding on humic substances, the influence of chemical differences is still unclear (Kretzschmar and Christl, 2001).

Humic substances are capable of interacting with metal ions to form metal-organic complexes of different stabilities and characteristics. Oxygen functional groups are involved in the formation of surface complexes with aqueous metal species and ion exchange with the displacement of protons. The capacity of humic and fulvic acids to combine with metals is usually attributed to their high contents of substituents such as carboxyl (COOH), hydroxyl (OH), and carbonyl (C=O) (Piccolo and Stevenson, 1982; Xiao and Thomas, 2004).

The mechanisms of interaction between divalent metal ions and oxygen functional groups on humic substances are illustrated in **Figure 1**. Previous investigations have suggested a number of chelate linkages. One possibility is a linkage between a metal and two adjacent hydroxyls in a benzenediol (catechol) component, as shown in **Reaction 1** (Stevenson, 1982; Dupuy and Douay, 2001). Several investigations have suggested two main types of chelate linkages, one involving two carboxylic groups in close proximity to form a phthalate-like ring, seen in **Reaction 2**. The other involves a carboxyl and an adjacent phenolic OH to form a salicylate-like ring, shown in **Reaction 3** (Schnitzer and Skinner, 1965; Gamble *et al.*, 1970; Piccolo and Stevenson, 1982). Infrared spectroscopic measurements of soil humic substances yielded results indicative of the participation of conjugated ketone structures, which are known to form complexes with transition metal ions (Piccolo and Stevenson, 1982). The mechanisms of interactions between ketone carbonyls and divalent metals are shown in **Reactions 4 and 5**.

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[2] Polydisperse – a term used to describe a polymer consisting of molecules with a variety of chain lengths and structures. Polydisperse substances can exist over a wide range of molecular masses; average weights are commonly used.

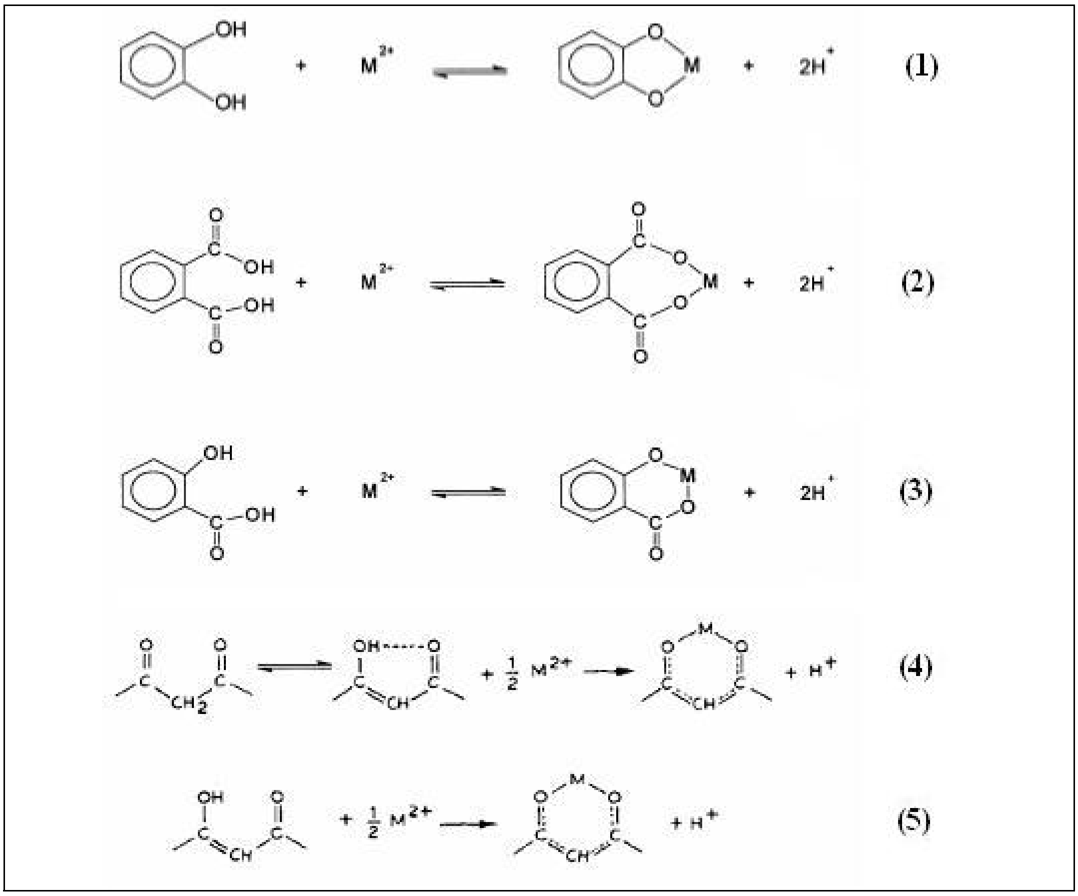

Figure 1: Mechanisms of complexation between metal ions and functional groups on humic substances (Piccolo and Stevenson, 1982; Dupuy and Douay, 2001)

The ease of dissociation of a particular –COOH group depends on the nature and position of the other functional groups close to it in the same molecule. Oxygen containing functional groups adjacent to the carboxylic acid group generally cause an increase in acid strength, and dissociation occurs at a lower pH. Phenols are generally much weaker acids than carboxylic acids, but their dissociation likewise depends on the nature of other functional groups nearby in the molecule. Phenol groups form strong complexes with metal ions (as seen in **Reaction 1**) and a phenol group adjacent to –COOH (**Reaction 3**) is a very effective chelator (Drever, 1997).

There is controversy as to which functional groups are more significant in metal binding, and whether the linkages are ionic or covalent. Covalent bonds may be formed at low degrees of metal-ion saturation, but bonding may become increasingly ionic in character as binding capacity is approached. The structures of humic acids are difficult to define because their compositions change with the type of soils and are never known exactly, adding to variations in experimental conditions. Nevertheless, the diversity of results obtained from numerous analyses of humic-metal chelation implies that the formation of mixed complexes is likely (Piccolo and Stevenson, 1982; Dupuy and Douay, 2001).

3.1.3 Surface complexes vs. diffuse ions

Complexation is one of the two important processes (the other being ion exchange) in metal ion adsorption on peat. It occurs whenever a molecular unit, such as a metal ion, acts as a central group and forms a close association with functional groups on the peat surface. In the case of humic substances on peat, the phenolic, carboxylic and carbonyl functional groups serve as ligands[3] that bind with metal ions. If the central group and ligands in a surface complex are in direct contact, the complex is called *inner-sphere*. If one or more water molecules are interposed between the central group and a surface ligand, the complex is *outer-sphere*. If all the ligands surrounding the central atom in a complex are water molecules, such as $Ca(H_2O)_6^{2+}$ for example, then it is a *solvation complex*. A solvated metal ion that does not form a complex with a charged surface functional group is denoted as a *diffuse ion* (Sposito, 1989). The different types of metal complexes are illustrated in **Figure 2**.

Outer-sphere complexation is usually a rapid process that is reversible. Adsorption by outer-sphere complexation is affected by the ionic strength of the aqueous phase, and occurs only on surfaces that are of opposite charge to the adsorbate. (In the case of metal-peat interaction, complexation is on negatively charged surface sites.) Outer-sphere complexation involves electrostatic interactions and are weaker than inner-sphere complexes (Sparks, 1995).

On the other hand, inner-sphere complexes are usually much more stable than outer-sphere complexes because it involves either ionic or covalent bonding, or a combination of both. The driving force for inner-sphere complexes is the heat evolved through strong bond formation between the central ion and the surface ligand (Sposito, 1989). Inner-sphere complexation is usually slower than outer-sphere complexation. It is often irreversible and adsorption by this mechanism is weakly affected by the ionic strength of the aqueous phase. Adsorption of ions via inner-sphere complexation can occur on a surface regardless of surface charge (Sparks, 1995).

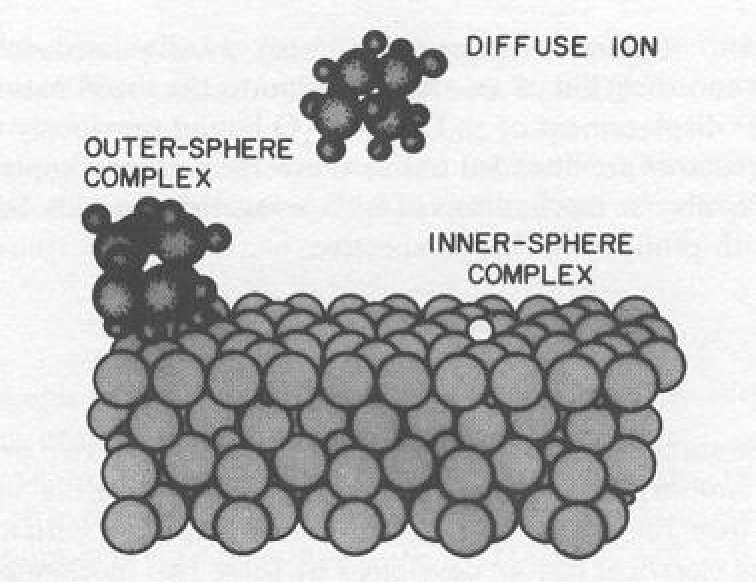

Figure 2: Types of complexes formed on surfaces and in aqueous solution (Sposito, 1989)

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[3] A ligand is a molecule or ion with at least one pair of unshared electrons available for coordinate bonding with cations.

Divalent heavy metals can undergo inner-sphere complexation either via one surface site on peat (monodentate complexation), or by attaching to two adsorption points on peat (bidentate), forming a chelate structure (Sparks, 1995).

Solvated ions that do not complex with a charged surface functional group, but instead neutralise surface charge only in a delocalised sense, is said to be adsorbed in a diffuse ion swarm. Ions that undergo inner-sphere surface complexation are said to be involved in specific adsorption. In contrast, diffuse-ion association and outer-sphere complexation are classified as non-specific adsorption. Only species adsorbed as fully solvated ions are readily exchangeable, with the molecular definition of “readily exchangeable” based on the diffuse ion swarm and outer-sphere complex mechanisms of adsorption (Sposito, 1989).

In real systems, outer and inner-sphere complexation can, and often do, occur simultaneously (Sparks, 1995).

3.1.4 Factors affecting heavy metal adsorption on peat

A number of factors are responsible for influencing the extent of heavy metal adsorption on peat. The specific surface area of the solid adsorbent is important, as the adsorptive capacity generally increases with an increase in specific surface area. Pore structure and particle size are related factors, as the surface area of nonporous adsorbents increases considerably with a decrease in particle size. However, for highly porous adsorbents, most of the surface area resides in the internal pore structure, resulting in the adsorptive capacity being independent of particle size (Faust and Aly, 1998). Under microscopic examination, peat exhibits a porous, cellular structure (McKay and Porter, 1997). The porous characteristic of peat contributes to the effectiveness of physical adsorption. However, the degree and rate of chemisorption of metals on peat is controlled by other factors, and surface area is only one contributor.

The number of available adsorption sites on peat is pH dependent. The dissociation of protons from carboxylic and phenolic groups determines the charge of the peat surface. Below pH 2.5 - 3.0, the surface is positively charged while at pH > 3.0, the surface is negatively charged and favours cation adsorption (Kalmykova et al., 2006a). The optimum pH for metal removal from aqueous solution also varies, depending on the target metal. Copper(II) is most effectively removed at pH 4.0, while Cd^{2+} and Zn^{2+} are more readily removed at pH levels greater than 5.0 and 5.5, respectively. The initial pH was found to be the controlling factor in the efficiency of Ni removal. The effective range is from pH 4.0 - 7.0, with the optimum at pH 7.0. Below the pH range of 3.0 - 3.5, the removal for most metal ions from solution ceases (Ho *et al.*, 1995; Brown, P.A. *et al.*, 2000). The effect of pH on metal cation adsorption is principally the result of changes in the net proton charge on particles. As pH increases, the amount of H^+ and its associated positive charge decreases, while the electrostatic attraction of an adsorbent for a metal cation is enhanced (Sposito, 1989).

The initial concentration of metals in aqueous solution is another factor to consider in sorption kinetics. Studies have shown that the greater the initial concentration, the longer the contact time needed for metal removal. Previous investigations have reported that peat is most efficient at removing metals from wastewater when the flow rates are slow, the quantity of wastewater to be treated is small, and the ion concentrations are low (Brown, P.A. *et al.*, 2000). However, in terms of total metal removed, the percentage of adsorption was found to be independent from the initial concentration when single-metal solutions with concentrations < 10 mg/L were used (Kalmykova et al., 2006a). Furthermore, equal initial concentrations for several metals do not mean that these will be removed from solution to an equal extent. Adsorption of metals on peat is preferential and can be governed by properties other than ionic strength of solution, as proposed earlier in **Section 2.2**.

Temperature is also an influencing factor that was observed in some studies on peat. Thermodynamic conditions for the spontaneity of adsorption results in the reduction of the equilibrium adsorptive capacity with an increase in temperature. Correspondingly, a decrease in temperature favours an increase in adsorptive capacity (Faust and Aly, 1998). Adsorption data for copper, nickel and zinc at varied temperatures (i.e., at 5, 10, 15 and 21°C) presented a decrease of sorption capacity upon the increase in temperature. This indicated that the uptake of these metals on peat is an exothermic process (Viraraghavan and Dronamraju, 1995). However, experiments on mercury indicated conversely, with sorption capacity increasing correspondingly with temperature (Viraraghavan and Kapoor, 1995). The varied effects of temperature increase on the uptake of different metals suggest that certain mechanisms of adsorption may be more relevant for some metals than for others. The effects of temperature changes, however, were not explored in this study.

The presence of competing metals is another factor affecting adsorption. The preference of peat for adsorption of one metal over another has been hypothesized by a number of authors as influenced by ionic properties such as electronegativity, ionic radius and standard reduction potential. This means predicted adsorption trends which may or may not coincide with observed results, as shown earlier in **Section 2.2**. Although the influence of ionic properties on metal adsorption by peat has yet to be conclusively proven, it is noteworthy of further investigation as an additional variable.

In summary, the effectiveness of peat in removing a target metal depends on a specific combination of peat particle size, solution pH, contact time and temperature. The preference of peat towards certain metals may possibly be accounted for by ionic properties that can affect physical interactions and chemical reactions on the adsorbent surface.

3.1.5 Displacement of adsorbed metals by competitive ions in solution

The process of metal ion adsorption is said to reach equilibrium when no change can be observed in the concentration of the metal on the solid surface or in the bulk solution. The addition of more ions into the system, whether it is the same metal or a second component, results in a shift in this equilibrium. In order for the system to regain stability, the proportion between the ions adsorbed on peat and the ions remaining in solution will change until equilibrium is re-achieved. The position of equilibrium is characteristic of the entire system and is dependent on the solutes, adsorbent, solvent, temperature and pH, among others (Faust and Aly, 1987). Considering all these conditions, the system will adapt in such a way that will result in the lowest energy in order to achieve the thermodynamic requirement for equilibrium. This may mean the release of ions originally adsorbed on the solid surface in favour of other species in solution. This is the basic premise of competitive displacement.

The first solutes to arrive at the bare peat surface are preferentially adsorbed on the most attractive sites or on positions where their potential energy will be at a minimum. As adsorption proceeds, the less active of the sites become occupied. Therefore, adsorption occurs on sites of progressively decreasing activity (Faust and Aly, 1998). By principle, the occupation of adsorption sites proceeds until all available positions are taken. In order for any additional solutes to be adsorbed on the solid surface, some ions may have to be released back into aqueous solution.

One mechanism described for the adsorption of metal ions on natural peat material involves ion exchange, in most cases the adsorption of metals on humic substances resulting in the release of H^+ and possibly with other exchangeable species such as Ca^{2+}, Mg^{2+}, Na^+ and K^+ (Sposito, 1989; Crist *et al.*, 1996). Ion exchange involves electrostatic interactions between an ion on a charged particle surface and ions in a diffuse cloud around the charged particle. It is usually rapid, diffusion-controlled[4], reversible, stoichiometric, and in most cases there is some selectivity of one ion over another by the exchanging surface. Stoichiometry in terms of ion-exchange means that any ions that leave the adsorbent surface are replaced by an equivalent amount of ions, with respect to ionic charge (Sparks, 1995). The same principle can apply to the displacement of an adsorbed heavy metal by a more preferred metal ion.

The displacement of an adsorbed metal can also be associated with the strength of complexation. Metal ions that go into inner-sphere complexes are more stable. A large amount of energy is needed to surpass that of the bonds formed, so it is not easy to dissociate the metal from its complexing ligand. Metals that form outer-sphere complexes, on the other hand, are readily exchangeable (Sposito, 1989) and are expected to be more easily displaced from the adsorbent surface. The formation of chelate structures, as illustrated in the reactions 1 to 3 in **Figure 1**, is also a factor, as it gives added stability to metal adsorption. Thus, the fraction of metals that are adsorbed mainly through electrostatic physical interaction and ion-exchange mechanisms are the ones that are relatively easier to displace from the peat surface.

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[4] In the case of the experiments in this study, however, the effects of slow diffusion is not relevant, as the peat-metal solutions are constantly agitated and mixed.

3.2 Analysis by ICP-MS

Inductively coupled plasma – mass spectrometry (ICP-MS) provides rapid, multi-element analysis with detection limits at single parts per trillion or below for about 40 to 60 elements in solution. The relative sensitivities are predictable enough that semi-quantitative analysis (with accuracy within a factor of 2 to 5) for up to 80 elements can be obtained using a single calibration solution containing a few elements and a blank solution (Olesik, 2000). **Figure 3** shows the basic ICP-MS instrumentation.

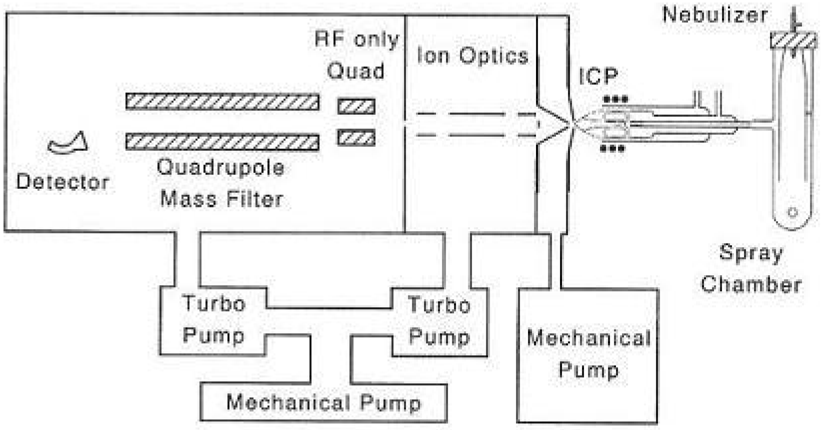

Figure 3: Schematic of ICP-MS instrumentation (Olesik, 2000)

The basic instrumentation consists of a sample introduction system, a nebulizer and spray chamber, an inductively coupled plasma source, a differentially pumped interface, ion optics, a mass spectrometer and a detector. The sample is pumped at a rate of around 0.4 to 1.0 mL/min to a nebulizer that produces an aerosol. The aerosol is modified as it passes through the cross-flow spray chamber (Scott-type spray chamber) and the aerosol drops that are too large to be vaporised effectively in the plasma are eliminated. The aerosol exiting the spray chamber enters the hot atmospheric pressure plasma gas (Ar, with flow rate of about 20L/min). The hot plasma converts the aerosol into atoms and ions, which diffuse toward the sampling orifice of the mass spectrometer (Olesik, 2000; Rauch, 2005).

After analyte ions pass through the sampling orifice, a fraction of the gas is sampled through the skimmer. A positive ion beam is formed as the electrons diffuse and charge separation occurs. A series of ion optics and typically a radio frequency-only quadrupole lens focus positive ions into the mass spectrometer. Ions of a particular mass-to-charge ratio exit the mass spectrometer and are detected (Olesik, 2000; Rauch, 2005). Detection limits for the target metals in this study are: a) 1 - 10 ppt for Cd, Cu, Ni, and Zn; b) < 1 ppt for Pb. Detection limits below 1 ppt (1 pg/mL) are routine as long as sources of contamination and reagent purity are carefully controlled.

Although ICP-MS is a highly successful and powerful technique, there are still some analytical problems that warrant improvement. Spectral overlaps, particularly those due to polyatomic ions, are of concern as these are difficult to identify with quadrupole mass spectrometers. Calcium oxide and hydroxide ions overlap with all five isotopes of nickel and both isotopes of zinc. The choice of acids to use in sample preparation for ICP-MS can also be affected by potential spectral overlaps. Chloride-containing molecular ions that produce intense signals make the use of nitric acid more preferred than hydrochloric acid. Deposition of sample on the sampler, skimmer, ion optics and other parts of the interface can lead to elevated blank measurement levels. In combination with chemical matrix effects, deposition can lead to a need to dilute samples further than necessary (Olesik, 2000).

Chapter 4: Experimental Methodology

Previous studies of competitive adsorption on peat commonly involved the simultaneous adsorption of metal ions from binary and ternary solutions. It is not only simultaneous adsorption in a multi-component system that needs to be understood. The interactions that occur once the adsorption sites of peat are occupied up to near capacity by metals should also be taken into account, as this can provide a more long term view of peat's effectiveness as an adsorbing medium.

Very few studies have been done about displacement on peat, mostly focusing on ion exchange of H^+ and Ca^{2+}, using relatively low metal concentrations (Crist et al., 1996). Competition and displacement between metals have been studied on soil and activated carbon (Christensen, 1987; Xiao and Thomas, 2004), but the dynamics of competitive displacement on peat still requires investigation. Hence a method for the observation of competitive metal displacement at high concentrations on peat needed to be developed.

This chapter provides an overview of the methodology employed during the course of the study. The detailed procedures used, as well as photographs of the materials and experimental set-up are found in **Appendices C** and **D,** respectively.

4.1 Materials used

4.1.1 Characterisation of peat adsorbent

A characterisation of the peat adsorbent was conducted for a related study (Kalmykova et al., 2006b), and the material used for the experiments in this project used sphagnum peat from the same batch. The peat material used for the experiments had a pH = 4.02 in nanopure water, humification degree[5] H3, water content 83.6 %, fiber content 77.5 %, bulk density 0.095 g cm^{-3}, saturated hydraulic conductivity 0.034 cm min^{-1}, and cation exchange capacity of 30.85 meq/100 g. The humic substance composition was 78 % humic acid and 22 % fulvic acid.

4.1.2 Experimental set-up

The experimental set-up was a similar to that for a batch experiment (Chauvet, 2003; Kalmykova, 2004), modified in such a way that buffer solutions can be passed through the

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[5] Degree of decomposition according to the Von Post Scale; criteria listed in **Appendix M**.

container in a flow-through mechanism. The in-flow and out-flow rates were controlled, such that constant volume was maintained for the peat-buffer suspension.

The experiments made use of fibreglass columns, measuring 48.8 cm in height and 6.5 cm in internal diameter. Each column was fitted with two glass filters (porosity = 0), at the inlet and outlet points of the column. The peat/metal/buffer solution in the column was kept in constant mixture by an overhead motor, to which a fibreglass stirrer was attached. Flow tubes were attached at the end of the filters, from the stock buffer to the inlet and from the outlet to the rinse collector. Buffer flow was facilitated by a peristaltic pump (Watson Marlow 302S). Images of the set up are shown in **Figure 4** and **Figure 5**.

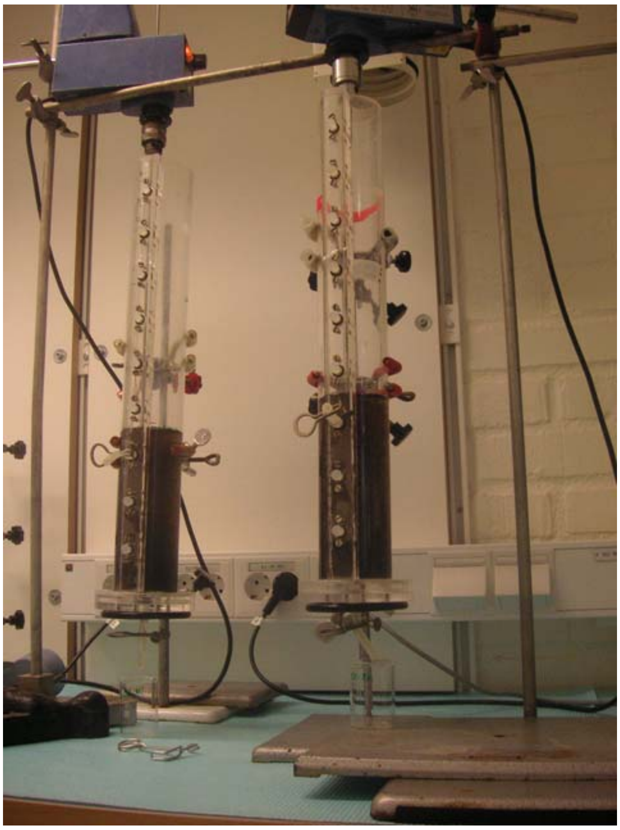

Figure 4: Modified column set-up for metal adsorption experiments on peat

Figure 5: Experimental set-up for metal displacement experiments on peat

4.1.3 Stock solutions used

Metal stock solutions (1000 ppm) were prepared from nitrate salts for each of the target metals (Cd, Cu, Ni, Pb, Zn). Buffer wash solutions at concentrations of 0.25M and 0.02M were also prepared at three pH levels. Acetate buffer solutions were prepared at pH 4 and pH 5.6, while biphosphate ($HPO_4{}^{-2}$) buffer solutions were prepared at pH 7. Details on the reagents and preparation protocol can be found in **Appendix C.**

4.1.4 Pre-treatment of peat

The peat used as adsorption substrate was ground and sieved to a size range of 0.5 – 0.125 mm. Prior to the batch and column experiments, pre-treatment was done by washing a designated amount of peat with 0.25 M buffer solution over coarse filter paper. The peat was washed until a clear filtrate was obtained. The volume of buffer required for pre-treatment varies, depending on the pH level. At least 500 mL is required for pH 4 buffer; greater volumes are needed for higher pH buffers. Peat pre-treatment was recommended to promote the adsorption and retention of metal ions on solid surfaces of peat, but not onto dissolved and movable humic acids (Kalmykova et al., 2006b).

After the wash solution has drained out of the filter, a 1-gram sample is taken for dry weight analysis. The sample is oven-dried at 105 – 110°C. Using the measured dry weight, the amount of treated peat to be used in the experiment column is calculated, such that the mass is equivalent to that of 1 gram of dry peat.

Technique considerations in the pre-treatment and dry-weighing of peat can be found in detail in **Appendix C.**

4.2 Experimental procedure

The following experiments were conducted in this study:

1. Kinetic experiment, using the Cd/Pb binary system
2. Competitive displacement of Cd, with Cu, Ni, Pb, and Zn as competitor metals
3. Competitive displacement of Pb, with Cd, Cu, Ni, and Zn as competitor metals

The protocol followed for the experiments are illustrated as schematics in the following sections.

4.2.1 Kinetic experiment

The first experiment was conducted in order to establish a time profile for the competitive adsorption of Cd and Pb on peat. The adsorbent was one gram (dry weight) of pre-treated peat, mixed with Cd^{2+} solution for 12 hours. The selection of the initial Cd concentration of 10 mg/L (10 000 µg/L) was based on previous batch experiments on peat. The liquid to solid ratio (L/S) was 500 (i.e., 1 g adsorbent to 500 mL aqueous metal solution), which was much higher than those employed in the earlier experiments (Chauvet, 2003; Kalmykova, 2004). The total solution volume was 500 mL.

After the 12-hour treatment, the column was rinsed with buffer solution of the same pH for another 12 hours at a flow rate of about 4.2 mL/min. Lead (Pb^{2+}) solution was then added, at 5 mg/L initial concentration. The column solution was maintained at pH 4 and adjusted with NaOH when necessary. The mixing time used on the peat and Cd/Pb solution was 24 hours. Liquid samples were then taken at set time intervals and prepared for analysis. The total experiment time was approximately 48 hours.

A 100 µL aliquot was taken from each of the column samples for dilution to 10 mL (corresponding to x100 dilution). These samples were then preserved with 1% HNO_3. The internal standard used was 10 ppb Rh. Samples were then analysed using ICP-MS (Perkin-Elmer ELAN 6000).

The purpose of the kinetic experiment was to determine the experimental mixing time that most closely approximates the adsorption equilibrium time. That is, the time at which Pb ceases to compete with and displace Cd. The mixing time obtained from this experiment, as well as information from related literature, will be used in the design of the metal competition/displacement experiments for the other binary systems in the study. **Figure 6** illustrates the basic schematic for the kinetic experiment, using a Cd/Pb binary system.

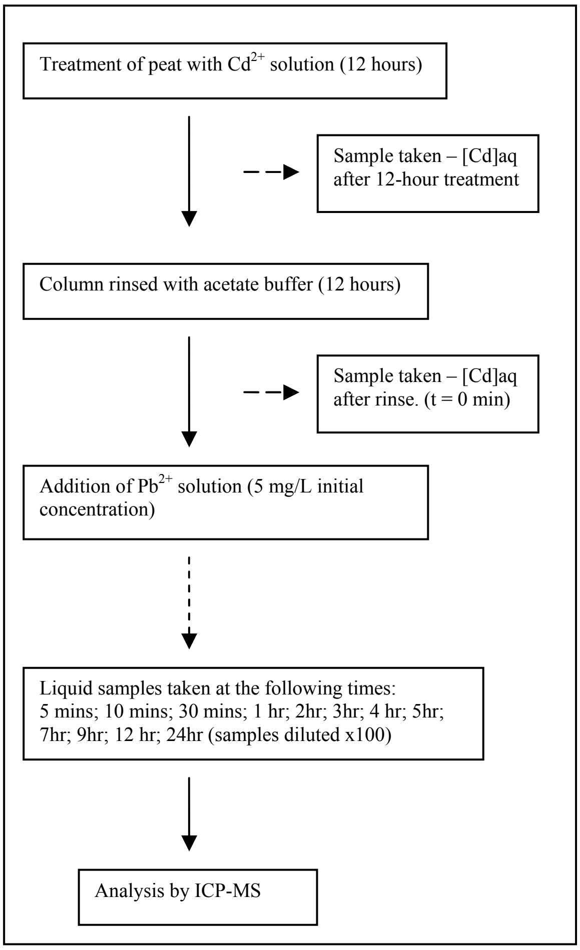

Figure 6: Schematic Diagram of the Cd/Pb Kinetic Experiment

4.2.2 Metal displacement experiments

The material set-up for the metal competitive displacement experiments were similar to the column used for the kinetic experiment. However in this case, instead of establishing a time profile, solution concentrations after the addition of the competitor metal are measured. The total volume for each binary solution was 500 mL. The metal pairs used in the analysis of Cd displacement were Cd/Cu, Cd/Ni, Cd/Pb and Cd/Zn. For the analysis of Pb displacement, the binary systems were Pb/Cd, Pb/Cu, Pb/Ni, and Pb/Zn.

After the 12-hour treatment of peat with the first metal (Cd or Pb) and the subsequent 12-hour buffer rinse (flow rate ~3 mL/min), the second metal (competitor ion) was introduced at an initial concentration = 500 μg/L. The binary solution was then allowed to mix according to the equilibrium time obtained from the kinetic experiment, which was 2 hours. After mixing, a liquid sample was taken from the column. The column was then rinsed with buffer for 1 hour (flow rate ~22 mL/min), to remove excess metals in solution, after which the competitor metal was added again at a higher concentration. This process is repeated until the highest concentration of the competitor metal (10 000 μg/L) has been added.

The protocol for the metal competition/displacement experiment is illustrated in clearer detail in **Figure 7**, using the Cd/Cu binary system as an example.

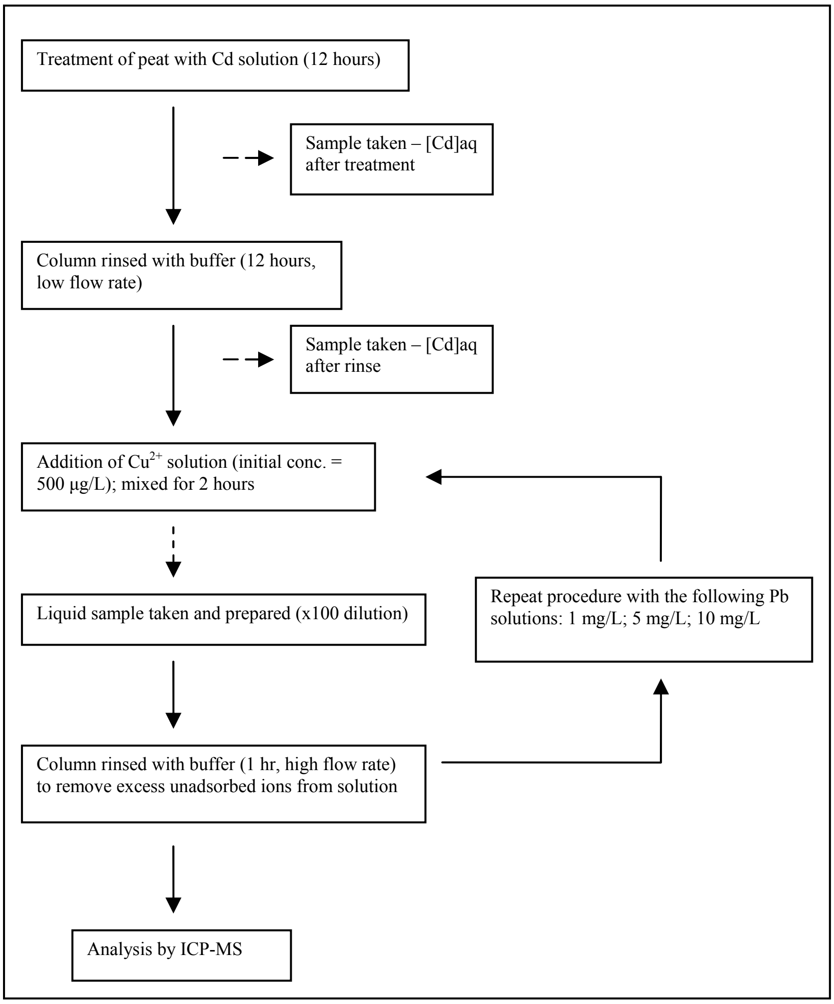

Figure 7: Schematic Diagram of Metal Displacement Experiment

As with the kinetic experiment, samples for introduction into ICP-MS were x100 diluted, preserved with 1% HNO_3 and treated with 10 µg/L Rh internal standard.

The key to the experimental design of the competitive displacement experiments is the sequential addition of the target displacement metal, followed by the competitor ion. In simple systems, little attention is given to the sequence of addition of reagents, but in studies of sorption competition this factor must not be neglected. The fact that the target metal (Cd or Pb) was brought into contact with the adsorbent first makes it a more successful competitor. Only a fraction of the target metal is released, even if the second metal is a very strong competitor. Simultaneous addition of both metals in the binary system could possibly prevent sorption of the target metal at otherwise identical experimental conditions (Kosmulski, 2001). The sequential addition of reagents, for example Cd + Cu, ensures that any additional Cd released in solution is indeed a fraction displaced from the peat surface.

Chapter 5: Results and Discussion

5.1 Kinetic experiment (Cd/Pb)

The results from the kinetic experiment yielded a 24-hour time profile for the adsorption of Cd and Pb ions, and the apparent displacement of Cd from peat. Although equilibrium conditions were not clearly obvious from the data obtained, the information was nevertheless useful in the derivation of the equilibrium time that was used in the subsequent competitive displacement experiments.

The first step was to mix the peat adsorbent for 12 hours in a pH 4 acetate buffer solution containing 10 000 µg/L of Cd^{2+}. This was done to ensure that as many adsorption sites as possible were saturated with Cd. The assumption was that, in order for Pb^{2+} to eventually be adsorbed on peat, Cd ions will have to be displaced from the peat surface into the surrounding buffer solution. After 12-hours of treatment, about 75 % of the initial 10 000 µg/L of Cd was adsorbed by peat.

The 12-hour buffer rinse was conducted to "wash away" excess unadsorbed Cd, in order to have as little background Cd^{2+} in aqueous solution as possible before the displacement by Pb^{2+}. The procedure reduced the concentration of the aqueous unadsorbed Cd from 2 706 µg/L to 385 µg/L, suggesting an 86 % removal of excess Cd in solution[6]. Although still a fair amount of excess Cd was left, 385 µg/L was taken as the background concentration to which the subsequent changes in aqueous Cd was measured against. The value was taken as the concentration at $t = 0$ *min*.

The time profile for the Cd/Pb system is presented in **<u>Figure 8</u>** (measured concentration values are tabulated in **Appendix E**). Aqueous concentrations of Cd and Pb were measured for samples taken at several points of the 24-hour mixing time. The goal was to determine the time at which the rates of adsorption and desorption of Cd^{2+} and Pb^{2+} were equal. This is the equilibrium time, ideally the point at which there are no subsequent changes in aqueous metal concentrations. The peat-metal solution is in a state of relative stability at this point, and it is taken as the optimal mixing time to be used in the competitive displacement experiments.

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[6] The 86 % excess Cd removal is only an assumed value, based on the amount of Cd left in solution. The rinsed buffer was not collected for the kinetic experiment set-up, so a confirmatory test was not made. Considerations on the analysis and interpretation of experimental results are found in **Appendix K**.

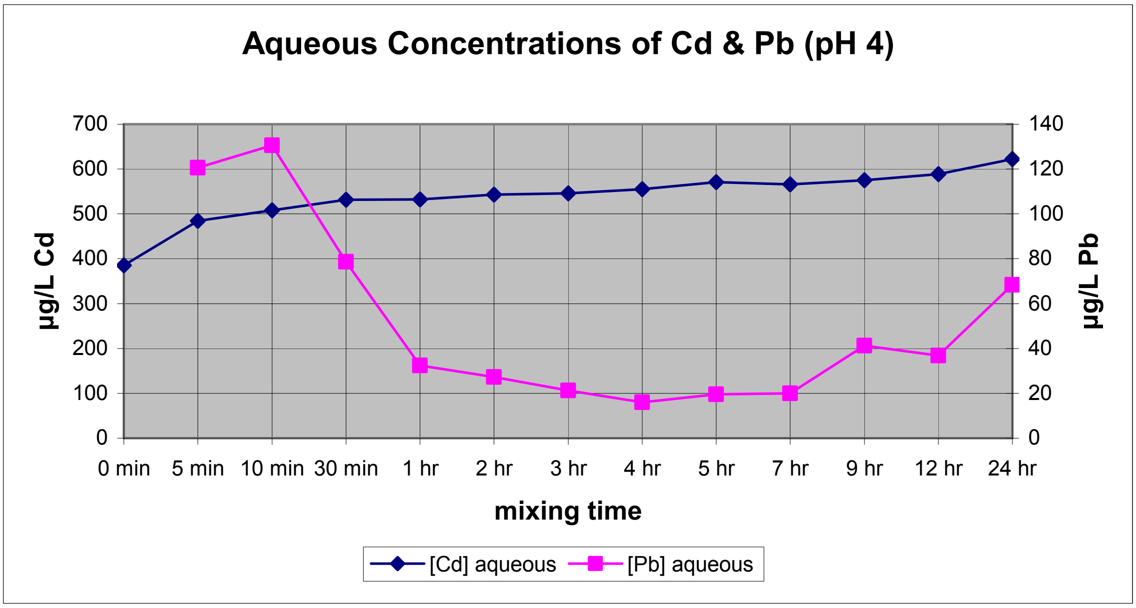

Figure 8: Aqueous concentrations of Cd and Pb at pH 4 (24-hour adsorption profile)

At 5 minutes after the addition of 5 000 µg/L of Pb, a Cd/Pb mass ratio of 2:1, the aqueous Cd concentration increased to 485 µg/L. The first 5 minutes of mixing with Pb resulted in the release of an additional 100 µg/L of Cd into solution, indicating a 6.74% displacement from peat. This percent displacement increased by 0.65% in the first 30 minutes. The concentration of aqueous Cd then gradually but continually increased until the end of the experimental run. This observation is indicative of a continuous desorption of Cd into solution in the presence of Pb.

The adsorption profile for Pb shows a maximum aqueous concentration 131 µg/L after the first 10 minutes of mixing, representing the highest value of unadsorbed Pb. This means that at least 97.4% of the initial Pb concentration was adsorbed within the first 10 minutes of reaction time. This percentage of adsorption increased in correspondence to the decrease in aqueous Pb over time. The concentration was fairly stable in the 2 – 7 hour time period (±6 µg/L), with re-increase in aqueous Pb after 7 hours of mixing.

Based on the data gathered from the kinetic experiment, the experimental time of 2 hours was derived. Considerations given to the selection of the experimental mixing time included the adsorption profile of Cd and Pb, as well as concerns on time management. The 2-hour mixing time seemed sufficient in terms of relative stability of aqueous ion concentrations and was also optimal in order to be able to test up to 4 additions of competing metal in the displacement experiments.

The contact time needed for adsorption equilibrium is dependent on the initial metal concentrations. Earlier experiments have shown that, for the initial concentrations of 25, 50, and 200 mg/L, the majority of metal ions were removed from solution during the first 5 hours (Hanzlik *et al.*, 2004). Equilibrium time can cover a wide range, from 10 – 30 seconds to several hundred hours. Most authors, however, seem to agree on a figure in the range of 20-60 minutes for most divalent ions (Brown, P.A. *et al.*, 2000). Given the motivations mentioned, it can be said that a 2-hour experimental mixing time would be sufficient for the purpose of the metal displacement experiments.

5.2 Metal displacement experiments

Two main sets of displacement experiments were conducted, using binary metal systems. The first set considered Cd as the target metal for displacement, with Cu, Ni, Pb and Zn as the competing metals. The second set of experiments studied the possibility of Pb displacement by Cd, Cu, Ni, and Zn. The complete data for all the binary systems studied are presented graphically in **Appendix F**.

Simple linear regression using least squares was the basic approach in the analysis of results from the displacement experiments. This was done considering the hypothesis that a metal that is displaced from the peat surface will show increasing aqueous concentration corresponding to increased additions of its competitor ion. The more suitable ion is preferentially adsorbed by peat. The less preferred ion will tend to stay in or be released to aqueous solution.

A best fit line (**y = *m*x + b**) was calculated for the concentration matrices. The Cd or Pb concentrations were set as the dependent y-values, with the additions of competing metal being the independent x-variables. Three main statistical values serve as indicators for the linear estimation[7]. The ***slope*** of the line, ***m***, is an indicator of the effect of competition between metals. The sign of the ***m***-value corresponds to the type of correlation. The magnitude of the ***m***-value is suggestive of how intensely the Cd or Pb concentrations increase/decrease upon metal additions.

The ***correlation coefficient***, **r**, describes the relationship between the aqueous concentration of the "displaced" metal and the concentration of the competing metal added to the system. The value of **r** can fall in the range of $-1 \leq \mathbf{r} \leq +1$. An **r**-value of -1 describes a perfect correlation with a negative slope of the linear estimate. An **r**-value of +1 indicates the positively-sloped counterpart. A value close to zero indicates that there is little to no correlation between the data sets (Miller and Miller, 2005).

Lastly, the ***coefficient of determination***, $\mathbf{R}^2$, was calculated to determine whether the linear estimate is the best fit for the correlation. As the least squares fit of a straight line to the data points improves, the value of $\mathbf{R}^2$ will get closer to 1, meaning there is no difference between the estimated y-value and the actual y-value. A high $\mathbf{R}^2$ value can indicate that the observed relation between independent and dependent variables is true and can be used to predict new conditions (Berthouex and Brown, 2002; Miller and Miller, 2005).

Thus, high $\mathbf{R}^2$ and **r** are indicative of a strong influence by competing metals on the release of Cd or Pb from the peat surface. Conversely, low values for $\mathbf{R}^2$ and **r** can mean that the amount of competing metal added to the solution may not be related to how much Cd or Pb is displaced from peat, suggesting that other factors are more significant[8].

In the analysis and comparison of displacing ability among the metals, competitiveness is inferred based on the statistical coefficients, as well as the effected release of Cd or Pb into solution.

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[7] The statistical coefficients were calculated using built-in functions in Microsoft Excel. The formulas used in the calculations are listed in **Appendix L**.

[8] Alternatively, low values for $\mathbf{R}^2$ and **r** can mean that the correlation between the variable may not be linear. Other curve fits (e.g., quadratic) may be more approximate.

5.2.1 Displacement of Cd by Cu, Ni, Pb, and Zn

Correlation of aqueous Cd concentrations vs. competing metal ions

Adsorption trends predicted by ionic properties and shown in earlier experiments indicate that Cd is generally a less-preferred adsorptive compared to the other metals in this study, as discussed in **Section 2.2**. Cadmium is thus a viable candidate for displacement. The competitive displacement of Cd by Cu, Ni, Pb and Zn was studied using the following metal pairs: Cd/Cu, Cd/Ni, Cd/Pb and Cd/Zn. The experiments were done under three pH conditions: pH 4, pH 5.6 and pH 7. The results are presented in **Tables 3 – 6**. Regression coefficients were calculated for each pH level[9].

The correlation coefficients for the metal pairs at pH 4 show a strongly direct proportion (**r** > 0.9) between the addition of competing metal and the release of Cd ions into solution. This indicates the relative ease of Cd desorption at low pH. According to previously determined binding data, Cd binding is strongly pH dependent and increases with increasing pH (Benedetti et al., 1995). It is thus expected for Cd to be more easily displaced at pH 4. Among the competitive metals, Ni was shown to be the most effective at pH 4, as higher concentrations of aqueous Cd were observed in the Cd/Ni system compared to the others.

Table 3: Correlation between aqueous Cd and Cu added to solution

	pH 4	pH 5.6	pH 7
Cu^{2+} added (µg/L)	Aqueous Cd (µg/L)	Aqueous Cd (µg/L)	Aqueous Cd (µg/L)
500	324	486	274
1000	299	293	355
5000	468	421	304
10000	954	697	481
r	**0.971**	**0.990***	**0.820**
R^2	**0.943**	**0.979***	**0.672**

*Not including the results for +500 µg/L Cu[10]

Table 4: Correlation between aqueous Cd and Ni added to solution

	pH 4	pH 5.6	pH 7
Ni^{2+} added (µg/L)	Aqueous Cd (µg/L)	Aqueous Cd (µg/L)	Aqueous Cd (µg/L)
500	921	4346	338
1000	1016	290	342
5000	1550	329	473
10000	2019	599	675
r	**0.995**	**0.941***	**0.997**
R^2	**0.990**	**0.886***	**0.995**

*Not including the results for +500 µg/L Ni

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[9] The calculations of regression coefficients (**r** and **R^2**) for the Cd/Ni, Cd/Pb, and Cd/Zn systems at pH 5.6 did not include the Cd concentrations after the addition of 500µg/L competing metal because the results obtained for these samples are suspect values. Details and motivations for the exclusion are found in **Appendix K**.

[10] For the sake of comparison, the Cd concentration after the addition of 500µg/L Cu was also excluded from the calculation. Calculation of the regression coefficients including all four concentrations results in **r = 0.801** and **R^2 = 0.641**, which are still quite significant levels.

Table 5: Correlation between aqueous Cd and Pb added to solution

	pH 4	pH 5.6	pH 7
Pb^{2+} added (µg/L)	**Aqueous Cd (µg/L)**	**Aqueous Cd (µg/L)**	**Aqueous Cd (µg/L)**
500	309	4235	157
1000	266	144	469
5000	342	180	328
10000	546	219	338
r	**0.948**	**0.9994***	**0.141**
R^2	**0.899**	**0.9998***	**0.020**

*Not including the results for +500 µg/L Ni

Table 6: Correlation between aqueous Cd and Zn added to solution

	pH 4	pH 5.6	pH 7
Zn^{2+} added (µg/L)	**Aqueous Cd (µg/L)**	**Aqueous Cd (µg/L)**	**Aqueous Cd (µg/L)**
500	501	4294	911
1000	475	216	665
5000	661	171	762
10000	1115	408	1470
r	**0.978**	**0.804***	**0.825**
R^2	**0.956**	**0.646***	**0.680**

*Not including the results for +500 µg/L Zn

Comparing the results obtained from the pH 4 and the pH 5.6 data sets, it appears that the pH dependence of Cd binding is validated. Aqueous concentrations of Cd at pH 5.6 are generally lower than those measured at pH 4. Copper was the most effective competitor at pH 5.6, as the measured Cd concentrations after the addition of 1 000, 5 000, and 10 000 µg/L of Cu were relatively higher than those after the addition of the other metals. Competitive behaviour among the metals cannot be fully assessed at the +500 µg/L stage. The results from the Cd/Ni, Cd/Pb, and Cd/Zn systems were not considered in the statistical calculations due to problems encountered in the experimental set-up (see **Appendix K**).

Aside from the relatively lower amounts of aqueous Cd, the experiments conducted at pH 5.6 also resulted in a different order of preference for adsorption, compared to those at pH 4. Given that the pH 4 and pH 5.6 binary systems used the same type of buffer (acetate buffer), this reduces the possibility of other interfering variables. Thus, the difference in outcomes between the two pH levels can be attributed mainly to the difference in H^+ concentration, in combination with the inherent chemical properties of the individual metal ions.

The differences in adsorption preference were more distinct at pH 7. Zinc was shown to be the most effective competitor, resulting in the highest concentrations of displaced Cd. Nickel and copper additions also resulted in significant releases of Cd, although the former exerted more effect than the latter. The Cd/Pb pair showed a distinctly different behaviour than the other three systems. The very low values of the correlation coefficients (**r** << 0.5 and **R^2** value close to zero) indicate that there is no relation between the concentration of Cd released and the amount of Pb added in the solution. The behaviour of the Cd/Pb system at pH 7 is greatly influenced by the formation of hydroxyl complexes and precipitates. These dynamics will be discussed later on in this section.

Figures 9 – 12 plot the concentrations of Cd in solution vs. the additions of Cu, Ni, Pb, and Zn, respectively. The graphs clearly indicate the pH level when the competing metals are more efficient in competitive adsorption and Cd displacement.

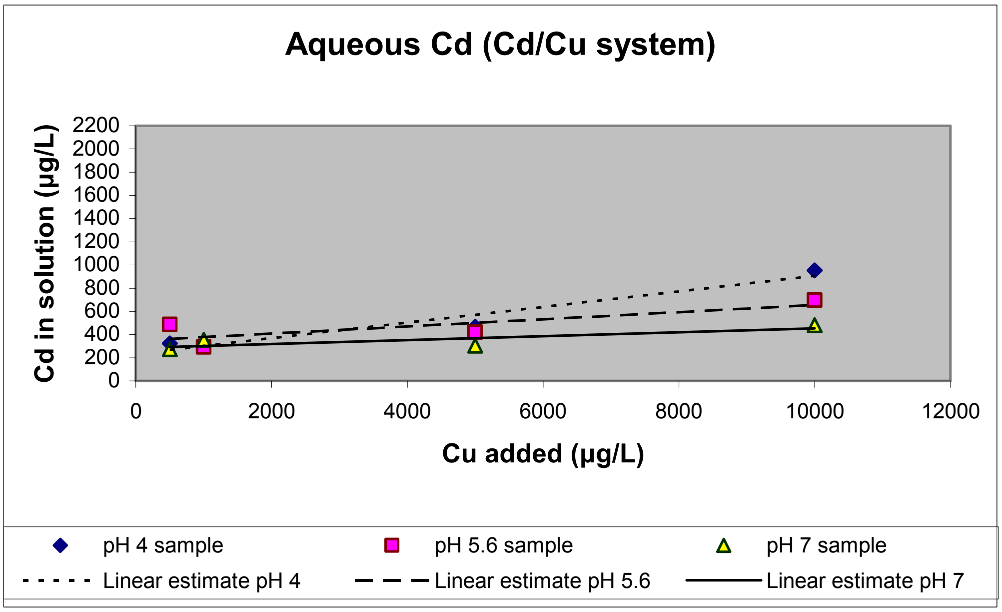

Figure 9: Aqueous Cd vs. Cu added to solution

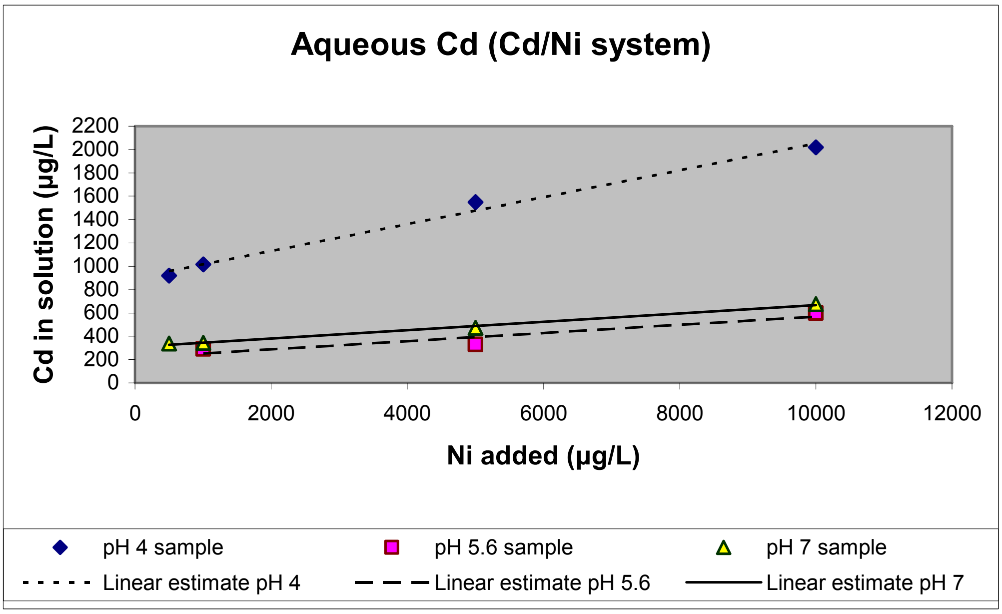

Figure 10: Aqueous Cd vs. Ni added to solution

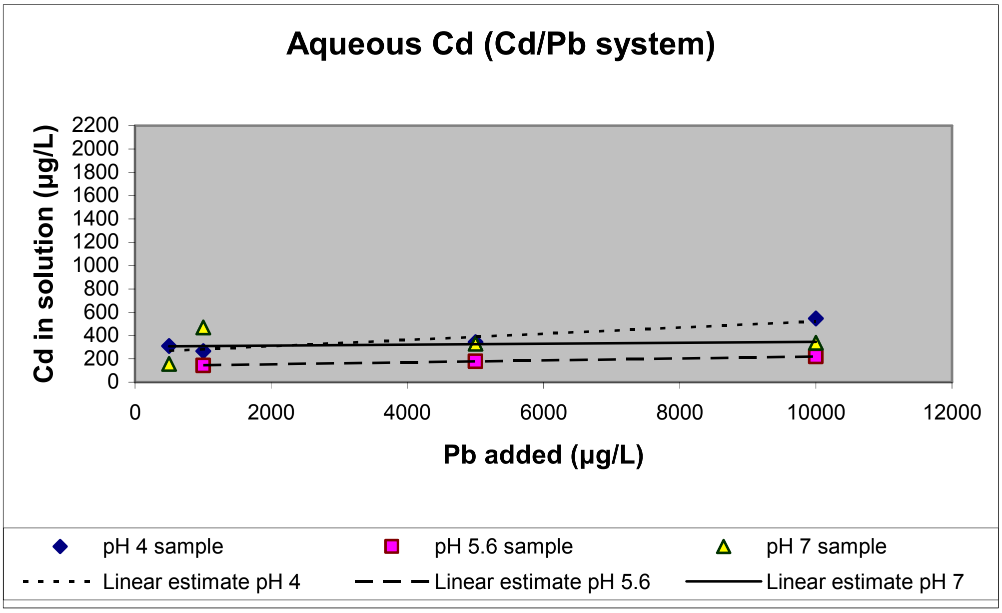

Figure 11: Aqueous Cd vs. Pb added to solution

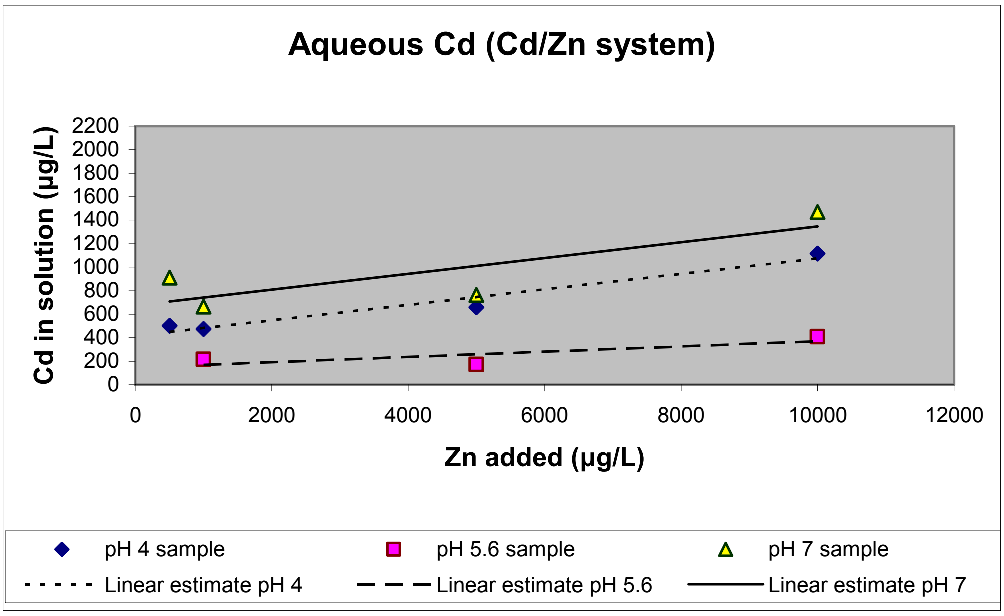

Figure 12: Aqueous Cd vs. Zn added to solution

The graphs show that at higher concentrations, Cu and Pb are most effective at pH 4, while Ni exhibited good competition throughout the entire concentration range. Zinc was distinctly more effective at pH 7, although it was almost as successful as Cu at pH 4. The extent of the effect of competitor metal addition on releases of aqueous Cd is also reflected by how steep the best fit line is. **Table 7** lists the slopes of linear estimate, ***m***, for the four metal binary systems at all tested pH levels. The greater the slope, the more intense is the effect of additional competing metal on the release and displacement of Cd.

Table 7: Slopes of linear estimate (*m*) of the metal binary systems

Metal pair	*pH 4*	*pH 5.6*	*pH 7*
Cd/Cu	0.067	0.031	0.017
Cd/Ni	0.115	0.035	0.036
Cd/Pb	0.027	0.008	0.004
Cd/Zn	0.066	0.022	0.067

It must be emphasized, however, that the linear estimates made for the Cd/Ni, Cd/Pb and Cd/Zn systems at pH 5.6 did not consider the Cd concentration resulting from the addition of 500 µg/L of competitor metal. The inclusion of 3 data points for these systems, instead of 4 data points as was done for Cd/Cu, lowers the reliability of slope comparison at pH 5.6. The analysis of Cd response using the linear slope would have been more meaningful if there were more data points in the calculations. Nevertheless, the ***m***-values are presented for the sake of comparison among the Cd-metal pairs.

Comparatively speaking, the systems with the highest slope values at pH 4 and pH 7 are Ni and Zn, respectively. At pH 5.6, a more reliable approach would be to compare the aqueous Cd concentrations after the addition of 1 000, 5 000, and 10 000 µg/L competitor metal, shown in **Tables 3 – 6**. Considering this, it can be seen that additions of Cu corresponded to greater aqueous concentrations of Cd.

To sum up the observations made at the three pH levels, the following sequences of "Cd-displacing ability" of the competing metals, considering *both* the magnitude of the correlation coefficient, **r**, and the amount of Cd released into solution were observed:

- **at pH 4: Ni > Zn > Cu > Pb**
- **at pH 5.6: Cu ≥ Pb > Ni > Zn**
- **at pH 7: Zn ≥ Ni > Cu > Pb**

Discussion of Cd displacement results

The observations made on the four binary metal systems are suggestive of a pH-dependent selectivity in terms of the ability of these ions to displace Cd. Aside from the variation in the amount of H^+ ions, different pH conditions also have an effect on the solubility and speciation of metals. The speciation of metal ions in aqueous solutions affects their interaction with oxygen functional groups on the adsorbent surface (Xiao and Thomas, 2004). The charge of the metallic species, and hence its degree of adsorption to the peat surface, is determined by what type of species is present. The formation of metal hydroxides such as $Cd(OH)_2$, $Cu(OH)_2$, and $Zn(OH)_2$ and the partial precipitation of these solutes from the aqueous phase at a given pH is a real consequence of the chemical properties of the components. The precipitation of some metal carbonates is also probable, as carbonates are often present in aqueous solutions, especially at a higher pH (Tombácz, 2002).

The success of Zn as a competitor ion at pH 7 can be seen as a function of speciation. The removal of Zn from aqueous solution is optimal at pH > 5.5 (Brown, P.A. *et al.*, 2000) and, compared to other divalent metal ions, zinc assumes the form Zn^{2+} up to around pH 8, before the $ZnCO_3$ salt starts to form. Copper and lead, on the other hand, are present mostly as Cu^{2+} and Pb^{2+} at pH < 7 and pH < 8, respectively. At pH 7, the species $CdCO_3$ also starts to form (Drever, 1997).

In batch experiments previously conducted with Ni, both complexation and ion-exchange played a role in sorption (Ho et al., 1995). The removal of Ni^{2+} from solution by adsorption was also shown to be optimal in the range of pH 4.0 – 7.0. In terms of adsorption at pH 4.0, Ni^{2+} is more likely to be preferred than Cd^{2+}, as the latter ion was to be more effectively adsorbed at pH > 5.0 (Brown, P.A. *et al.*, 2000). Furthermore, the influence of ionic potential on adsorption via ionic bonding (see **Table 2**) can account for the preference towards Ni in the ion exchange mechanism.

Lead was shown to be effective in competing with Cd ions at pH 4 and 5.6. However, at pH 7, the species of Pb present were not favourable for competitive adsorption. At higher pH, the aqueous chemistry of Pb is determined by the solubility of $Pb(OH)_{2(s)}$ and $PbCO_{3(s)}$. The ionic Pb^{2+} species is readily formed in solution at pH levels < 6 (Faust and Aly, 1987; Drever, 1997). This partly explains the low correlation between Cd concentrations and Pb additions at pH 7. The other factor is that the release of aqueous Cd, in this case, is more a result of cadmium speciation behaviour than Pb competition. At pH < 7, the aqueous Cd ions are in the form of Cd^{2+}. The hydrolysis of cadmium ions starts at pH > 7 when $Cd(OH)^+(aq)$, $Cd(OH)_2(s)$, $Cd(OH)_3^-(aq)$, and $Cd(OH)_4^{2-}(aq)$ species are established in dilute solutions (Xiao and Thomas, 2004). The hydrated forms of Cd at this stage are mostly not positively charged, hence are not favoured for adsorption on peat. The Cd fraction in aqueous solution is more likely desorbed species due to hydrolysis and not necessarily due to the presence of Pb. The influence of pH-dependent speciation and other relevant characteristics of Pb will be discussed in further detail in the **Section 5.2.2**, where Pb is the target of displacement by Cd, Cu, Ni and Zn.

A number of factors contribute to the effectiveness of Cu as a competitor ion. Aside from inherent ionic properties that make Cu ions favourable for a number of adsorption-related interactions (see **Table 2**), the mechanism of Cu adsorption is thought to be different from those of the other divalent metal ions. The reaction of Cu with humic acids is one of chelate ring formation, or bidentate inner-sphere complexation (Sposito, 1989). The chelation involves adjacent aromatic –COOH and phenolic OH groups or, less commonly, two adjacent –COOH groups which participate in ion-exchange reactions by binding metal ions with the release of H^+ ions (Brown, P.A. *et al.*, 2000), as shown in **Reactions 2 and 3** in **Figure 1.** As for most other divalent metal ions, it is believed that peat and humic acids likely bind as hydrated ions, forming outer-sphere complexes (Bloom and McBride, 1979). Given that inner-sphere complexes are stronger than outer-sphere, this gives Cu a competitive edge in terms of complexation-driven adsorption. This is shown in the dominance of Cu in terms of complexing strength and intrinsic binding, compared to Cd and the other divalent metals in this study, as shown in **Table 2**. Furthermore, surface sorption of Cu also proceeds through mechanisms other than those involving humic acids. In a previous experiment, when humic acids were extracted from peat, the remaining material exhibited an increase in Cu sorption, contrary to an expected decrease. This is suggestive that, although binding by humic acids is important, the formation of humic acid complexes is not the sole contributing factor (Brown, P.A. *et al.*, 2000).

Another way of analysing the displacement of Cd is by looking at the changes in aqueous Cd concentration relative to background levels after buffer rinse. Recall that after the 12-hr saturation of peat with Cd, the mixture was rinsed with buffer for another 12 hours, in order to remove excess Cd and reduce background Cd levels in solution prior to the addition of the competing metal. A 1-hour rinse was also done after each addition of competitor metal, for the same reason of reducing background levels, this time for both Cd and the other metal ion. (Refer to the schematic, **Figure 7** in **Chapter 4**.) The purpose of the buffer rinse steps was to lower background concentrations of Cd as much as possible in order for any additional increases to be indicative of displacement of Cd that was originally adsorbed on peat. The aqueous Cd concentrations after each buffer rinse and metal addition are shown for the Cd/Cu system in **Figure 13**.

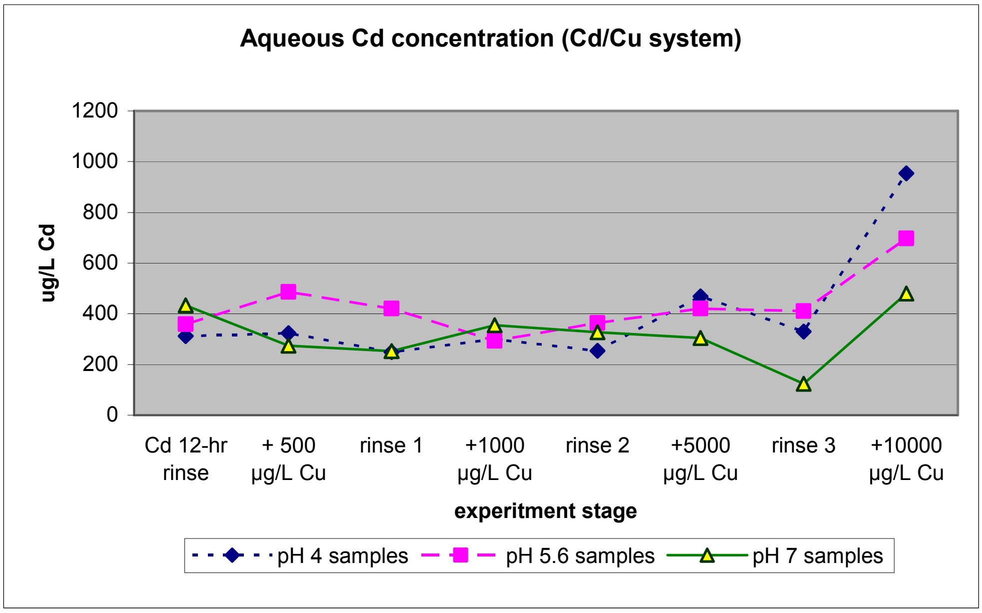

Figure 13: Aqueous Cd concentrations at selected stages of the Cd/Cu experiments

The changes in aqueous Cd after Cu addition, relative to background levels in solution after rinse, were then calculated and expressed as **ΔCd** (e.g., $[Cd]_{aq,\ after\ +1000\mu g/L\ Cu} - [Cd]_{aq,\ after\ rinse\ 1}$). The values are tabulated in **Table 8**.

Table 8: Changes in aqueous Cd relative to rinsed background levels

	pH 4	pH 5.6	pH 7
Cu addition stage:	**Δ Cd** (µg/L)	**Δ Cd** (µg/L)	**Δ Cd** (µg/L)
+ 500 µg/L Cu^{2+}	12	127	-160
+ 1 000 µg/L Cu^{2+}	50	-128	102
+ 5 000 µg/L Cu^{2+}	215	57	-23
+ 10 000 µg/L Cu^{2+}	624	286	356

The **ΔCd** is an indicator of pH influence in the ease of Cd displacement from peat. At pH 4, there is clearly an increase in the amount of additional Cd in solution. The more Cu ions are added, the more additional Cd is released into solution. The pattern is not as distinct at pH 5.6 and pH 7, which suggests that the process of Cd displacement by Cu is not as easy at higher pH. This is supported by earlier observations of Cd being more effectively adsorbed at pH > 5.0 (Brown, P.A. *et al.*, 2000). Nevertheless, at sufficiently high amounts, Cu is able to effect a displacement of Cd from peat at pH 5.6 and 7. The corresponding graphs and data tables for the other Cd binary systems are found in **Appendix G**.

Aside from the explanations that have already been mentioned in this section, there are other contributing factors that have to be noted. For example, two kinds of buffer solutions were used in the experiments. The experiments at pH 4 and pH 5.6 made use of an acetate buffer

(HOAc-NaOAc solution), while the pH 7 systems were essentially in phosphate based buffer solutions (HNO_3-Na_2HPO_4). Despite the relatively low strength of the buffers used (20 mM), the differences in anion components, as well as the differences in the amount of Na^+ in solution may influence metal-ligand interactions, as well as other factors related to adsorption and displacement. Previous studies have found that the presence of Na^+ reduced the sorption of some metals (Dissanayake and Weerasooriya, 1981; Brown, P.A. *et al.*, 2000). The reduction of adsorption when monovalent ions are present indicates a buffering action of sorption site. To some extent, metal adsorption by ion-exchange may involve the exchange of the heavy metals with Na^+ as well as H^+ ions. Furthermore, although some anions such as NO_3^- do not have the ability to form complexes with metal ions, other anions (e.g., PO_4^{3-}) may significantly influence the speciation of several metal ions, such as Cu^{2+}, Cd^{2+}, Pb^{2+} and Zn^{2+} (Tombácz, 2002). Nitrate salts were used in the preparation of the metal stock solutions. The effect of the phosphate buffer on metal speciation, however, was not explored in this study. Sufficient information in terms of metal-HPO_4 complexation constants was not available.

In conclusion, the competitive displacement of Cd from the peat surface is a function of the following factors: a) the pH-dependent speciation of Cd; b) the pH-dependent speciation of the competing metals; and, c) the type and strength of complexation of Cd compared to that of the competing metal. The results obtained from the experiments were consistent with predicted and observed behaviour in related studies.

5.2.2 Displacement of Pb by Cd, Cu, Ni, and Zn

Competitive displacement of Pb was studied using the following binary metal systems: Pb/Cd, Pb/Cu, Pb/Ni, and Pb/Zn. The analysis of the displacement behaviour of Pb comes in two parts. First, a correlation of aqueous Pb concentration vs. additions of competing metal ions is presented and discussed. Further analysis of results is then made through accounting of the mass balance of the Pb/metal systems studied. Aside from validating the information derived from the correlation calculations, the mass balance also serves to test the efficiency of the experimental design.

Correlation of aqueous Pb concentrations vs. competing metal ions

Previous studies have shown that Pb has relatively high efficiency for adsorption and metal cation exchange (see **Table 2** in **Section 2.2**). Its smaller hydration radius and higher intrinsic binding constant, among others, makes it more favourable for adsorption compared with the other metals in the experiments, except for Cu. It is thus expected that there were significantly lower concentrations of aqueous Pb released in the Pb-displacement experiments, compared to the releases of aqueous Cd in the Cd-displacement experiments.

Graphical representations of the aqueous Pb concentrations at the three pH levels, with respect to the amount of Cd, Cu, Ni, or Zn added to solution, are illustrated in **Figures 14 – 17**.

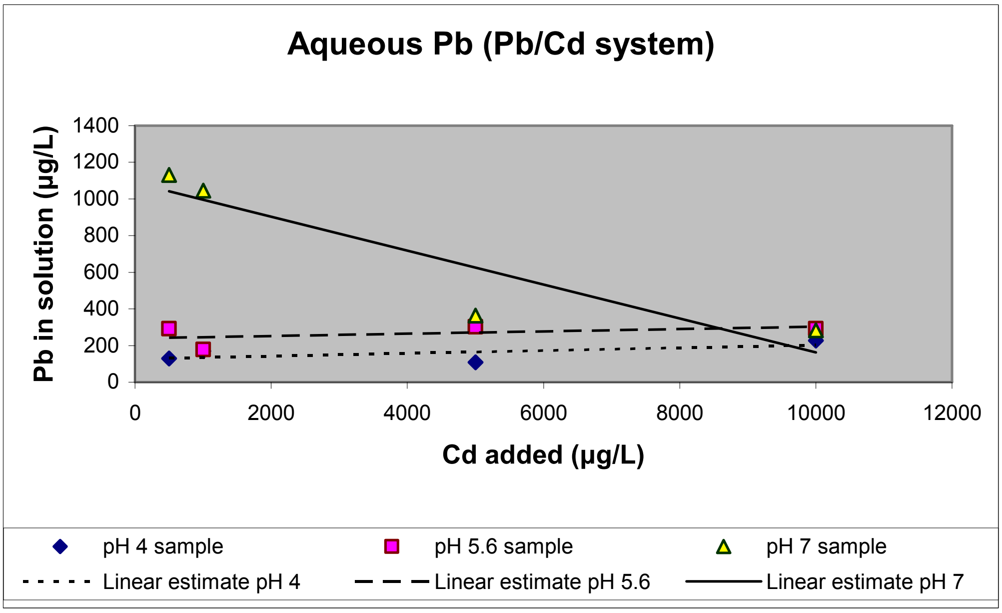

Figure 14: Aqueous Pb vs. Cd added to solution

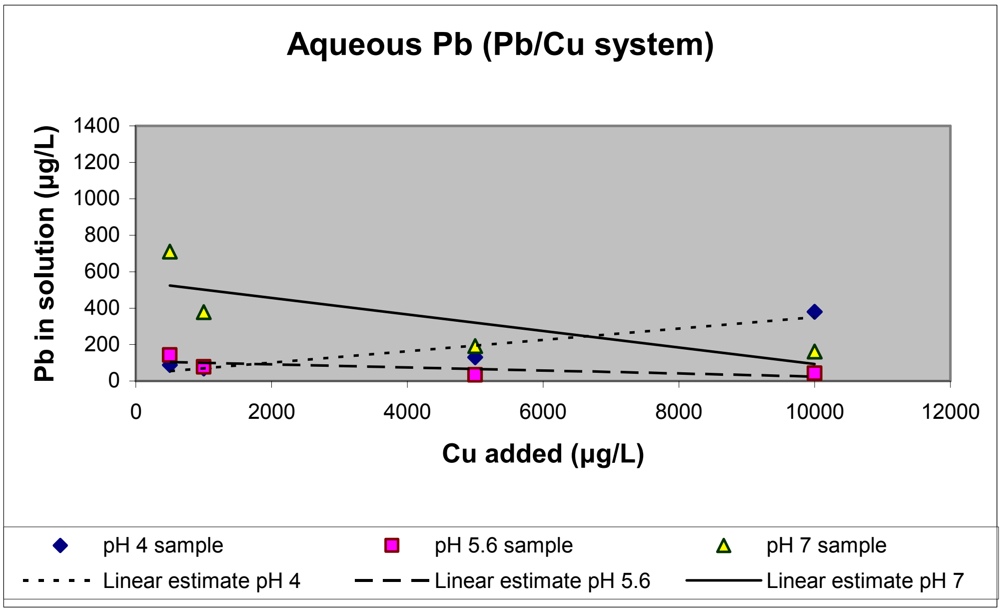

Figure 15: Aqueous Pb vs. Cu added to solution

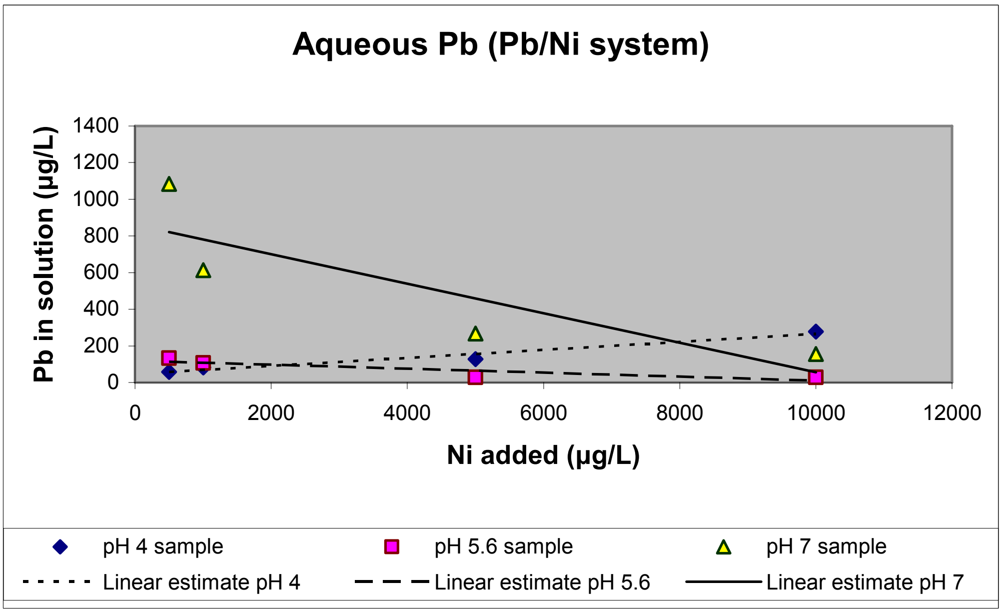

Figure 16: Aqueous Pb vs. Ni added to solution

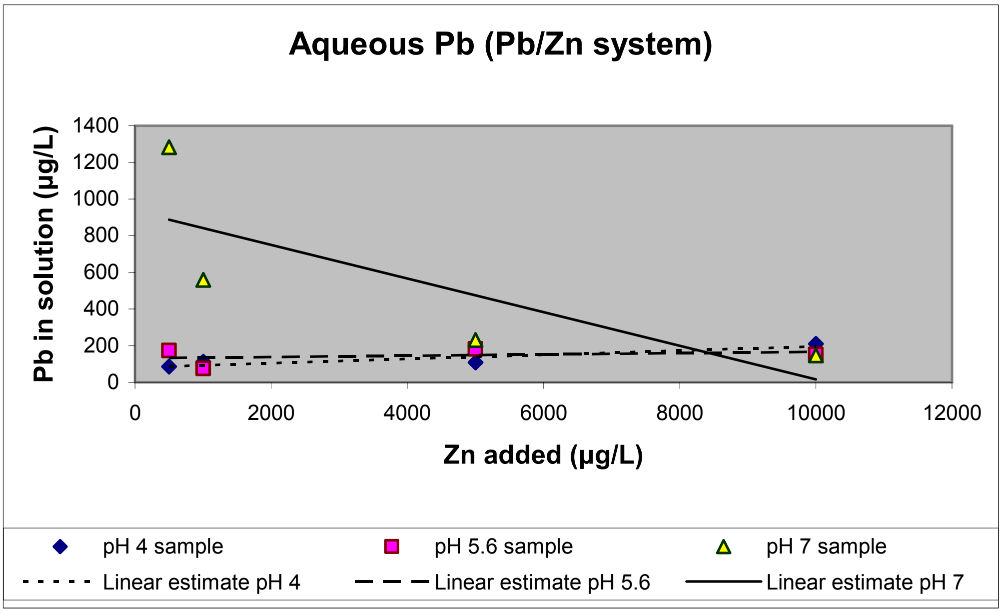

Figure 17: Aqueous Pb vs. Zn added to solution

The behaviour of the Pb-metal binary systems at pH 7 was found to contrast starkly with that observed at pH 4 and 5.6, obviously reflecting the difference in Pb speciation at these pH levels. The concentrations of aqueous Pb at pH 7 are primarily due to the inherent properties of Pb itself and may have little or nothing to do with the characteristics of the competing metal. The analysis of Pb-displacement at pH 7 may also be irrelevant because it is not certain which fraction of Pb was adsorbed on peat and which has complexed and/or precipitated out from solution[11].

Primary focus is thus given to the behaviour of the systems at pH 4 and pH 5.6. The correlation data between aqueous Pb and the additions of Cd, Cu, Ni, and Zn are shown in **Tables 9 – 12**.

Table 9: Correlation between aqueous Pb and Cd added to solution

	pH 4	pH 5.6	pH 7
Cd^{2+} added (µg/L)	Aqueous Pb (µg/L)	Aqueous Pb (µg/L)	Aqueous Pb (µg/L)
500	129	292	1131
1000	170	178	1045
5000	108	303	364
10000	227	291	283
r	**0.623**	**0.463**	**- 0.918**
R^2	**0.338**	**0.214**	**0.843**

---

[11] During preparation of buffer solutions containing Pb and HPO_4^{2-} at pH 7, some white turbidity was observed.

Table 10: Correlation between aqueous Pb and Cu added to solution

	pH 4	pH 5.6	pH 7
Cu^{2+} added (µg/L)	**Aqueous Pb (µg/L)**	**Aqueous Pb (µg/L)**	**Aqueous Pb (µg/L)**
500	88	142	710
1000	69	78	378
5000	131	33	191
10000	380	42	161
r	**0.950**	**- 0.738**	**- 0.792**
R^2	**0.903**	**0.544**	**0.627**

Table 11: Correlation between aqueous Pb and Ni added to solution

	pH 4	pH 5.6	pH 7
Ni^{2+} added (µg/L)	**Aqueous Pb (µg/L)**	**Aqueous Pb (µg/L)**	**Aqueous Pb (µg/L)**
500	58	133	1083
1000	82	107	613
5000	127	27	267
10000	278	29	155
r	**0.980**	**- 0.873**	**- 0.852**
R^2	**0.959**	**0.763**	**0.726**

Table 12: Correlation between aqueous Pb and Zn added to solution

	pH 4	pH 5.6	pH 7
Zn^{2+} added (µg/L)	**Aqueous Pb (µg/L)**	**Aqueous Pb (µg/L)**	**Aqueous Pb (µg/L)**
500	85	172	1283
1000	112	75	559
5000	109	182	231
10000	209	152	147
r	**0.918**	**0.305**	**- 0.781**
R^2	**0.843**	**0.093**	**0.610**

The correlation coefficients obtained from the Pb/Cu, Pb/Ni, and Pb/Zn systems at pH 4 show a strong connection between the addition of competing metal and the concentration of Pb measured in aqueous solution (**r** > 0.9). While at pH 5.6, low correlation coefficient values were obtained (**r** < 0.5), suggesting that the aqueous Pb concentration has little to do with the addition of the competitor metal. The negative **r**-values obtained for the pH 7 systems support the inference that analysis of Pb displacement by competing metals at pH 7 is irrelevant.

In summary, considering *both* the magnitude of the correlation coefficient, **r**, and the amount of Pb released into solution, the following sequence of “Pb-displacing ability” can be derived from binary systems at **pH 4: Ni ≥ Cu > Zn > Cd**.

Discussion of Pb displacement results

As is the case with Cd, the displacement of Pb is also a function of pH-dependent speciation. The aqueous chemistry of Pb is controlled by the solubilities of $Pb(OH)_{2(s)}$ and $PbCO_{3(s)}$ (Faust and Aly, 1998). Ionic Pb^{2+} essentially is found below pH 6, above which the $PbCO_{3(s)}$ starts to form (Drever, 1997). Pb species start to undergo hydrolysis initially to $Pb(OH)^{+}_{(aq)}$ at pH > 4-5. A small amount of $Pb(OH)^{+}_{(aq)}$ may be present at pH 5.6. In the pH range 6 – 13, the complex species $Pb(OH)^{+}_{(aq)}$, $Pb(OH)_{2(aq)}$, and $Pb(OH)_3{}^{-}_{(aq)}$ are known to exist (Xiao and Thomas, 2004).

The speciation of Pb at pH 4, pH 5.6 and pH 7 naturally has consequences on adsorption and displacement behaviour. Complexation that leads to a decrease in positive charge (< 2+) means a decreased preference by negatively charged adsorption sites, compared to a competitive divalent metal ion. This leads to a higher likelihood of displacement of adsorbed Pb species from the peat surface. As pH increases, speciation moves towards precipitation from solution, making Pb-removal by humic acid adsorption less efficient. These influences were manifested in the results obtained from the competitive displacement experiments on Pb.

Taking the overall release of aqueous Pb into consideration, Cu was shown to be more competitive than Ni and Zn at pH 4. One contributing factor may be that Cu^{2+} has the ability to form strong inner-sphere chelates with humic acids. Even if Pb^{2+} is in itself a strongly adsorbing metal ion, its electron configuration makes it less favourable for chelation compared to Cu, Ni, and Zn. Bonding and electron pairing in the chelation of transition metals mainly involves electrons in the *d*-orbital, and the electron configuration of Cu, Ni and Zn facilitates this type of covalent bonding. Lead, on the other hand, differs in electron configuration because as its *d*-orbital electrons are surrounded by the 6s-orbitals and 6p-orbitals, making the chelate-forming electrons less accessible compared to Cu, Ni, and Zn (Datukan, 2006). Thus, even if Pb is overall a strongly adsorbing metal, there is still a possibility of displacement by these competing metals. This also supports the idea that Pb adsorption peat proceeds through mechanisms other than humic acid chelation.

The outcome of the experiments on Pb/Cd at pH 4 differs from those of the other systems. There is no clear trend in terms of increasing additions of Cd. This suggests that the release of aqueous Pb is a result of desorption due to properties inherent to Pb, and not because Cd is a more preferred adsorbate. The total increase in ionic strength can also explain the unadsorbed aqueous Pb concentration measured at the end of the experiment.

At pH 5.6, the releases of Pb ions into solution do not follow a specific pattern when comparing results among all the systems studied. This indicates that the amount of aqueous Pb is a result of its own speciation, and not necessarily due to the nature of the competing ion. Hydrolysis of Pb ions begins at pH 4 – 5; at pH 5.6, there is already a fraction present as $Pb(OH)^{+}$ ions. The lower positive charge of the hydrolysed fraction makes it easier to be displaced into solution, even at low concentration additions of the competing divalent metal. The influencing factors in this case are the higher charge (2+) of the competitor and the overall increase in ionic strength. The observed decrease in aqueous Pb concentration after additions of Cu and Ni, shown in **Table 10** and **Table 11** respectively, may just be a result of the washing away of Pb in the successive buffer rinses in the experiments.

As was done in the analysis of Cd displacement in the previous section, the occurrence of Pb displacement can be examined in terms of changes in aqueous Pb concentration at vital stages of the competition experiment. An example using the Pb/Ni experiments is shown in

Figure 18. The changes in aqueous Pb after each Ni addition (**ΔPb**) were likewise calculated relative to background levels in solution after rinse (e.g., $[Pb]_{aq,\ after\ +1000\mu g/L\ Cu} - [Pb]_{aq,\ after\ rinse\ 1}$). The values obtained for **ΔPb** are shown in **Table 13**.

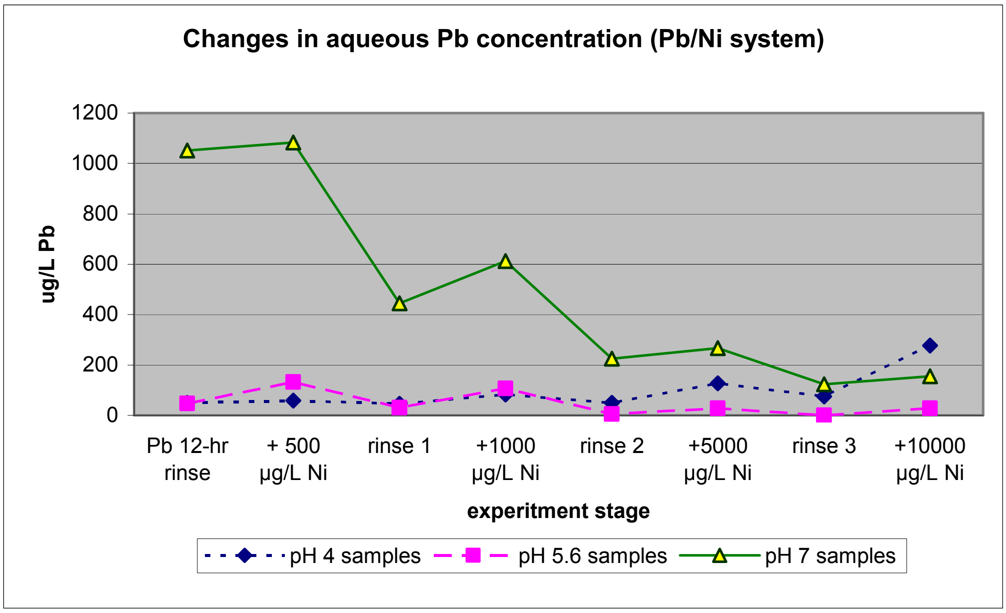

Figure 18: Aqueous Pb concentrations at selected stages of the Pb/Ni experiments

Table 13: Changes in aqueous Pb relative to rinsed background levels

	pH 4	**pH 5.6**	**pH 7**
Ni addition stage:	**Δ Pb** (µg/L)	**Δ Pb** (µg/L)	**Δ Pb** (µg/L)
+ 500 µg/L Ni^{2+}	9	85	32
+ 1 000 µg/L Ni^{2+}	36	76	168
+ 5 000 µg/L Ni^{2+}	77	23	42
+ 10 000 µg/L Ni^{2+}	203	30	32

Comparing the changes in aqueous Pb observed for the three pH levels, it can be seen that it is only at pH 4 where the changes correspond in proportion to the amount of competing Ni added. It is more clearly inferred at pH 4 that the releases of Pb ions occurred as a result of competitive adsorption and increasing ionic strength. For the pH 5.6 experiment, the greater changes occurred at lower Ni concentrations. The release of Pb in this case was a function of its own desorption and had less to do with increases in aqueous Ni concentration. As for the experiment at pH 7, it is visible that buffer rinsing resulted in the washing away of aqueous Pb and that increases in Pb ions at the higher ionic strengths are smaller. The inverse proportion only meant that most of the aqueous Pb that was present at earlier stages of the experiment has been progressively taken away from the solution by each buffer rinse.

The observations in terms of pH-dependent behaviour were more or less similar for the other Pb/metal pairs. The illustrations and calculations for the other three Pb binary systems are shown in **Appendix H**.

Mass balance calculations on the Pb/metal binary systems

In the experiments carried out on the Pb/metal binary systems, the rinsed buffer solutions were collected separately for each column. Samples from the collected rinse were also taken and prepared for ICP-MS similarly as for the other experimental samples. One sample was taken for the collected 12-hr rinse buffer and another from the collected rinse 3 buffer, which was the rinse period before the addition of 10 000 μg/L competing metal. The volumes of the collected rinse buffers were noted. These steps were done in the interest of making mass balance calculations in terms of amounts of Pb present in the different components of the experimental set-up.

By multiplying the concentration of aqueous Pb (μg/L) by the volume of the collected rinse buffer (L), the amount of Pb that was washed away (μg) is determined. This can then be compared to the amounts left in the column. The distribution of amounts in the experimental set-up is expected to be such that:

$$\text{mass of }\mathrm{Pb}_{(aq)}\text{ in column before rinse} = \text{mass of Pb(aq) in column after rinse} + \text{mass of }\mathrm{Pb}_{(aq)}\text{ in collected rinse buffer}$$

The purpose of the mass balance is to test the efficiency of the experimental set-up. The analysis of competitive adsorption and displacement in the experiments were based on measurements of aqueous species of metals. Doing a mass balance of the different experimental compartments can give an idea of how closely the measurements approximate actual concentrations. It can also pinpoint possible sources of inaccuracy, for the sake of further development of the analytical method.

The mass balance of Pb in the Pb/Ni experiments was taken as an example and is shown in **Table 14**. Mass balance calculations for the other metal pairs are found in **Appendix I**.

Table 14: Mass balance of Pb (in μg) at rinse periods in the Pb/Ni experiments

Rinse period	*A*	*B*	*C*	*B+C*	Difference/Notes
	In column, before rinse	In column, after rinse	In collected rinse buffer		***A = B+C?***
pH 4					
12-hour	138	25	168	193	A < B+C by 55 μg; excessive amount in collected rinse
Rinse 3	63	37	58	96	A < B+C by 32 μg; excessive amount in collected rinse
pH 5.6					
12-hour	311	24	94	118	A > B+C; 192 μg lost during rinse (unaccounted for)
Rinse 3	14	0	8	8	A > B+C; 6 μg lost during rinse (unaccounted for)
pH 7					
12-hour	4420	526	1903	2428	A > B+C; 1992 μg lost while rinse (unaccounted for)
Rinse 3	133	61	97	158	A < B+C by 25 μg; excessive amount in collected rinse

Depending on the metal and pH level observed, the imbalances in mass distribution have implications on the experimental results, as these are sources of uncertainty. The excess amount in the 12-hour rinse at pH 4 suggests that competition with H^+ may account for the desorption of Pb^{2+}. The excess 55 µg is a significant value relative to the amount of Pb released after addition of 500 µg/L Ni, which was 29 µg Pb. This raises uncertainty as to whether Pb release at that point was due to Ni or because of simple desorption. However, the results obtained for the higher additions of Ni, as shown in **Table 11**, validate the supposition that Ni competition is an important factor in Pb desorption.

For the Pb/Ni experiment at pH 5.6, there were amounts of Pb that were unaccounted for and seemed to be "lost" during rinse periods. Plausible explanations could be re-adsorption on peat or adhesion of Pb to pump tubes and container walls. As for the experiment at pH 7, the relatively large unaccounted amount of aqueous Pb lost during the 12-hour rinse, 1992 µg, is likely due to the precipitation of Pb out of solution. Losses due to adhesion to pump tubes and container walls could also have occurred. The attachment of metal to the equipment

The imbalances in the mass balance determinations can also be due to experimental factors other than adhesion of Pb to equipment surfaces. For example, the buffer collection container may not have been shaken properly prior to the taking of sample for ICP-MS analysis, making the sample less representative of the entire volume. There may also be errors in total volume measurement, as graduated cylinders were used. Contamination of glass filters and pump tubing is minimised by acid washing prior to each experiment, but is still a possible factor.

All of the above explanations remain as conjecture, however, unless a complete mass balance is done to include the sampling and analysis of solid peat to determine the actual amount adsorbed on the surface.

5.2.3 Blank tests

Given that the experiments relied on the analysis of aqueous metal concentrations alone, it is necessary to determine which ions were released due to competitive displacement and which ones were originally contained in the peat material that was used. The tests are also indicative of possible contamination from the columns and other equipment used in the experiment. In order to have an idea of background levels of metals on peat, blank tests were done at the three pH levels (pH 4, pH 5.6, pH 7).

The results show that up to a maximum of 30 µg/L Zn is released in solution at pH 4, 53 µg/L at pH 5.6, and 9 µg/L at pH 7. There was also a concentration of 19 µg/L Cu and 0.5 µg/L Ni at pH 4 that can be attributed to natural releases from peat. The concentrations of 9 µg/L Pb and 6 µg/L Cd at pH 5.6 and pH 7, respectively, may be due to some metal adsorbed to small peat particles that were fastened to the glass filters from previous experimental runs.

A graphical presentation of the results from the blank tests is found in **Appendix J**.

The aqueous metal releases in the blank tests are not of great concern. The competitor metals, Cu, Ni, and Zn, were added in concentrations much larger than those measured in the blank tests. The measurements of Cd and Pb in the blank are likewise insignificant compared to the concentrations measured in the experiments. However, the detection of these metals calls attention to possible contamination in the glassware and other equipment, which is always a consideration to be cautious about.

5.2.4 Analysis of displacement using molar ratios: Cd/Cu and Pb/Cu systems at pH 4

The premise regarding the displacement of a metal ion from the peat surface is that displacement occurs when a more preferred competitor dislodges and takes its place on the adsorption site previously occupied. This can be considered as some form of ion-exchange, where equal amounts of ion charges are traded between the peat surface and the surrounding aqueous solution. The replacement of equal amounts of ion charges means that the ion-exchange is stoichiometric. Thus, the moles of ions released in solution should equal the moles of ions adsorbed.

A following example is shown, using the Cd/Cu and Pb/Cu systems at pH 4. The number of moles of Cd and Pb in aqueous solution was compared with the number of moles of Cu that was adsorbed on peat after each Cu-addition. Stoichiometric balance would mean that: ***moles of Cd (or Pb) released in solution = moles of Cu adsorbed on peat***. The results obtained from the ICP-MS analysis were in terms of concentrations (µg/L), so the analysis results were converted to µmoles of metal using this formula:

$$\mu mol = \frac{[Me^{2+}]*V}{AW}$$

Where:
$[Me^{2+}]$ = concentration of metal (µg/L)
V = volume of solution (0.5 L)
AW = atomic weight of the metal

The concentrations of metal (presumably) displaced vs. concentrations adsorbed on peat, as well as the corresponding conversions to µmoles, are shown in **Table 15**.

Table 15: Comparative analysis of aqueous Cd and Pb versus adsorbed Cu

Experiment Stage	Cd/Cu system at pH 4		Pb/Cu system at pH 4	
	A. metal concentrations (µg/L)			
	$[Cd^{2+}]_{aqueous}$	$[Cu^{2+}]_{adsorbed}$	$[Pb^{2+}]_{aqueous}$	$[Cu^{2+}]_{adsorbed}$
+ 500 µg/L Cu^{2+}	324	451	88	500
+ 1 000 µg/L Cu^{2+}	299	924	69	1000
+ 5 000 µg/L Cu^{2+}	468	4625	131	4735
+ 10 000 µg/L Cu^{2+}	954	7309	380	7792
	B. molar quantity (µmoles)			
	µmol Cd^{2+}	µmol Cu^{2+}	µmol Pb^{2+}	µmol Cu^{2+}
+ 500 µg/L Cu^{2+}	1.44	3.55	0.21	3.93
+ 1 000 µg/L Cu^{2+}	1.33	7.27	0.17	7.87
+ 5 000 µg/L Cu^{2+}	2.08	36.39	0.32	37.26
+ 10 000 µg/L Cu^{2+}	4.24	57.51	0.92	61.31

The calculated values did not support the premise of 1:1 stoichiometry in the case of the experiments in this study. This has mainly to do with experimental design. First of all, the experiments were designed in terms of mass ratios (instead of mole ratios). Furthermore, there were multiple additions of competing Cu ions, compared to a single addition of Cd and Pb at the start of the experiments (10 000 µg/L). It is worthy to note that Cu adsorption at pH 4 was 90 – 100% for the first three additions, then dropped to 73 – 77% after the addition of 10 000 µg/L. The decrease in adsorption percentage suggests that peat is approaching its saturation point with regards to additional adsorption of Cu. This may be taken as an indicator that the peat adsorbent may not have been fully saturated; there are still available, although perhaps less attractive, sites for Cu adsorption. Nevertheless, the increased releases of Cu and Pb after the higher additions of Cu indicate that Cu has more successfully competed with Cd and Pb for the more preferred adsorption sites[12].

Although the experiments performed are good illustrations of how displacement of metals proceeds by competitive adsorption, a more appropriate experimental design, using mole ratios of the competing metal pairs, would be necessary in order to determine reaction stoichiometry. A stoichiometric analysis of competitive adsorption can better test the occurrence of metal displacement and is instrumental in determining the type of reaction mechanisms involved.

5.3 Evaluation of the experimental method

As this is the first stage of methodology development for the analysis of metal displacement, there are a number of aspects that need to be verified and developed. In terms of experimental design, a number of issues need to be addressed.

When the experiments were conducted in this study, they were done in such a way that optimises the number of pH conditions and metal pairs in terms of time management and sample allocation. As such, only one sample was taken for each experimental stage. Although the ICP-MS takes multiple readings per sample and returns a standard deviation value, it can be useful in terms of method development to make replicate ICP samples of 3 per column sample as a means of validation. Errors may have been introduced with the x100 dilution of the ICP sample. Focus can be given on only one binary metal system at three pH levels, to check the data spread and the precision of the experimental method.

Another matter that should be noted is that, although the ICP-MS is a highly reliable analytical instrument, calibration curves are created for each analysis run; this means a different calibration curve for each batch of samples. The careful preparation of standards is thus of importance, in order to maintain consistency as much as possible in calibration.

The experimental method has some limitations that can serve as sources of systematic and random errors. The buffer rinse period, which is an important part of the experiment, can contribute uncertainty and error due to two main factors. The irregularity of the pumping mechanism during long hours of operation results in unequal in-flow and out-flow rates. At times, constant volume is maintained in the column by manual adjustment. Related to this is the size of the peat particles used in the experiment in relation to the porosity of the outlet

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[12] As discussed earlier in **Section 3.1.5**, the most attractive sites on peat are positions where the potential energy of the adsorbed species will be at a minimum. The release of Cd and Pb in favour of Cu adsorption implies that an attachment of Cu is more energetically preferred than those of Cd and Pb.

filters. Clogs in the outlet filter can slow down buffer flow rates. Other experimental considerations that may be useful for method developers are discussed **Appendix K**.

One possible aspect to be explored in terms of method development is the possibility of directly sampling adsorbed metal concentrations on peat, to complement with information acquired using aqueous samples. This will help in developing a more “close-fit” system to better analyse metal distribution and mass flows.

In overall assessment, experimental method conducted in this study was a very good initial tool towards understanding competitive metal displacement mechanisms on peat. The information derived from the experiments is useful in familiarizing the effects of pH, ionic strength, and other solution properties on adsorption dynamics. Further improvements on the analysis method, however, are necessary in order to better test the viability of peat material as an effective, long term treatment alternative to metal-contaminated waters.

Chapter 6: Conclusions and Recommendations

Competitive adsorption and displacement of metals are complicated processes that are influenced by a multitude of factors. The occurrence of more than one possible adsorption mechanism on peat contributes to the multi-faceted nature of these interactions. The binding of metal ions is thought to occur through a combination of physical electrostatic adsorption, ion-exchange, complexation, and chelation reactions. The extent of adsorption and the mechanisms involved are also influenced by pH, initial metal concentration, the presence and properties of competing metals in solution, and contact time with peat. Metal speciation is important, as the associated properties of ion charge, size and solubility determine how effectively a particular metal adsorbs and how likely it will be displaced by a more preferred competitor.

From the experiments performed, the ease of Cd displacement was shown as a product of the inherent characteristics of both Cd and the competing metals. Aside from pH-dependent speciation, other properties such as electron configuration and ion size are thought to influence metal binding to organic matter. Periodic properties explain the preference of peat towards Cu, Ni or Zn over Cd, as these influence the distribution of charge and the type and strength of complexes formed. The electron configuration of Cu, Ni, and Zn enables these metals to form strong chelates via electron pairing in the *d*-orbital. Lead was also shown to be less easily displaced than Cd, due in part to properties that are more favourable for binding, such as a higher electronegativity and smaller hydrated radius, which give lead a greater affinity for the negatively charged adsorption sites on peat. However, the effectiveness of Pb adsorption is also strongly pH-dependent due to the influence of speciation on ion charge. The analysis of possible displacement by Cu, Ni and Zn is viable at $pH < 7$, before Pb precipitates from solution.

Recommendations for method development include the improvements in the experimental set-up, such that the system becomes more of a closed loop and that mass balance is better accounted for. Adjustments in the mechanism of buffer rinsing also have to be made to improve efficiency. The precision of the experimental method also needs to be analysed to detect other areas of improvement.

Some recommendations for further study include the investigation of temperature effects, as well as the effect of Mg, Ca and Fe on ion-exchange and redox reactions, with appropriate modifications on the method developed in this project. The analysis of metal pairs using molar ratios instead of mass loading will be useful in understanding the stoichiometry involved in the reactions. It is also advisable to try working at higher initial concentrations for selected metal systems, as adsorption behaviour is expected to be different from that at low concentrations. Analysis of higher concentrations also better approximate the conditions in contaminated waste water.

In conclusion, peat is a viable material for the treatment of metal-contaminated water, as it is able to bind metals through several mechanisms. However, the long-term efficiency of peat as an adsorbent in terms of metal selectivity, as well as the time and pH range of its metal binding capacity, needs to be considered in planning wastewater treatment alternatives. The possible displacement of adsorbed ions upon additional metal loadings is a material limitation that has to be addressed and remedied in order for peat to be developed as part of any wide-scale treatment of toxic heavy metals.

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APPENDICES

APPENDIX A: Glossary of terms

This section contains some useful definitions of relevant terminology.

Adsorbate	The material that accumulates at an interface; it is the substance in the adsorbed state
Adsorbent	Solid material on which adsorption occurs
Adsorption	A surface phenomenon defined as the increase in concentration of a particular component at the surface or interface between two phases
Adsorptive	Adsorbable substance in the fluid phase. A molecule or an ion in the soil solution that potentially can be adsorbed.
Chelation	The reaction between a metal ion and a chelating reagent. Chelating reagents are substances with multiple sites available for bonding with metal ions; such bonding typically results in the formation of stable five- or six-membered rings.
Chemisorption	Adsorption involving chemical bonding
Conjugated	Referring to an organic compound, containing two or more double bonds each separated from the other by a single bond
Counterions	Ions with charge opposite that of the solid adsorbent surface
Divalent metals	Metals that are available for reaction in a valence state of two (i.e., carrying a positive electric charge of two units)
Physisorption	Adsorption without chemical bonding
Fulvic acid	The coloured material which remains in solution after the removal of humic acid by acidification.
Functional group	An atom or group of atoms in an organic compound that gives the compound some of its characteristic properties, such as the C=O functional group in aldehydes and ketones, or –COOH in carboxylic acids
Humic acid	A type of humic substance, it is the dark-coloured organic material which can be extracted from soil by various reagents and which is insoluble in dilute acid.
Humic substances	A general category of naturally occurring, biogenic, heterogeneous organic substances that can generally be characterised as being yellow to black in colour, of high molecular weight, and refractory. Humic substances can be subdivided into humic acid (HA), fulvic acid (FA) and humin.
Ion exchange	The interchange between an ion in solution and another ion on a charged surface

Ionic strength	A property of a solution that depends on the total concentration of ions in the solution as well as on the charge carried by each of these ions, usually denoted as $\boldsymbol{\mu}$. (Formula: $\mu = \frac{1}{2} \Sigma c_i Z_i^2$, where c_i is the molar concentration of each ion and Z_i is its charge).
Irving-Williams Order	The order of complex stability of transition metals with organic ligands ($Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < \mathbf{Cu^{2+}} > Zn^{2+}$).
Isotope	Atoms of the same element containing different numbers of neutrons and therefore having different masses.
Ligand	A molecule or ion with at least one pair of unshared electrons available for coordinate bonding with cations
Monolayer capacity	Either the chemisorbed amount required to occupy all surface sites or physisorbed amount required to cover the adsorbent surface
Non-humic substances	Compounds belonging to a known class of biochemistry, such as amino acids, carbohydrates, fats, waxes, resins, and organic acids.
Polydisperse	A term used to describe a polymer consisting of molecules with a variety of chain lengths and structures. Polydisperse substances can exist over a wide range of molecular masses; average weights are commonly used.
Specific surface area	Surface area per unit mass
Stoichiometry	The relationships among the quantities of reactants and products involved in chemical reactions (usually involves mole ratios).
Substituent	In organic chemistry, a substituent is an atom or group of atoms substituted in place of a hydrogen atom on the parent chain of a hydrocarbon. The suffix “-yl” is used when naming organic compounds that contain a substituent.
Surface coverage	Ratio of the amount of adsorbed substance to monolayer capacity

APPENDIX B: Literature Summary of Adsorption Trends: Cd, Cu, Ni, Pb, Zn (Also including H^+, Na^+, Ca^{2+}, Mg^{2+} and Fe)

This section contains a summary of metal adsorption trends found in literature.

Author/year	*Source/ Experiment – Medium*	*Property – process (effect)*	*Adsorption trend (predicted by property or observed in experiment)*	*Explanation*
(Helfferich, 1962)	Textbook information – soils in (Sparks, 1995)	Charge and hydrated radius – *electrostatic ion exchange* (polarization)	$Pb^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+}$	Selectivity sequence or lyotropic series shows that ions with the higher charge and the smaller hydrated radius will be preferred, because of **greater polarization**. **Trend according to electrostatic ion exchange**: for a given group of elements in the periodic table with the same valence, ions with the smallest hydrated radius will be preferred. If dealing with ions of a different valence, generally the higher charged ion will be preferred.
(Ong and Swanson, 1966)	In (Brown, P.A. *et al.*, 2000) – peat	Ionic potential (ratio of charge to ionic radius)		Metals having the greatest ionic potential would be removed first, and if the sites were still undersaturated, then those having lower ionic potential would be removed in sequence.
(Pakarinen *et al.*, 1981)	Peat	*Sorption of metals*	$Pb^{2+} > Cu^{2+} > Zn^{2+}$	
(Maslennikov and Kiselva, 1989)	Peat	Affinity for peat	$Cu^{2+}> Zn^{2+}> Fe^{2+}> Ca^{2+}$	
(Sposito, 1989)	Textbook information – soils	Ionic radius	$Na^{+} > Ca^{2+} > Cd^{2+} > Zn^{2+}$	The **tendency to form inner-sphere complexes** increases with increasing ionic radius. Metal cations with larger ionic radii will create a smaller electric field and will be **less likely to remain solvated** in the face of competition by a surface functional group. A larger R implies a larger spread of the electron configuration in space and a **greater tendency for a metal ion to polarise** (distort) in response to the electric field of a charged surface functional group. (Polarization is necessary for covalent bonding.)

		Electron configuration (Irving-Willams order)	$Cu^{2+} > Ni^{2+}$	For transition metal ions, ionic radius is not adequate as a single predictor of adsorption affinity (electron configuration has an important role in complexation).
(Chistova *et al.*, 1990)	Granulated peat	Affinity for peat	$Fe^{3+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$	
		Cation chelation capacity w/peat	$Fe^{3+} > Pb^{2+} > Cu^{2+} > Ni^{2+}$	
(Chen *et al.*, 1990)	Eutrophic peat	*Metal ion-exchange*	Pb > Cu > Ca > Mg, Zn	
	Oligotrophic peat	*Metal ion-exchange*	Pb > Ca > Cu > Mg, Zn	
(McBride, 1994)	Textbook information – soils	Electronegativity (covalent bond strength) in (McBride, 1994; Brown, T.L. *et al.*, 2000)	Cu > Ni > Pb > Cd > Ca > Zn 2.0 > 1.91 > 1.87 > 1.7 > 1.0 > 1.65	The more electronegative metals should form the **strongest covalent bonds** with O atoms on any particular mineral surface. *The affinity of humus for Ca^{2+} is higher than predicted by Electronegativity; certain complexing or chelating groups may select based on ionic size
		Charge-to-radius ratio (electrostatics – effect on ionic bonding)	Ni > Cu > Zn > Cd > Pb	The strongest bond should be formed by the metal with the greatest charge-to-radius ratio.
		Metal radius (Irving-Williams series of complexing strength)	Cu > Ni, Zn > Ca ($Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < \mathbf{Cu^{2+}} > Zn^{2+}$)	For any particular type of Lewis base (e.g., carboxylate), metals of smaller radius generally from the stronger complex. (Considering divalent metal ions.)
(Drever, 1997)	Textbook information – natural waters	Intrinsic binding constants (binding and complexing between metals and dissolved humics)	$Cu^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+} > Ca^{2+}$ Log binding constant: -0.72 > -0.81 > -1.04 > -1.63 > -2.67	Related to pH metallic speciation in reducing or oxidising environments. The numbers are a good indicator of the relative extent of complexing to be expected between the individual metals and natural dissolved organic matter. A larger –log means weaker binding
(McKay and Porter, 1997)	Peat (initial pH 4.5)	Pauling Electronegativity	Cu > Cd > Zn 1.9 > 1.69 > 1.65	
		Standard reduction potential	Cu > Cd > Zn 0.341 > -0.403 > -0.762	
(Brown, T.L. *et al.*, 2000)	Textbook information – aqueous solutions	Activity series – *redox*	Cu > H > Pb > Ni > Fe > Cd > Zn > Mg > Na > Ca	Activity series arranged according to standard reduction potential.

(Xiao and Thomas, 2004)	Oxidised nanoporous activated carbon	Hydrated ion size (smaller size, greater affinity)	$Pb^{2+} > Cd^{2+} > Ca^{2+}$	Pb has the smallest hydrated ion size, thus greater adsorption affinity.
(Kalmykova *et al.*, 2006a)	Peat	Adsorption efficiency	Cu > Pb > Zn > Cr	
(Kalmykova *et al.*, 2006b)		Sorption capacity (µg/g) Uptake (% removed)	Pb > Cu > Ni > Cd > Zn	

APPENDIX C: Preparatory procedures for the metal adsorption experiments on peat

This section contains laboratory protocol for the preparation of reagents and materials used in the metal adsorption experiments. The procedures were based on protocol applied in the experiments by Kalmykova (2004; 2006).

A. Preparation of metal stock solutions

Metal stock solutions, each with a concentration of 1000 ppm (1 g/L) were prepared from metal nitrate salts. A calculated amount of salt was weighed, transferred into a volumetric flask, and then diluted to 100 mL. Preservation of the stock solutions was done by adding 1 mL HNO_3.

The formula used for the calculation of the weight of salt:

$$weight\ of\ M(NO_3)_2 = 0.1 * \frac{MW_{M(NO_3)_2}}{(AW_M)(stoichiometric\ ratio)}$$

Where: *MW* = molecular weight of the metal nitrate salt
AW = atomic weight of the target metal
Stoichiometric ratio = the number of moles of metal per mole of salt

B. Preparation of buffer solutions

The reagents needed for buffer preparation were:

- Acetate buffer (pH 4, pH 5.6): sodium acetate and acetic acid
- Phospate buffer (pH 7): Na_2HPO4, HNO_3

The proportion of acid and base were prepared in accordance to the scheme presented in the following table:

Purpose	Strength, mM	pH	Volume, ml	Acid, grams	Base, grams
For batch with ash and displacement tests with peat	20	**4**	**5 000**	**5,068**	**1,271**
			10 000	**10,136**	**2,5428**
		5.6	**500**	**0,066**	**0,722**
			1 000	**0,132**	**1,444**
			5 000	**0,6726**	**7,276**
			10 000	**1.345**	**14,552**
		7 (phosphate!)	**1 000**	**0,59**	**2,67**
			5 000	**2,483**	**10,77**
			10 000	**4,965**	**21,54**

For washing of peat	250	4	2 000	27, 7946	7,1366
			5 000	61,9896	17, 8497
		5.6	5 000	7,08	92,86
		7	500	2,67	14,684
			5 000	26.72	146,98

C. Pre-treatment of peat

The pre-treatment of peat for each experimental run was comprised of two stages: 1) rinsing with 0.25 M buffer solution; and, 2) determination of dry weight. The following procedures were applied.

1. Pre-treatment with 0.25 M buffer

- Prepare 0.25 M buffer solution of the pH level that will be used in the experiment.
- Weigh dry 0.5 – 0.125 mm sized peat, with some extra amount which may be lost during the pre-treatment (~0.5 g extra).
- Place the peat in a small, clear plastic bag and add a few milliliters of buffer. Seal the bag and mix vigorously until all the peat is thoroughly moistened.
- Prepare a funnel with fluted coarse filter paper in it, and a large Erlenmeyer flask for collecting the buffer washing.
- Transfer the peat onto the fluted filter and continue washing with buffer (at least 0.5 L for pH 4 and until the water becomes clean / colourless for the higher pH).
- Let the fluid run out and take a sample (about 1 g) for the determination of the dry weight.

2. Determination of dry weight

- Scoop out a small amount of peat (1 g) from the treated batch and place in a ceramic crucible (keep uncovered).
- Place the crucible in the oven, temperature at 105 – 110°C, and leave for at least 30 min or until it’s dry (may even be overnight in some cases).
- Determine the dry weight and recalculate how much wet peat you should take so that it corresponds to the for example 1 g of dry peat.

The following formulas were used in the calculations:

$$percentage\ moisture = \frac{weight\ before\ drying - weight\ after\ drying}{weight\ before\ drying}$$

$$percentage\ solid = 1 - percentage\ moisture$$

$$wet\ weight\ of\ peat * \left(percentage\ solid\right) = 1.0\ g\ dry\ weight\ of\ peat$$

APPENDIX D: Experiment photographs

This section shows some of the materials and equipment used, as well as the experimental set-up.

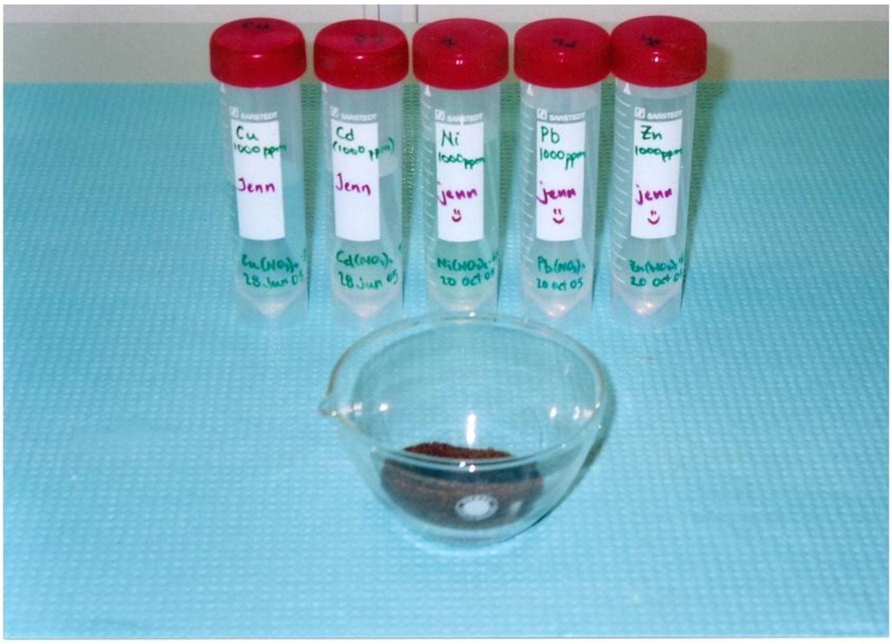


Figure I: Metal nitrate solutions and dried peat

Figure II: Glass filters – outlet filter (1.35 x 1.5 cm) and inlet filter (2.5 x 1.3 cm)

Figure III: Watson-Marlow 302S peristaltic pump

Figure IV: Peat samples in crucibles – for dry weight determination

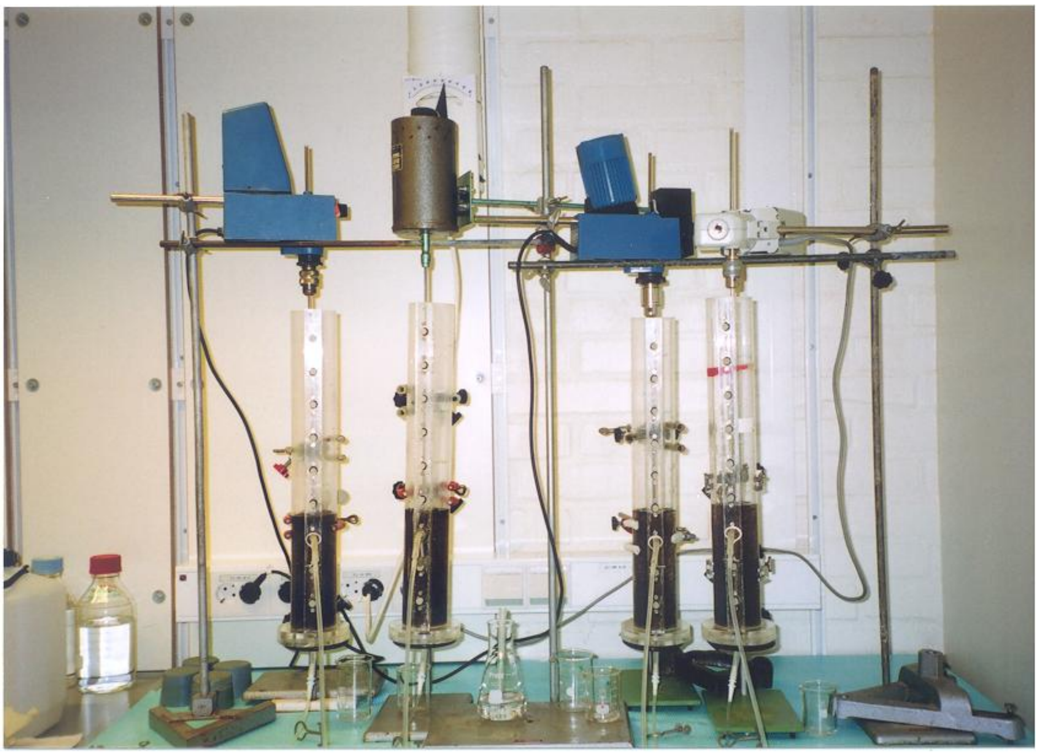


Figure V: Experimental columns with overhead motors

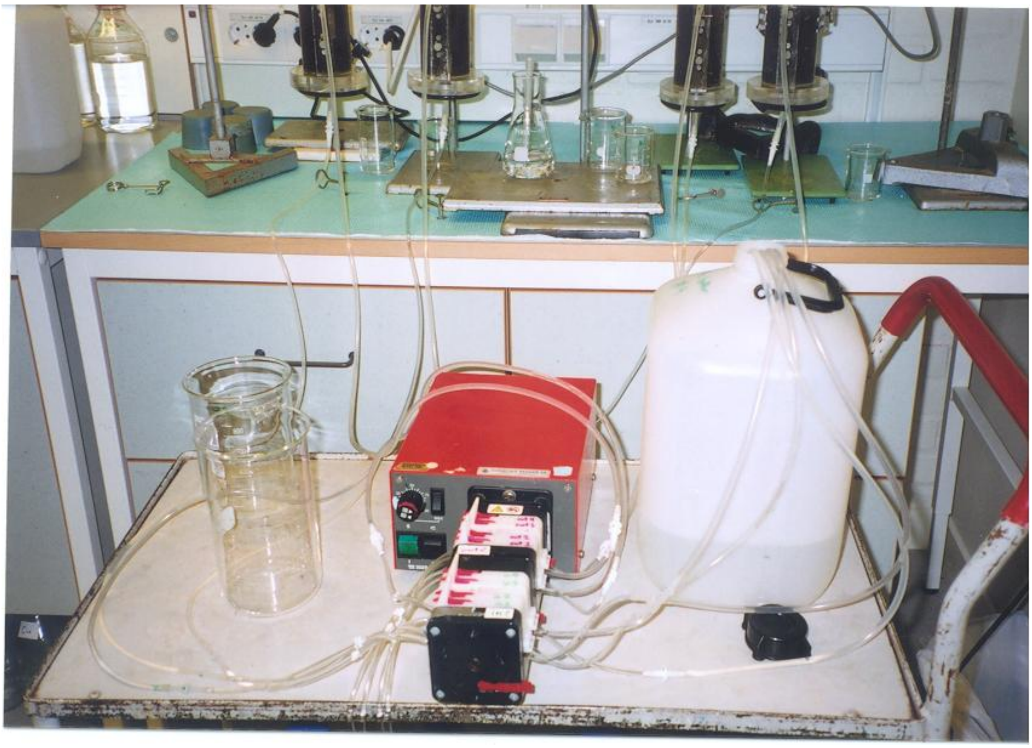


Figure VI: Peristaltic pump with tubing connected for buffer rinse

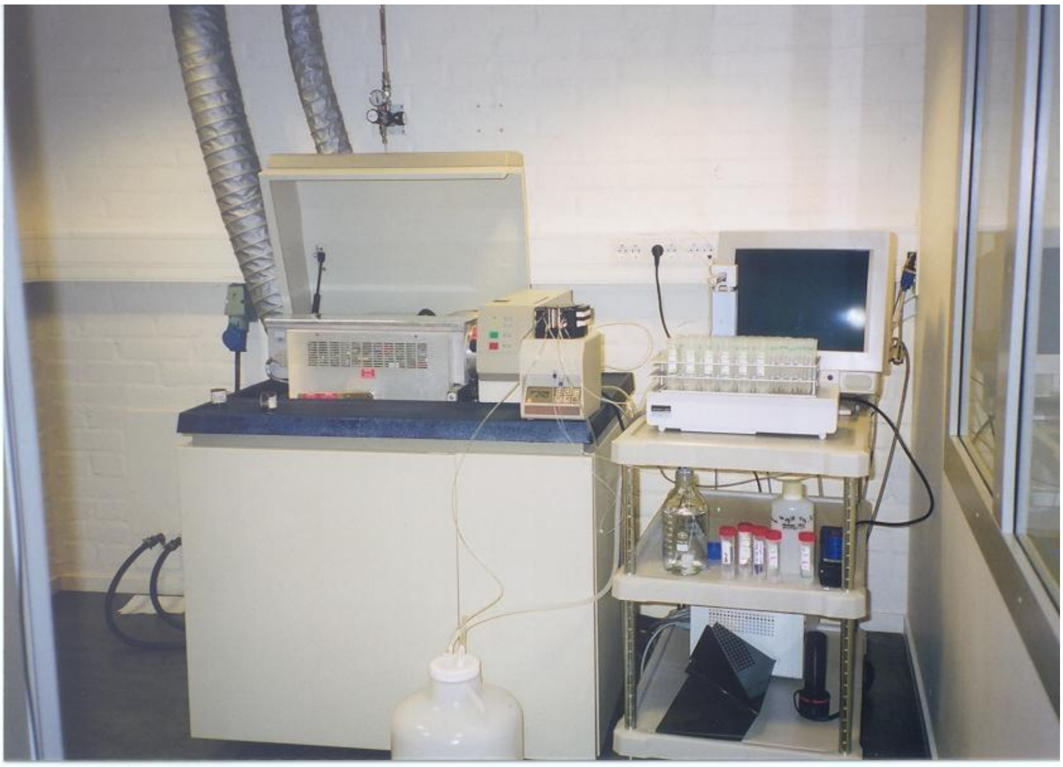


Figure VII: ICP-MS instrumentation (Perkin-Elmer ELAN 6000)

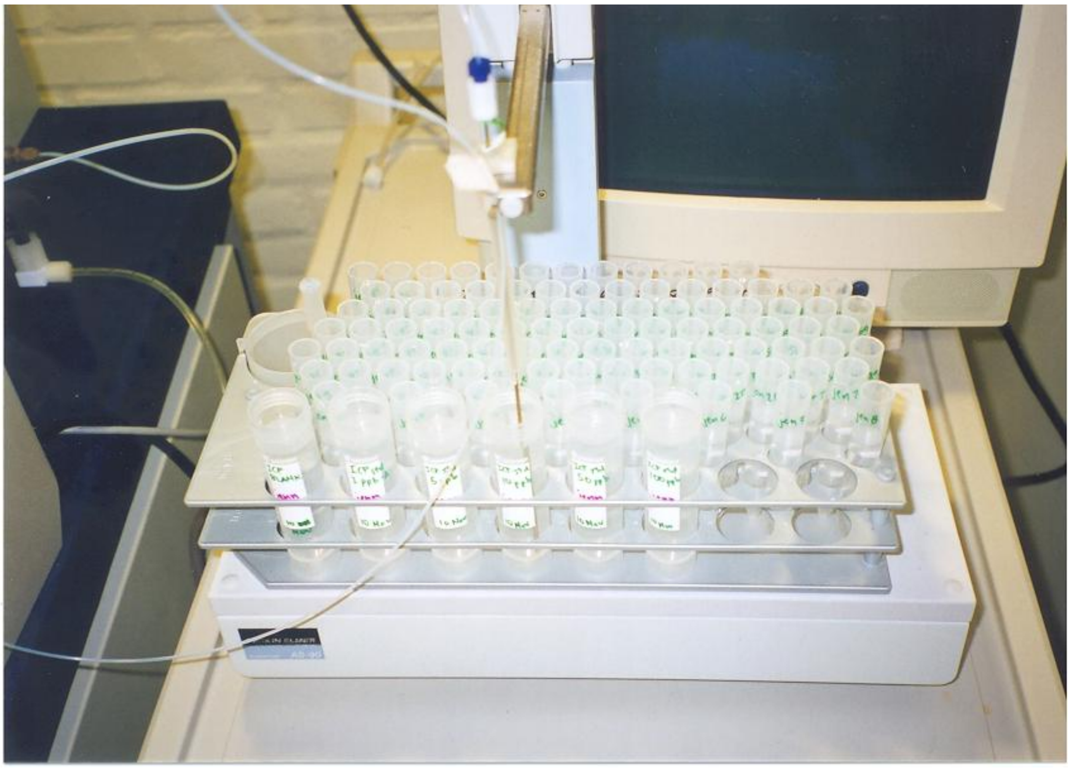
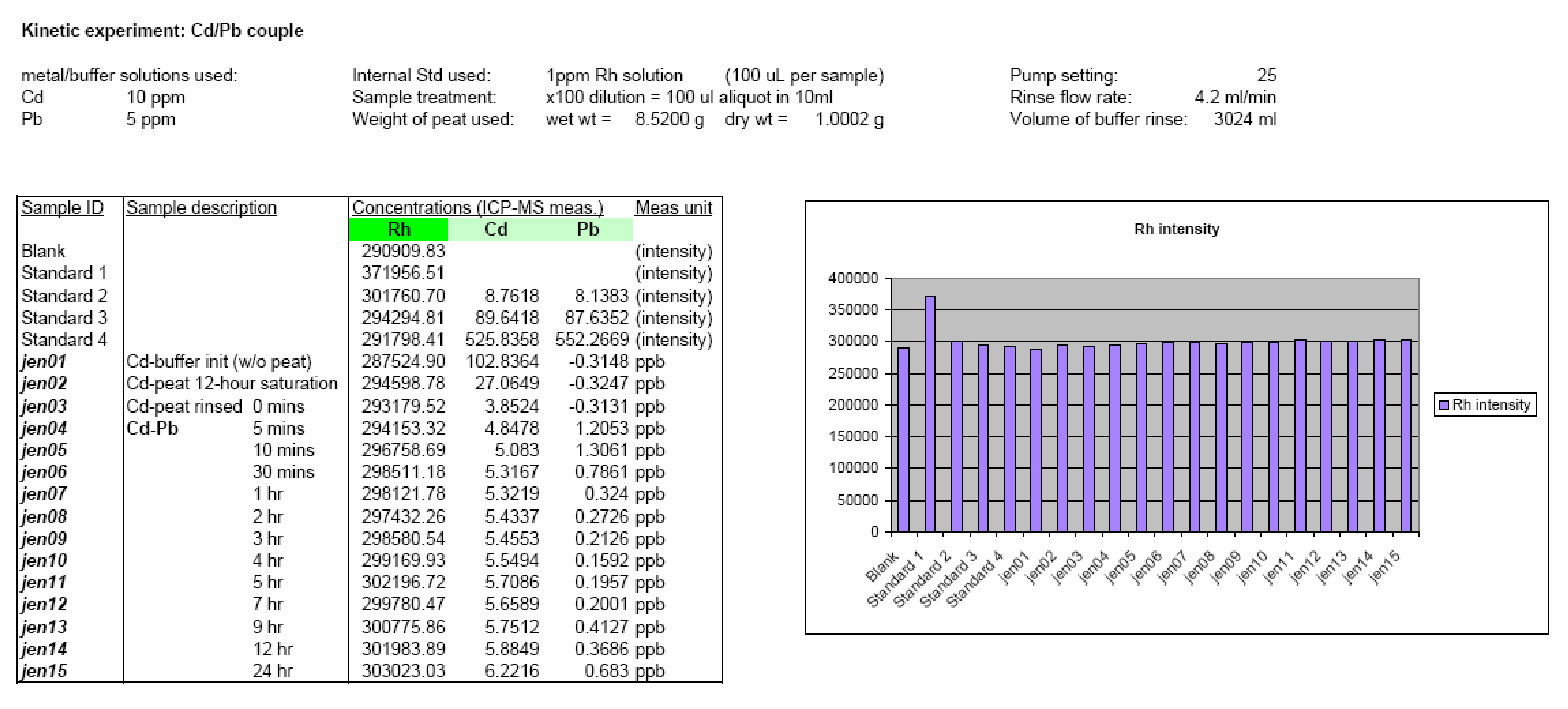


Figure VIII: Loaded standards and samples

APPENDIX E: ICP-MS results - kinetic experiment

This section contains the detailed results and calculations for the kinetic experiment, using a Cd/Pb system.



Kinetic experiment: Cd/Pb couple

metal/buffer solutions used:
Cd 10 ppm
Pb 5 ppm

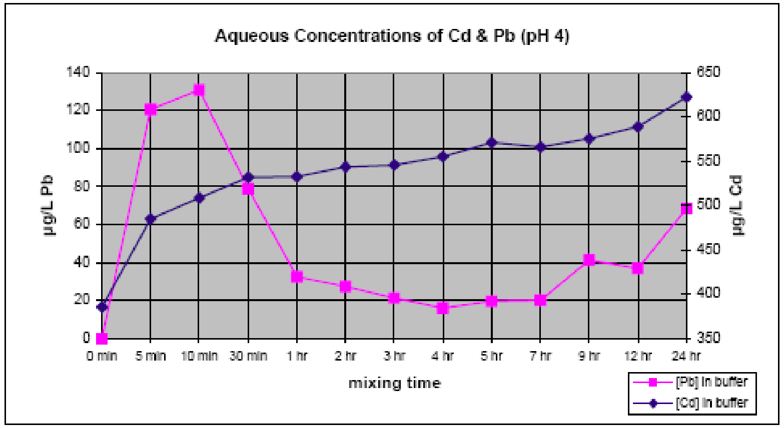
Internal Std used: 1ppm Rh solution (100 uL per sample)
Sample treatment: x100 dilution = 100 ul aliquot in 10ml
Weight of peat used: wet wt = 8.5200 g dry wt = 1.0002 g

Pump setting: 25
Rinse flow rate: 4.2 ml/min
Volume of buffer rinse: 3024 ml

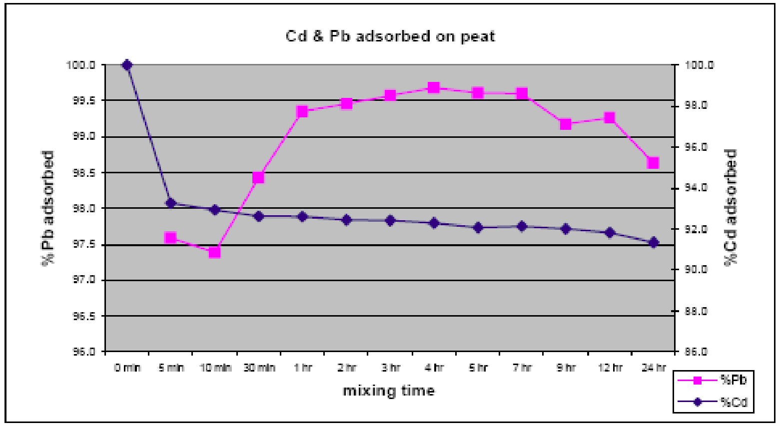
Sample ID	Sample description		Concentrations (ICP-MS meas.)			Meas unit
			Rh	Cd	Pb	
Blank			290909.83			(intensity)
Standard 1			371956.51			(intensity)
Standard 2			301760.70	8.7618	8.1383	(intensity)
Standard 3			294294.81	89.6418	87.6352	(intensity)
Standard 4			291798.41	525.8358	552.2669	(intensity)
jen01	Cd-buffer init (w/o peat)		287524.90	102.8364	-0.3148	ppb
jen02	Cd-peat 12-hour saturation		294598.78	27.0649	-0.3247	ppb
jen03	Cd-peat rinsed	0 mins	293179.52	3.8524	-0.3131	ppb
jen04	Cd-Pb	5 mins	294153.32	4.8478	1.2053	ppb
jen05		10 mins	296758.69	5.083	1.3061	ppb
jen06		30 mins	298511.18	5.3167	0.7861	ppb
jen07		1 hr	298121.78	5.3219	0.324	ppb
jen08		2 hr	297432.26	5.4337	0.2726	ppb
jen09		3 hr	298580.54	5.4553	0.2126	ppb
jen10		4 hr	299169.93	5.5494	0.1592	ppb
jen11		5 hr	302196.72	5.7086	0.1957	ppb
jen12		7 hr	299780.47	5.6589	0.2001	ppb
jen13		9 hr	300775.86	5.7512	0.4127	ppb
jen14		12 hr	301983.89	5.8849	0.3686	ppb
jen15		24 hr	303023.03	6.2216	0.683	ppb

Appendix E: ICP-MS results – kinetic experiment

Sample ID	Sample description	Concentrations (aqueous, µg/L)	
		Cd	Pb
jen01	Cd-buffer init (w/o peat)	10284	-31
jen02	Cd-peat 12-hour saturation	2706	-32
jen03	Cd-peat rinsed 0 min	385	0
jen04	Cd-Pb 5 min	485	121
jen05	10 min	508	131
jen06	30 min	532	79
jen07	1 hr	532	32
jen08	2 hr	543	27
jen09	3 hr	546	21
jen10	4 hr	555	16
jen11	5 hr	571	20
jen12	7 hr	566	20
jen13	9 hr	575	41
jen14	12 hr	588	37
jen15	24 hr	622	68



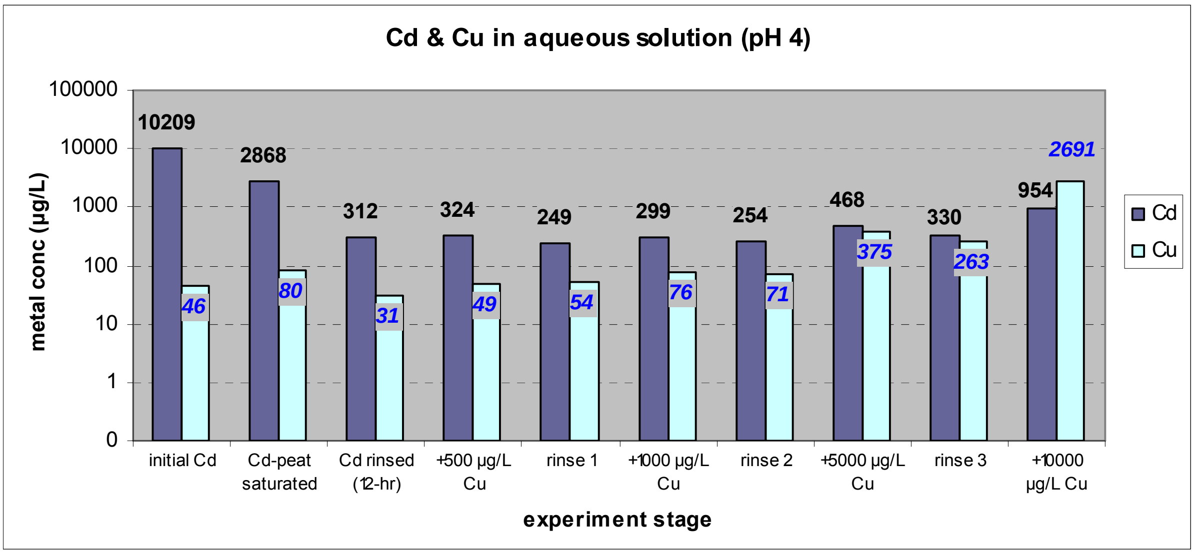
Sample ID	Sample description	Concentrations (adsorbed, µg/L)		(%adsorbed or %released)		
		Cd	Pb	Cd	Pb	Cd
				%adsorbed	%adsorbed	%released
jen01	Cd-buffer init (w/o peat)	0				
jen02	Cd-peat 12-hour saturation	7577				
jen03	Cd-peat rinsed 0 min	7192		100		
jen04	Cd-Pb 5 min	6707	4879	93.3	97.6	6.74
jen05	10 min	6684	4869	92.9	97.4	7.07
jen06	30 min	6660	4921	92.6	98.4	7.39
jen07	1 hr	6660	4968	92.6	99.4	7.40
jen08	2 hr	6649	4973	92.4	99.5	7.56
jen09	3 hr	6646	4979	92.4	99.6	7.59
jen10	4 hr	6637	4984	92.3	99.7	7.72
jen11	5 hr	6621	4980	92.1	99.6	7.94
jen12	7 hr	6626	4980	92.1	99.6	7.87
jen13	9 hr	6617	4959	92.0	99.2	8.00
jen14	12 hr	6603	4963	91.8	99.3	8.18
jen15	24 hr	6570	4932	91.3	98.6	8.65

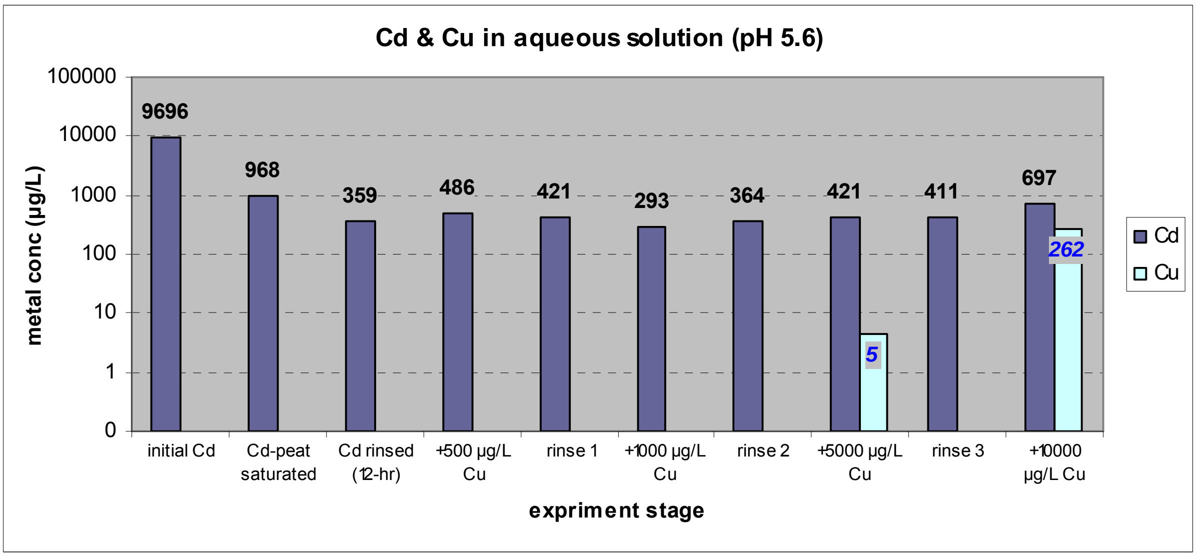


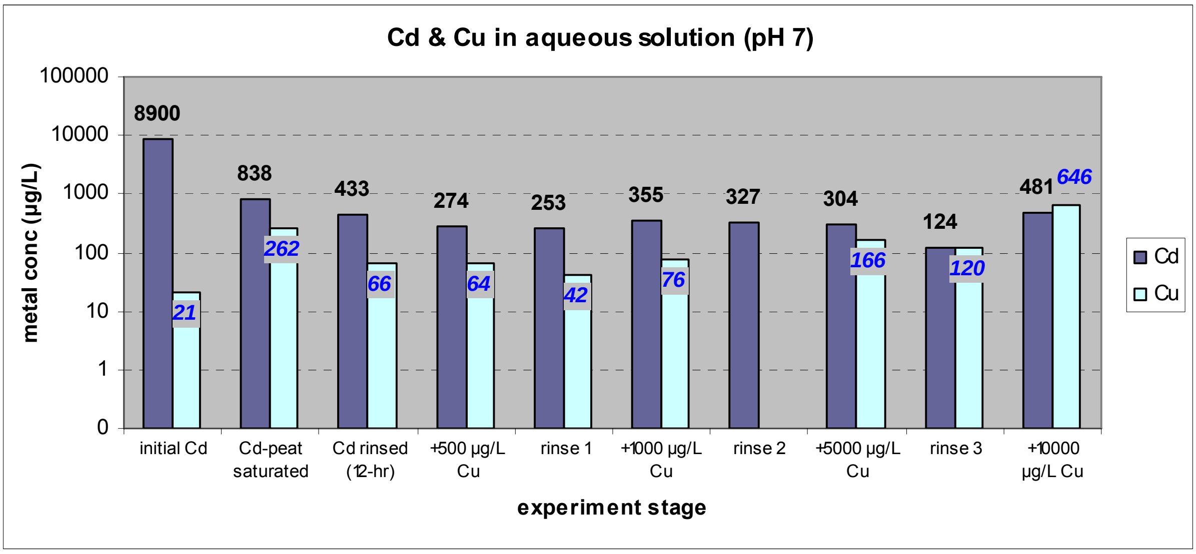
APPENDIX F: ICP-MS results for the metal displacement experiments

The complete data for all the binary systems studied are presented graphically in this section.

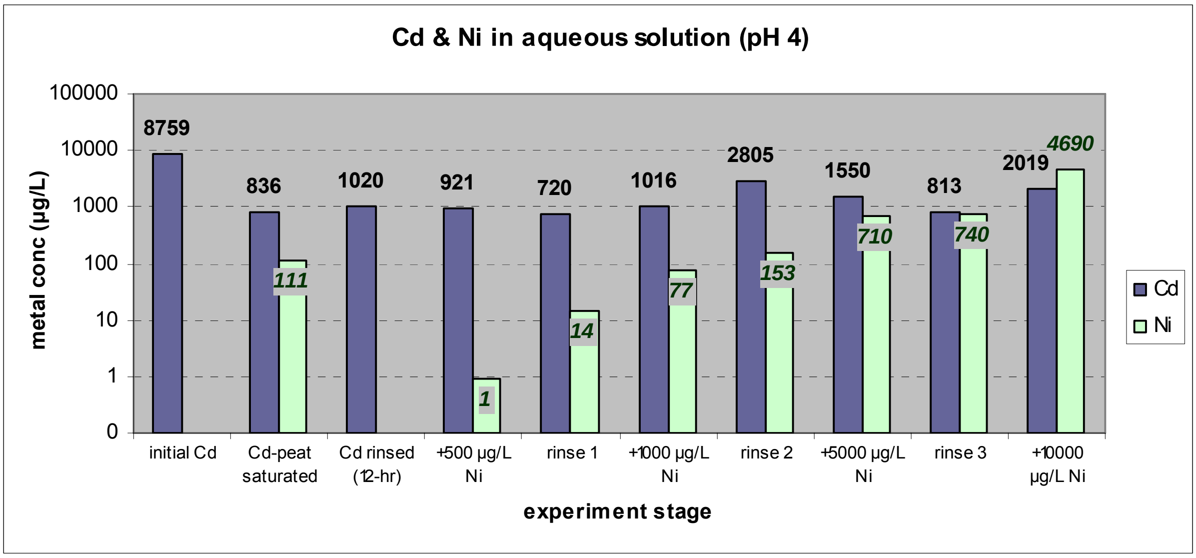
<u>Cd/Cu experiments</u>

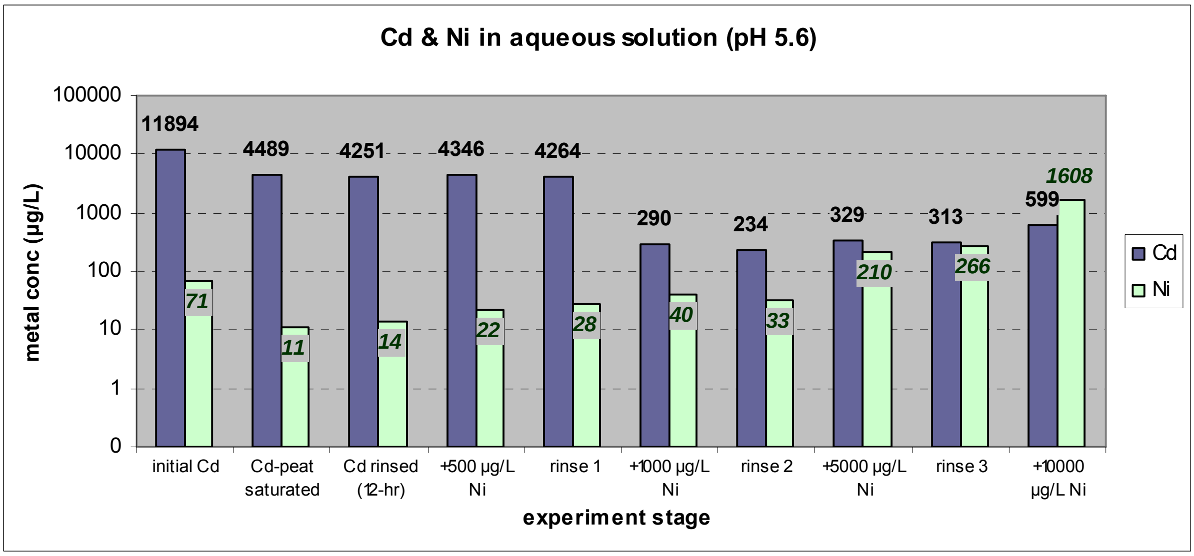


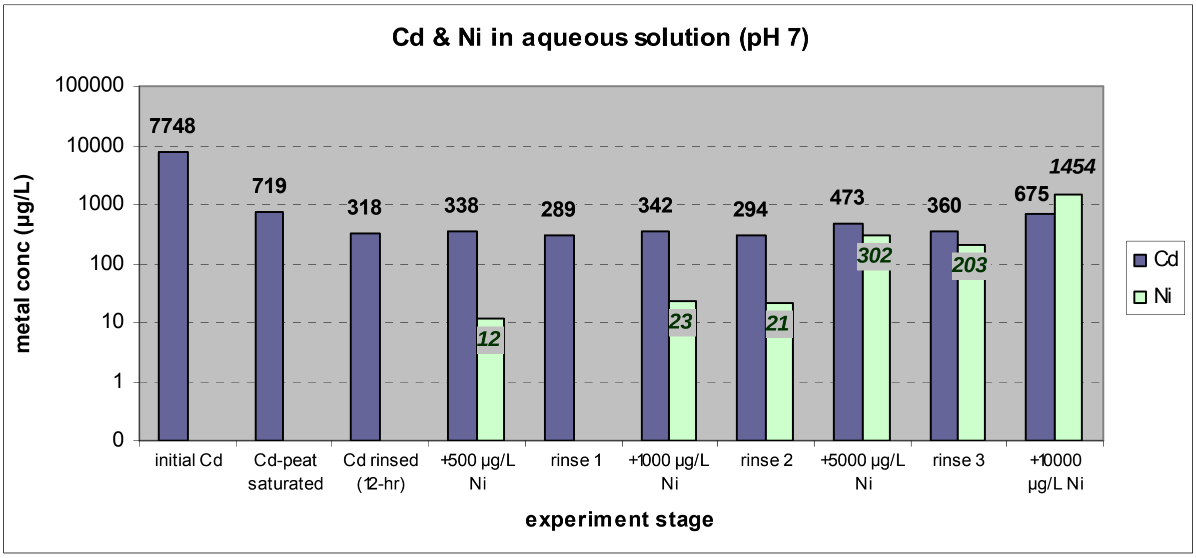




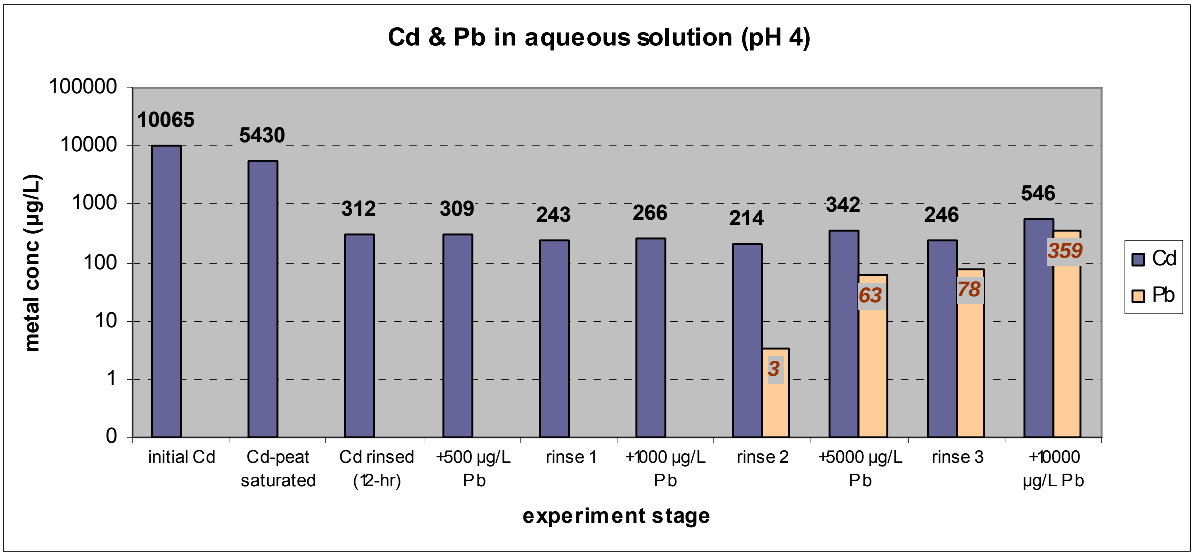
Cd/Ni experiments

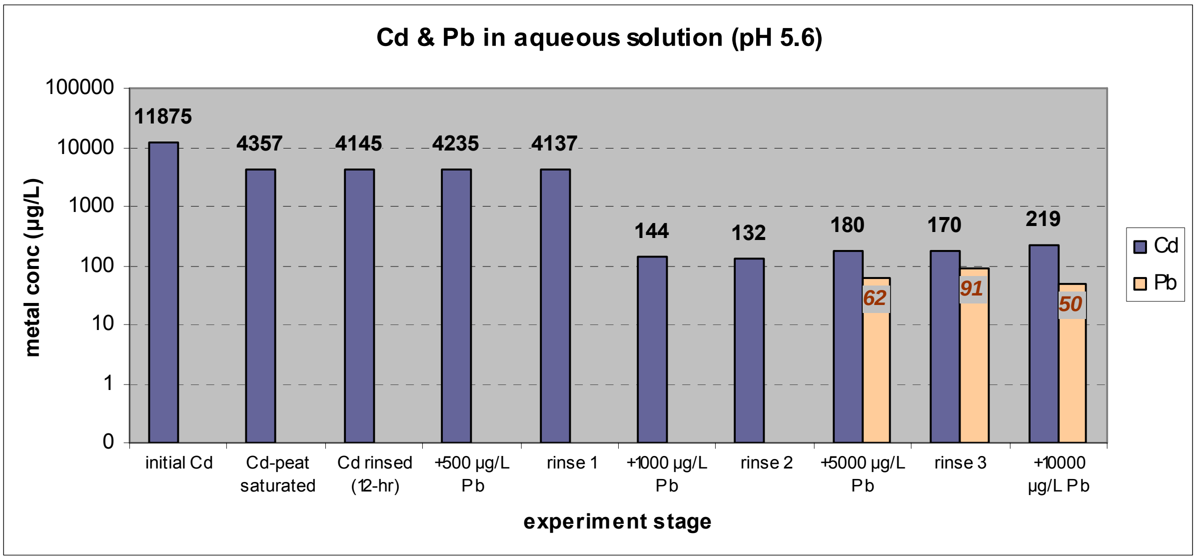


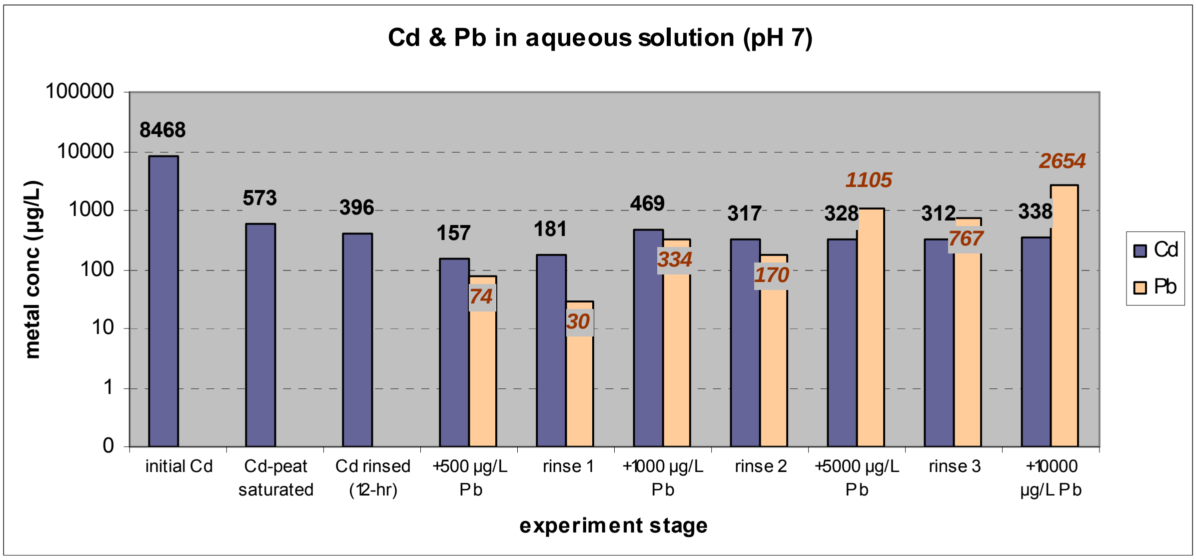




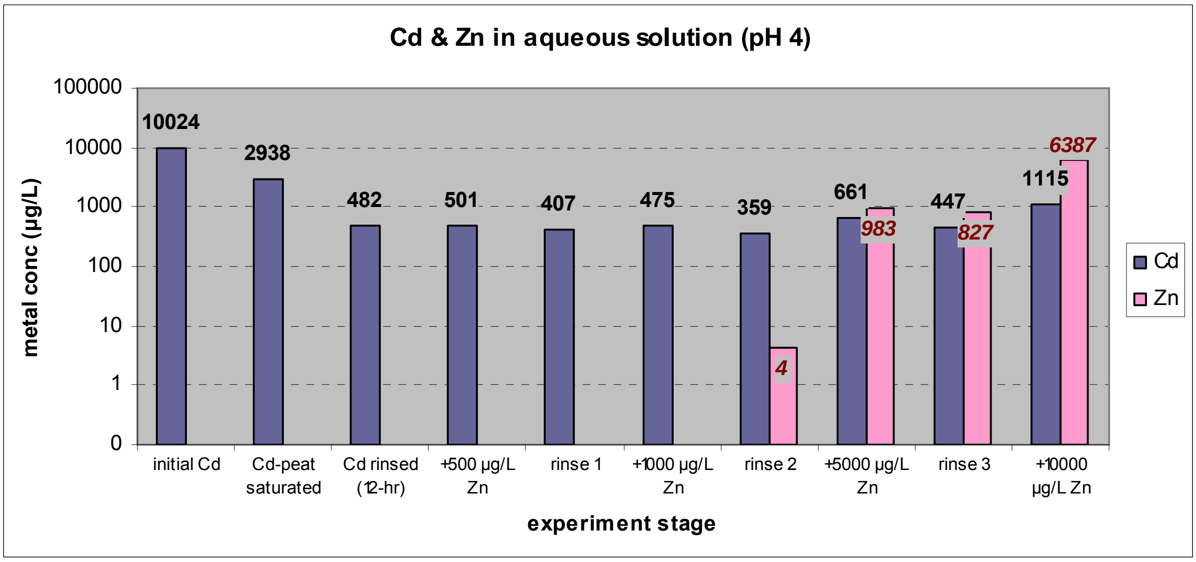
Cd/Pb experiments

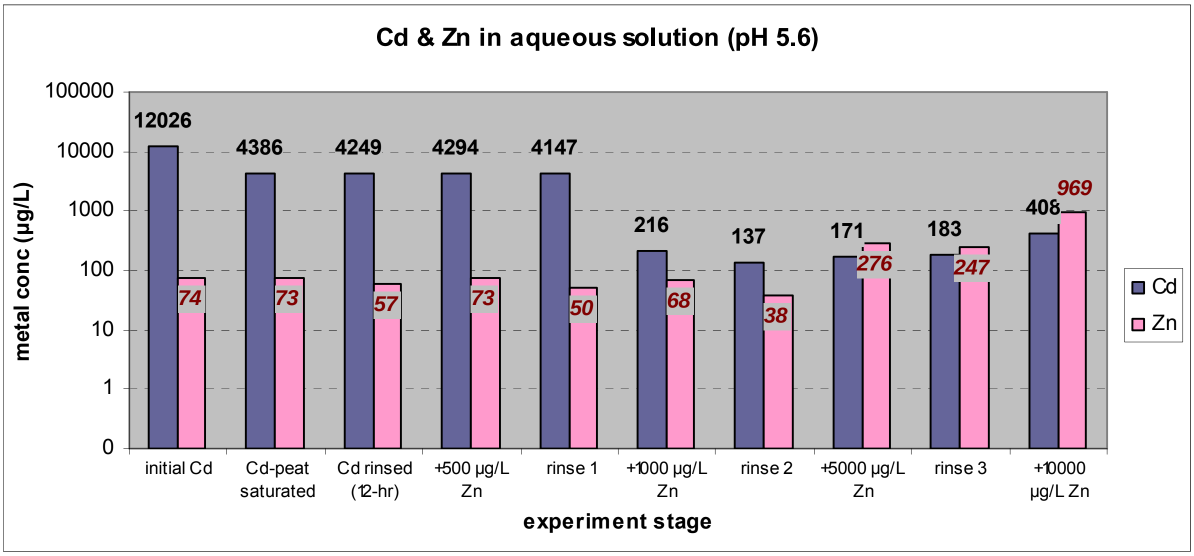


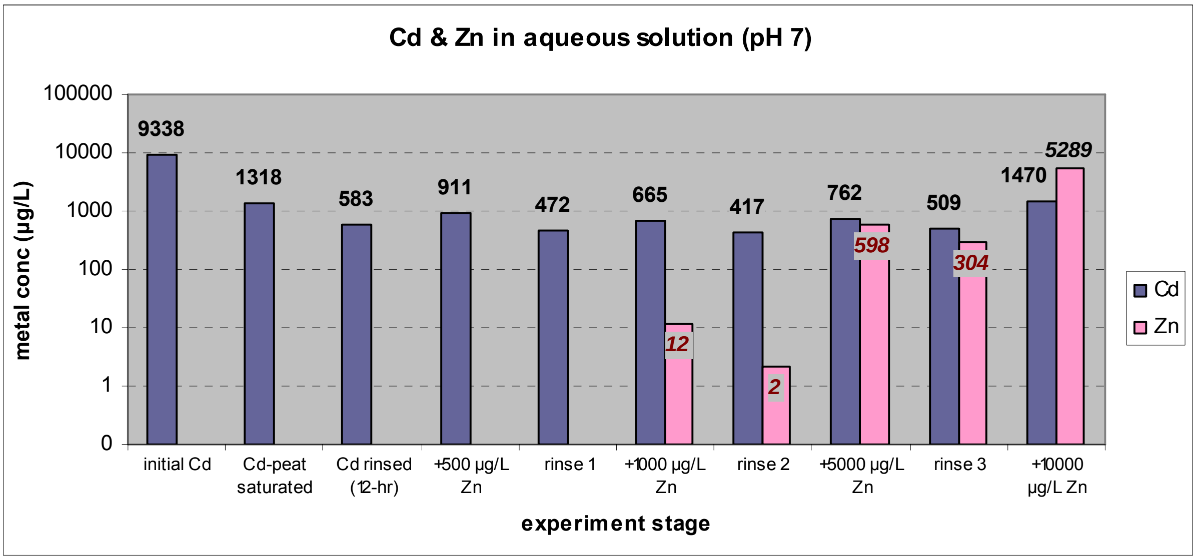




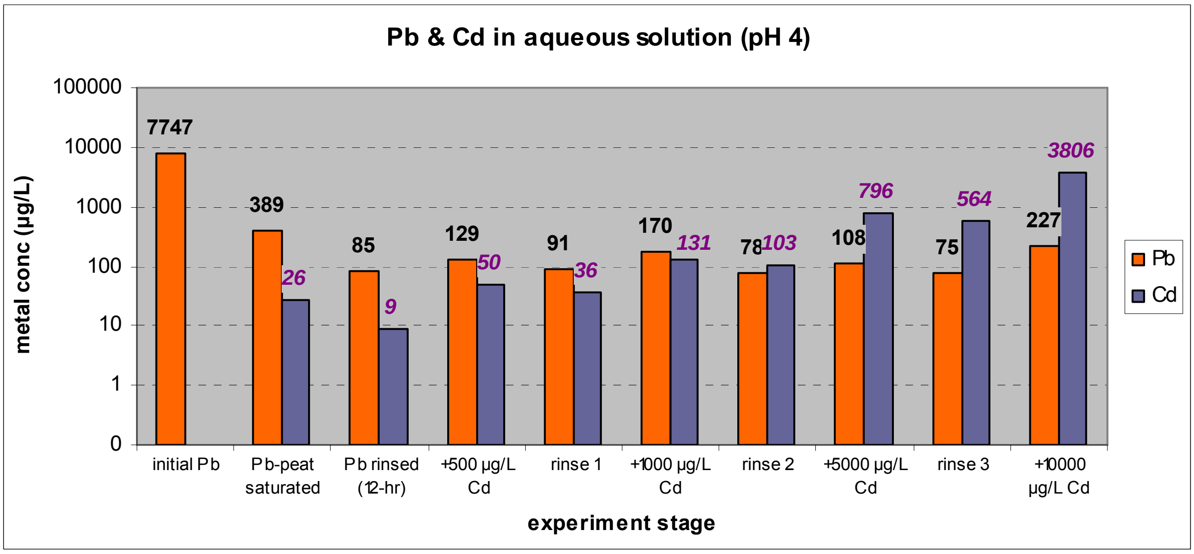
Cd/Zn experiments

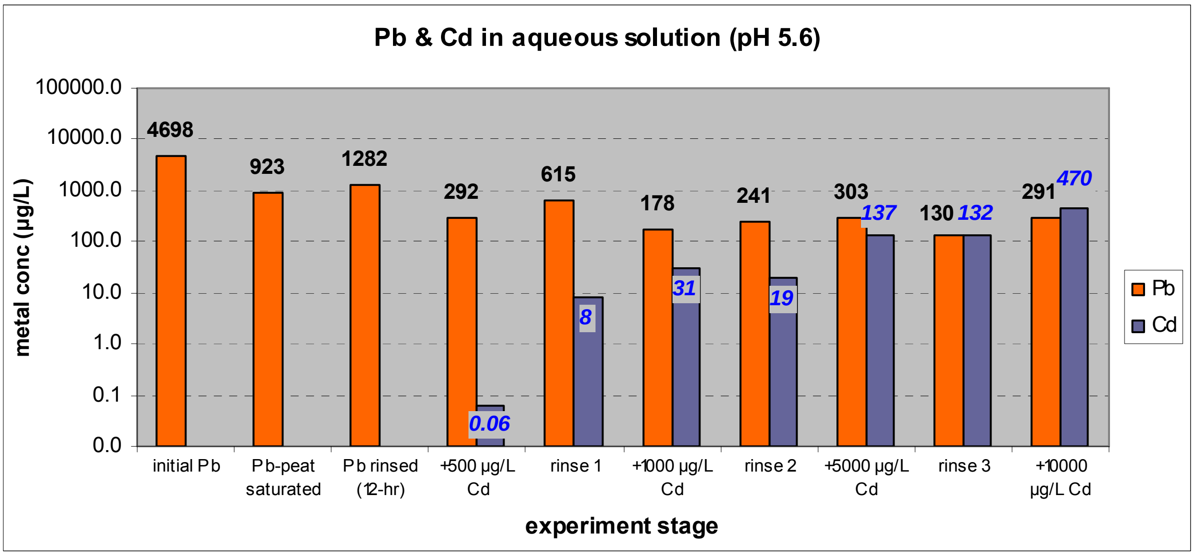


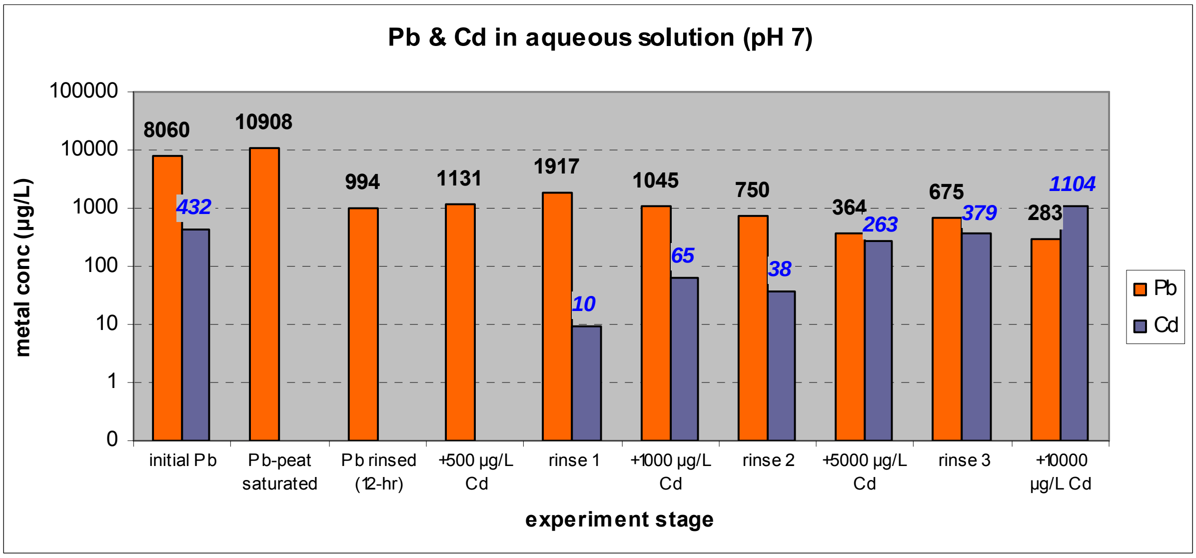




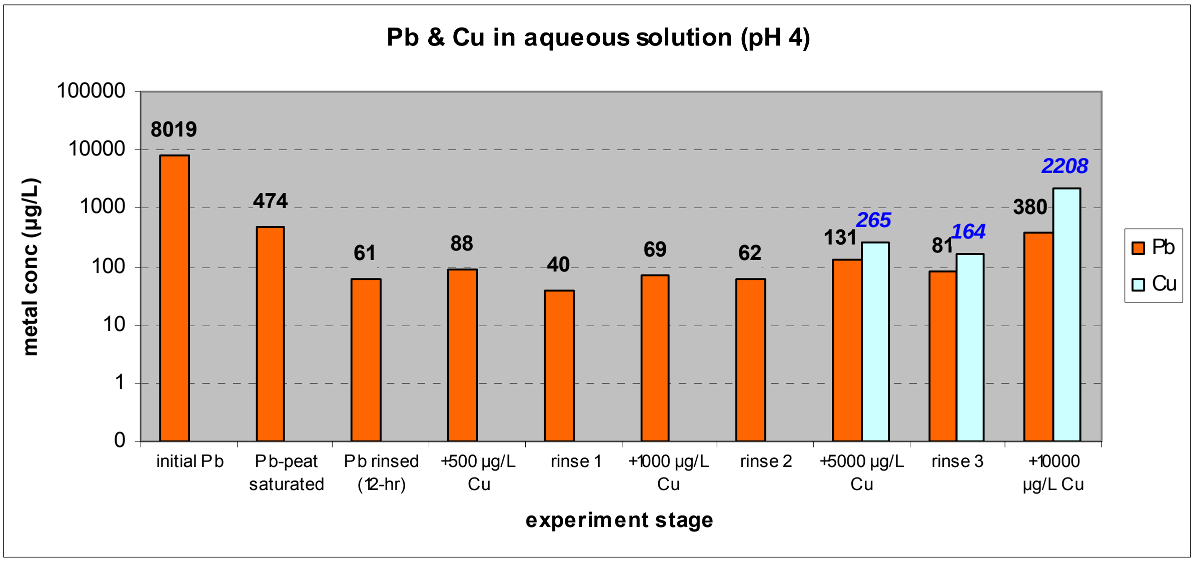
Pb/Cd experiments

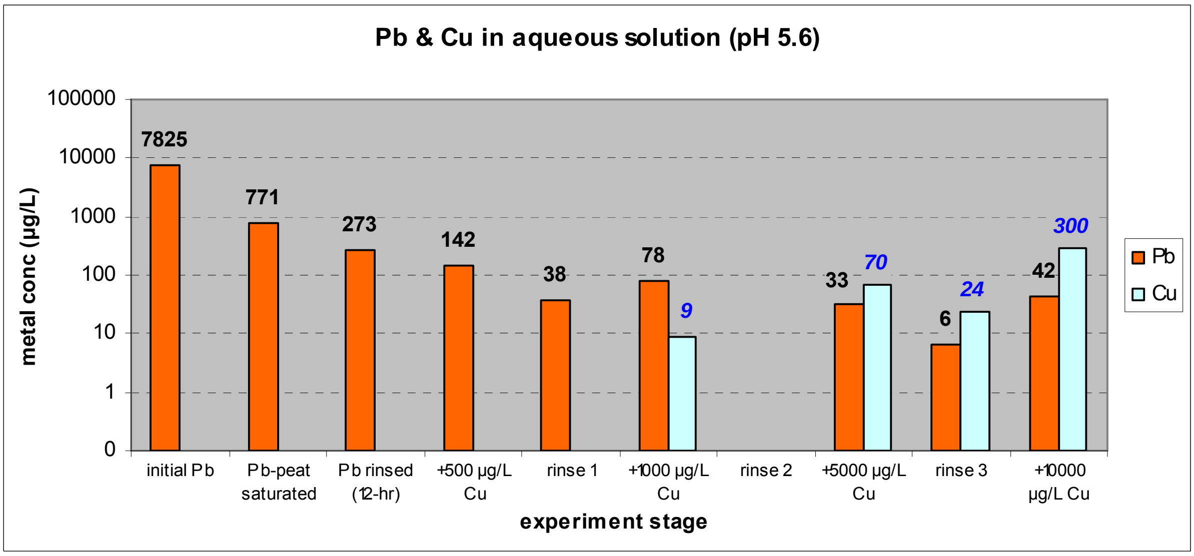


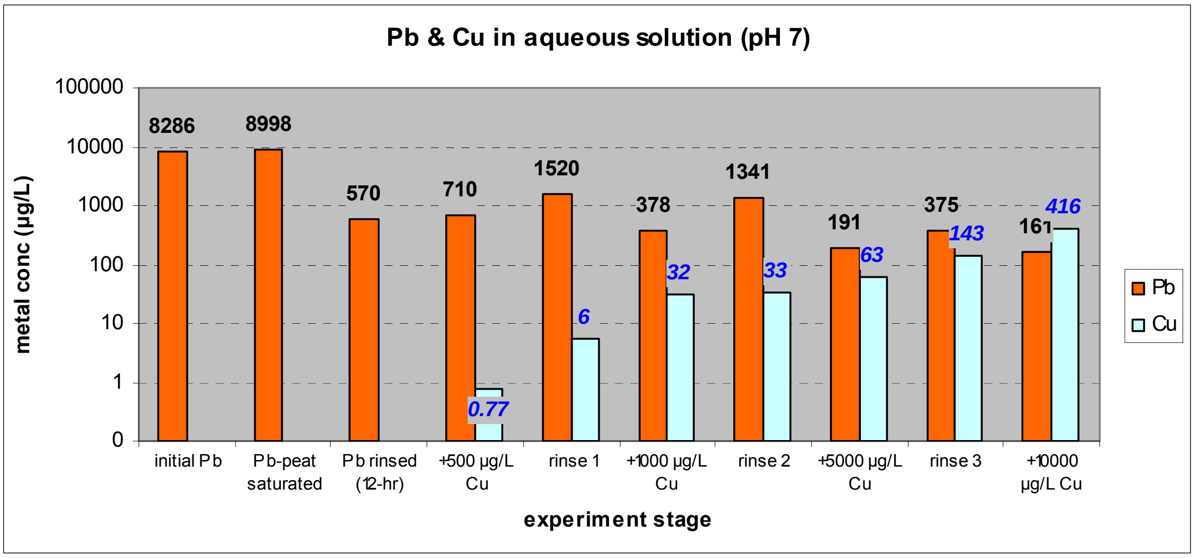




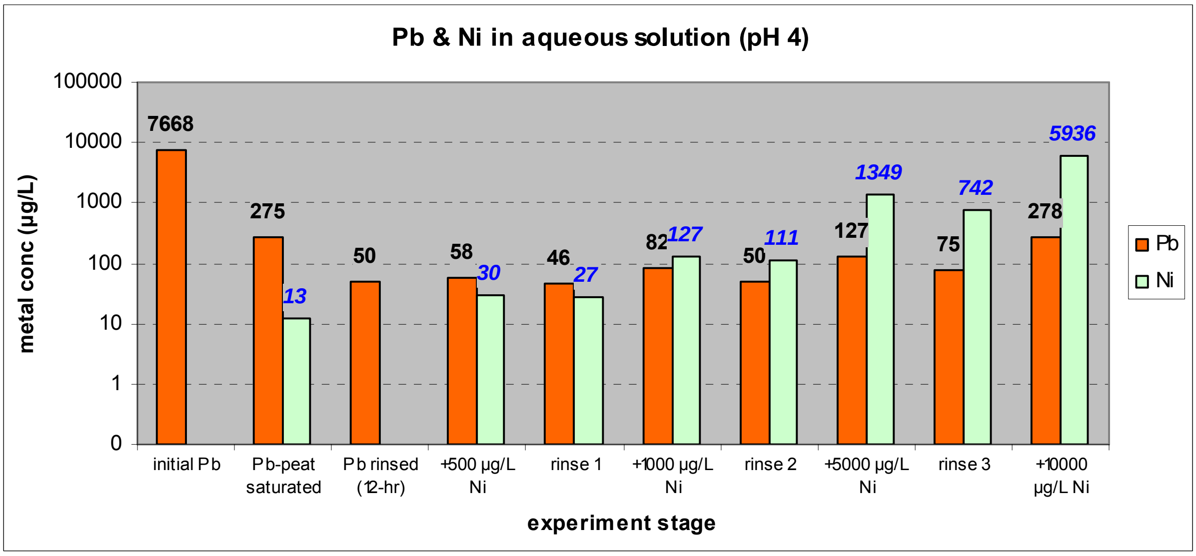
Pb/Cu experiments

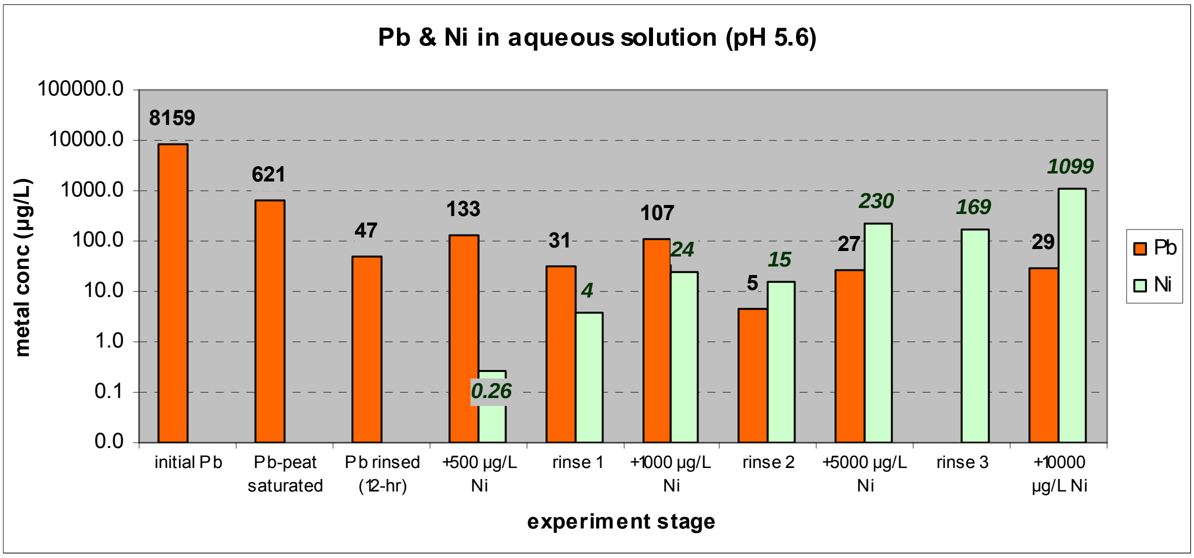


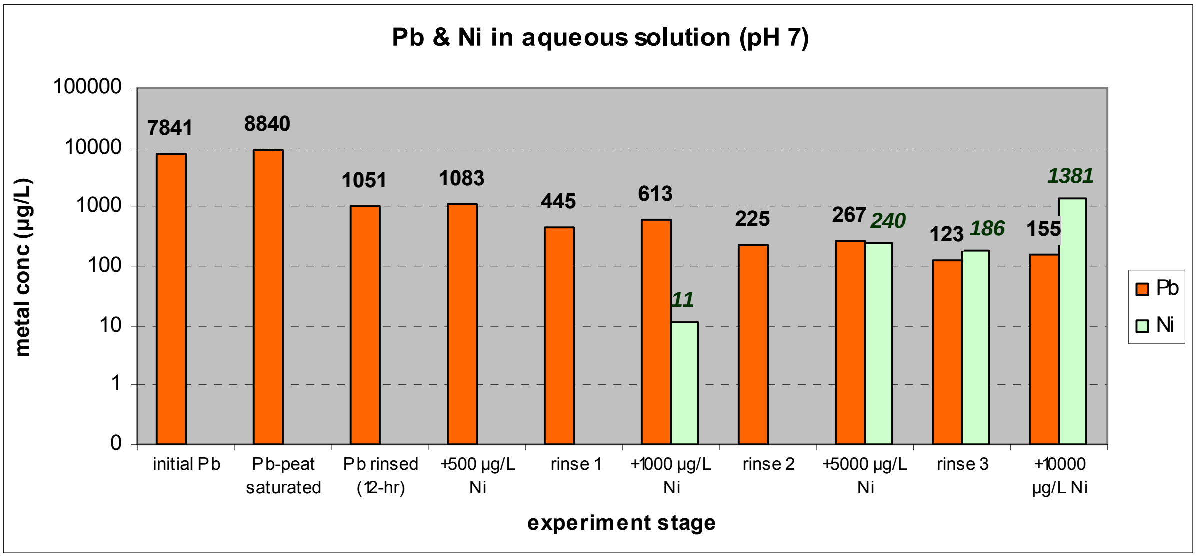




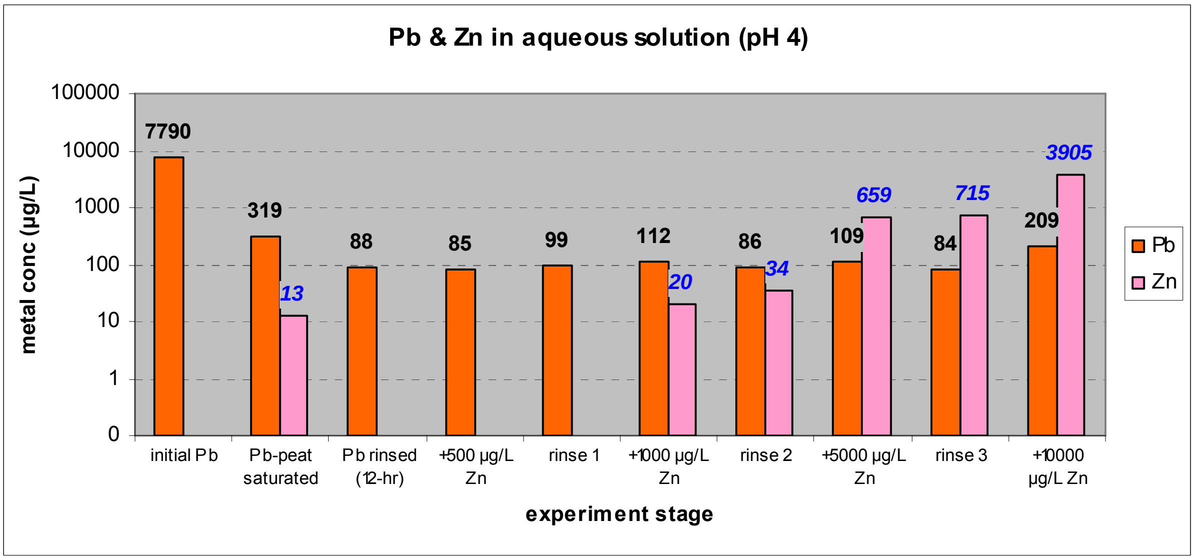
Pb/Ni experiments

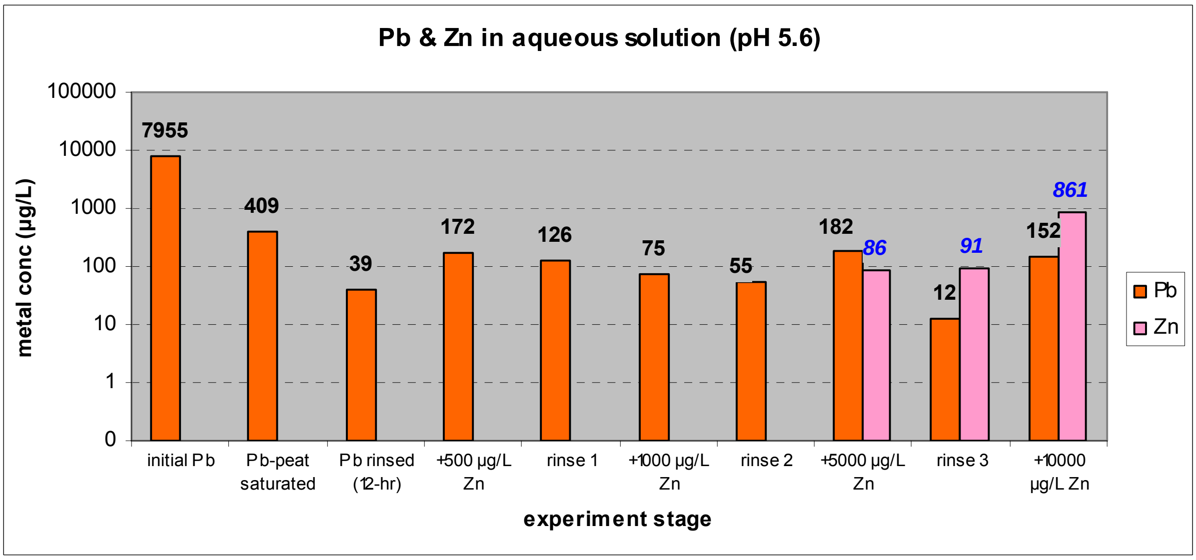


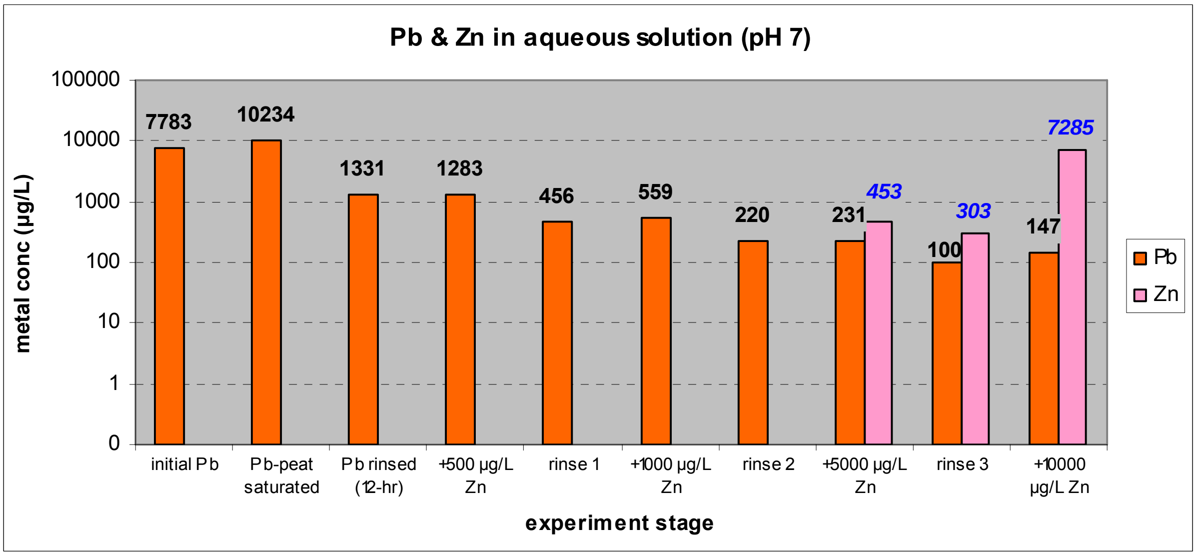




Pb/Zn experiments



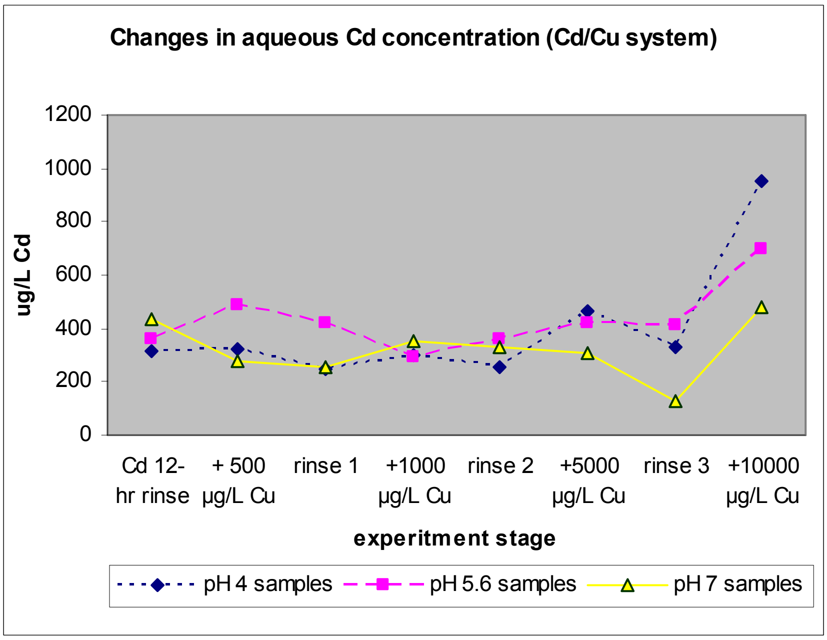




APPENDIX G: ΔCd – tables and graphs

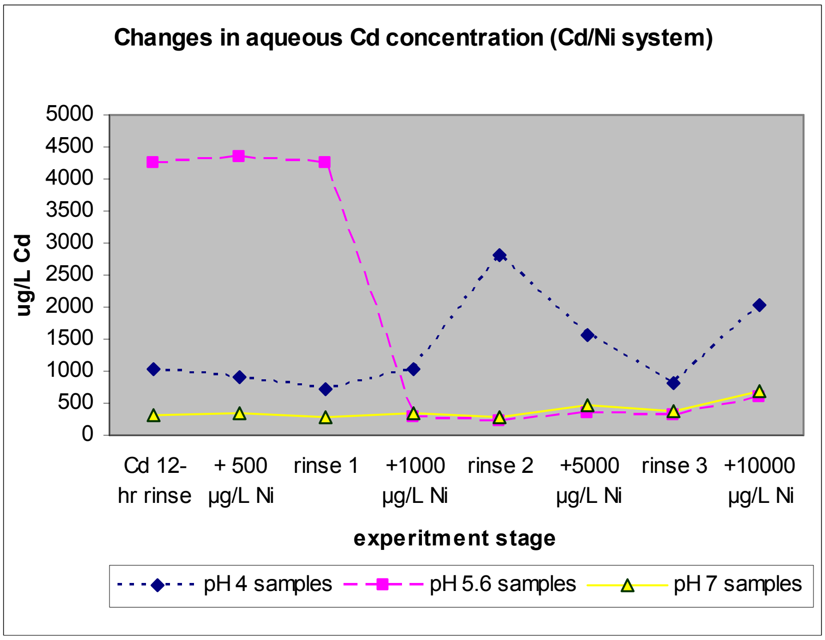
This section graphically presents the changes in aqueous Cd concentration (ΔCd) *after the addition of the competitor metal ion and relative to "rinsed" concentration levels.*

Cd/Cu experiments



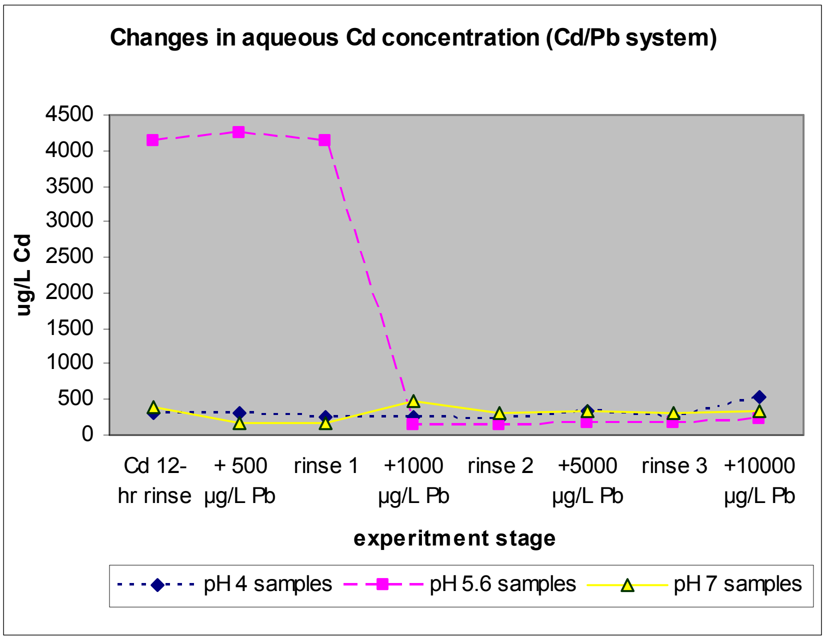
Cu added (μg/L)	pH 4	pH 5.6	pH 7
	Δ Cd (μg/L)	**Δ Cd** (μg/L)	**Δ Cd** (μg/L)
+ 500	12	127	-160
+ 1 000	50	-128	102
+ 5 000	215	57	-23
+ 10 000	624	286	356

Cd/Ni experiments



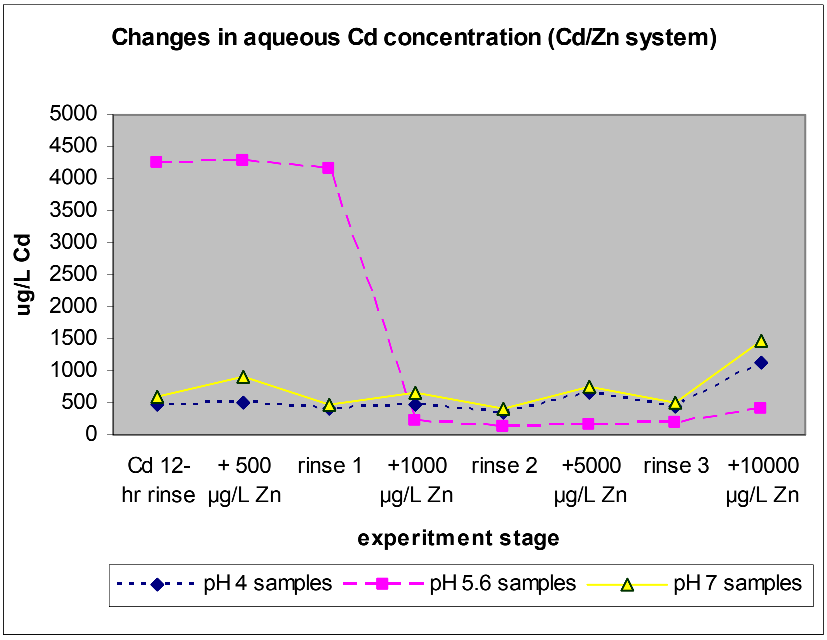
Ni added (μg/L)	pH 4	pH 5.6	pH 7
	Δ Cd (μg/L)	**Δ Cd** (μg/L)	**Δ Cd** (μg/L)
+ 500	-99	95	19
+ 1 000	296	-3974	53
+ 5 000	-1255	94	180
+ 10 000	1205	286	315

Cd/Pb experiments



Pb added (µg/L)	pH 4	pH 5.6	pH 7
	Δ Cd (µg/L)	Δ Cd (µg/L)	Δ Cd (µg/L)
+ 500	-2	89	-239
+ 1 000	23	-3993	289
+ 5 000	128	48	11
+ 10 000	300	49	26

Cd/Zn experiments

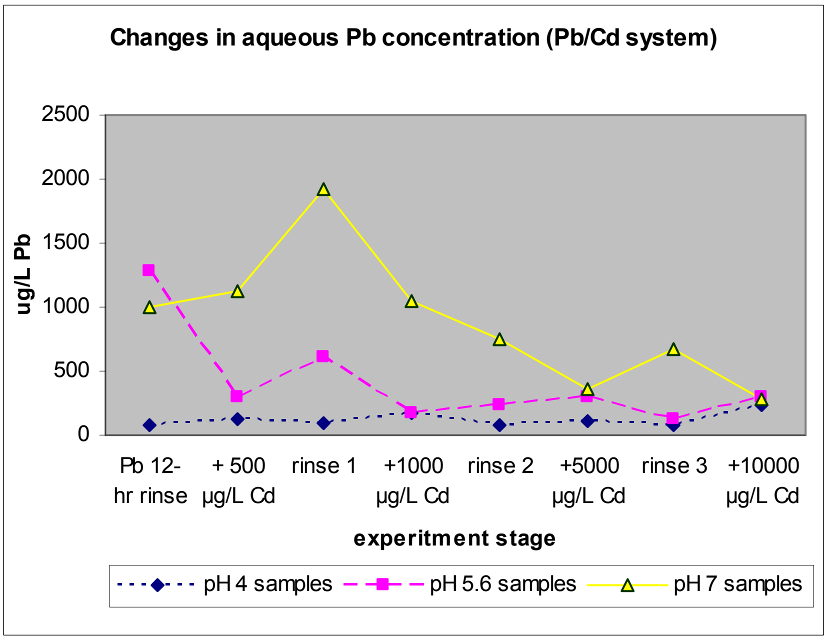


Zn added (µg/L)	pH 4	pH 5.6	pH 7
	Δ Cd (µg/L)	Δ Cd (µg/L)	Δ Cd (µg/L)
+ 500	19	45	328
+ 1 000	68	-3931	194
+ 5 000	302	34	345
+ 10 000	668	225	961

APPENDIX H: ΔPb – tables and graphs

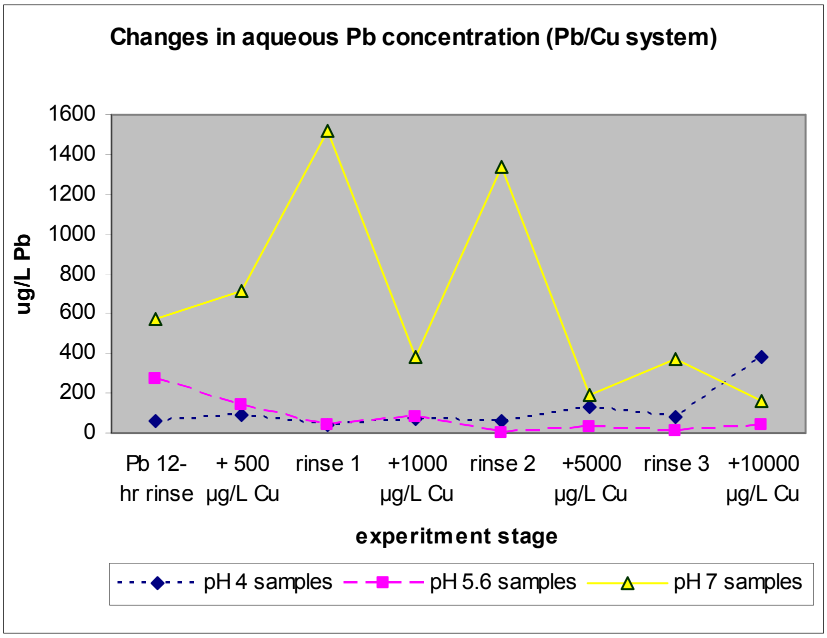
This section graphically presents the changes in aqueous Pb concentration (ΔPb) *after the addition of the competitor metal ion and relative to "rinsed" concentration levels.*

Pb/Cd experiments



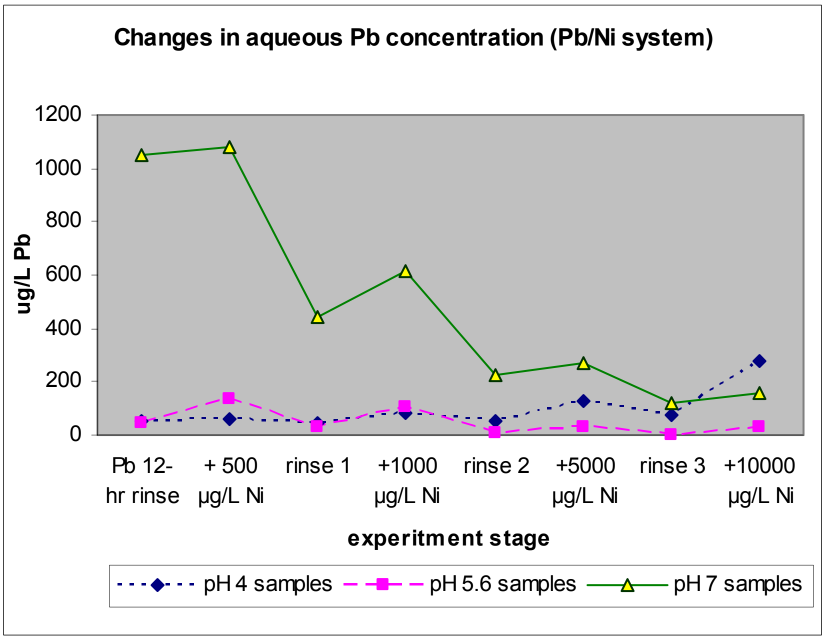
Cd added (µg/L)	pH 4	pH 5.6	pH 7
	Δ Pb (µg/L)	Δ Pb (µg/L)	Δ Pb (µg/L)
+ 500	45	-990	137
+ 1 000	79	-438	-871
+ 5 000	31	63	-386
+ 10 000	152	162	-392

Pb/Cu experiments



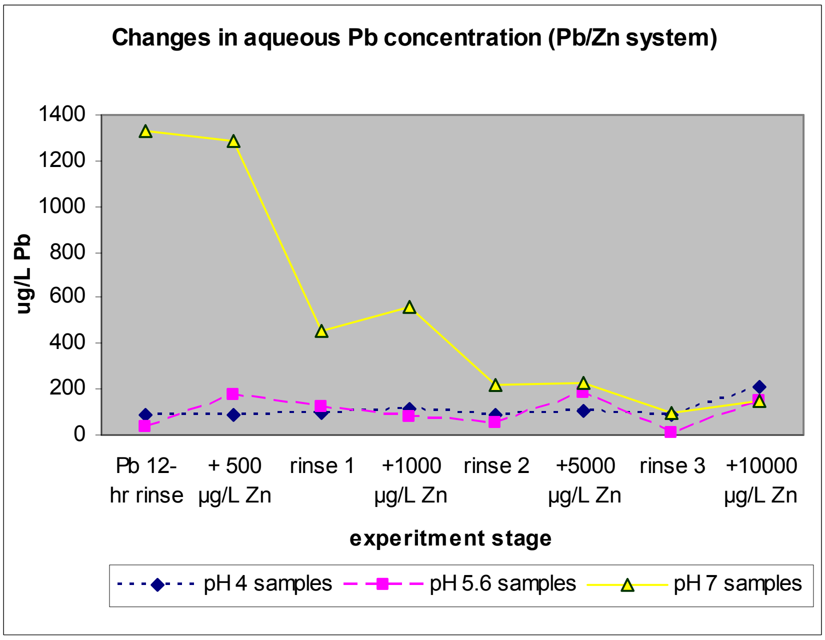
Cu added (µg/L)	pH 4	pH 5.6	pH 7
	Δ Pb (µg/L)	Δ Pb (µg/L)	Δ Pb (µg/L)
+ 500	28	-131	140
+ 1 000	29	40	-1143
+ 5 000	69	33	-1150
+ 10 000	299	36	-214

Pb/Ni experiments



Ni added (µg/L)	pH 4	pH 5.6	pH 7
	Δ Pb (µg/L)	Δ Pb (µg/L)	Δ Pb (µg/L)
+ 500	9	85	32
+ 1 000	36	76	168
+ 5 000	77	23	42
+ 10 000	203	29	32

Pb/Zn experiments



Zn added (µg/L)	pH 4	pH 5.6	pH 7
	Δ Pb (µg/L)	Δ Pb (µg/L)	Δ Pb (µg/L)
+ 500	-3	134	-48
+ 1 000	13	-51	103
+ 5 000	22	127	10
+ 10 000	125	140	46

APPENDIX I: Mass balance calculations

This section presents the results of the mass balance calculations on the experiments conducted, with Pb as the target for displacement. Calculations were done using Excel. The mass of Pb (in µg) was calculated by multiplying the measured concentration (µg/L) by the volume in the column (0.5 L) or the volume in the collected rinse. The purpose of the mass balance is to check if the distribution of Pb among the different compartments can be accounted for.

Pb/Cd experiments

Rinse period	*A*	*B*	*C*	*B+C*	Difference/Notes
Pb/Cd	In column, before rinse	In column, after rinse	In collected rinse buffer		***A = B+C?***
pH 4					
12-hour	195	42	117	159	A > B+C; 36 µg lost during rinse (unaccounted for)
Rinse 3	54	37	53	90	A < B+C by 36 µg; excessive amount in collected rinse
pH 5.6					
12-hour	461	641	458	1099	A < B+C by 637µg; excessive amount in collected rinse
Rinse 3	152	65	38	103	A > B+C; 49 µg lost during rinse (unaccounted for)
pH 7					
12-hour	5454	497	2226	2723	A > B+C; 2731 µg lost during rinse (unaccounted for)
Rinse 3	182	338	85	423	A < B+C by 241µg; excessive amount in collected rinse

Pb/Cu experiments

Rinse period	*A*	*B*	*C*	*B+C*	Difference/Notes
Pb/Cu	In column, before rinse	In column, after rinse	In collected rinse buffer		***A = B+C?***
pH 4					
12-hour	237	30	193	223	A > B+C; 14 µg lost during rinse (unaccounted for)
Rinse 3	65	40	70	110	A < B+C by 45 µg; excessive amount in collected rinse
pH 5.6					
12-hour	386	137	33	170	A > B+C; 216 µg lost during rinse (unaccounted for)
Rinse 3	17	3	18	21	A < B+C by 5 µg; excessive amount in collected rinse
pH 7					
12-hour	4499	285	2136	2421	A > B+C; 2078 µg lost during rinse (unaccounted for)
Rinse 3	96	188	43	230	A < B+C by 135 µg; excessive amount in collected rinse

Pb/Ni experiments

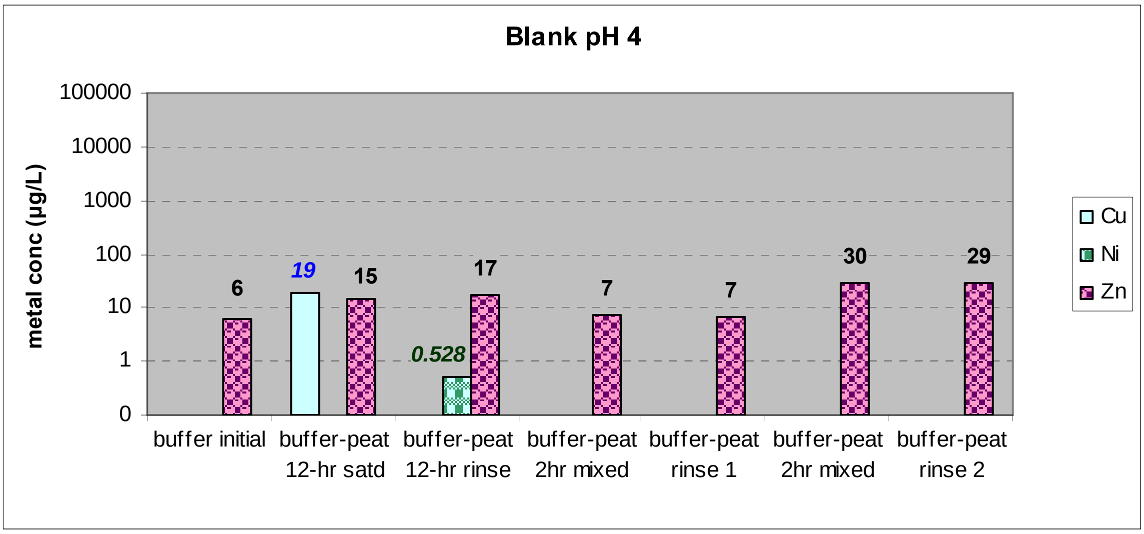
Rinse period	*A*	*B*	*C*	*B+C*	Difference/Notes
Pb/Ni	In column, before rinse	In column, after rinse	In collected rinse buffer		***A = B+C?***
pH 4					
12-hour	138	25	168	193	A < B+C by 55 µg; excessive amount in collected rinse
Rinse 3	63	37	58	96	A < B+C by 32 µg; excessive amount in collected rinse
pH 5.6					
12-hour	311	24	94	118	A > B+C; 192 µg lost during rinse (unaccounted for)
Rinse 3	14	0	8	8	A > B+C; 6 µg lost during rinse (unaccounted for)
pH 7					
12-hour	4420	526	1903	2428	A > B+C; 1992 µg lost while rinse (unaccounted for)
Rinse 3	133	61	97	158	A < B+C by 25 µg; excessive amount in collected rinse

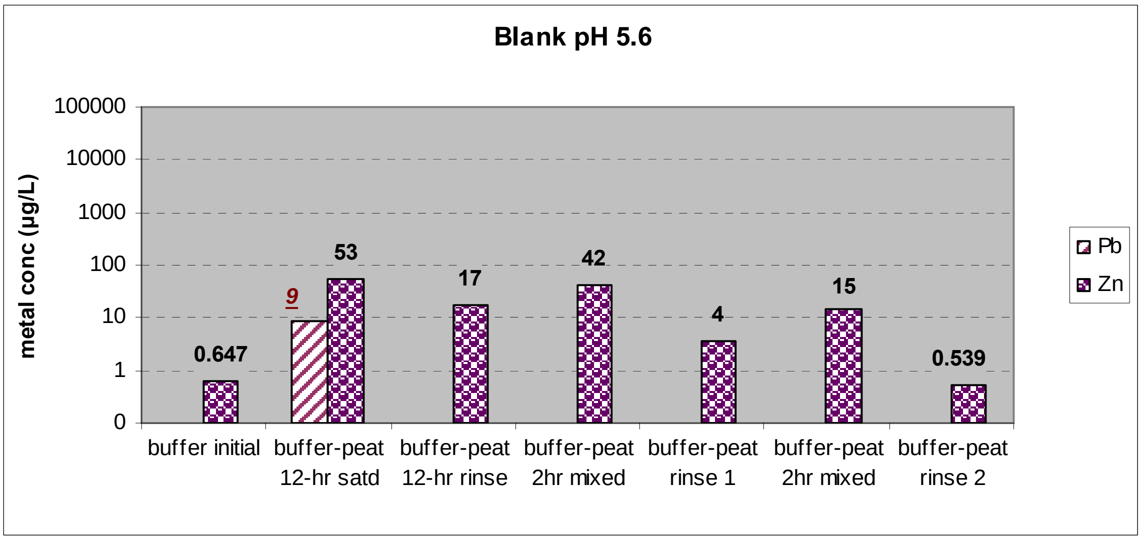
Pb/Zn experiments

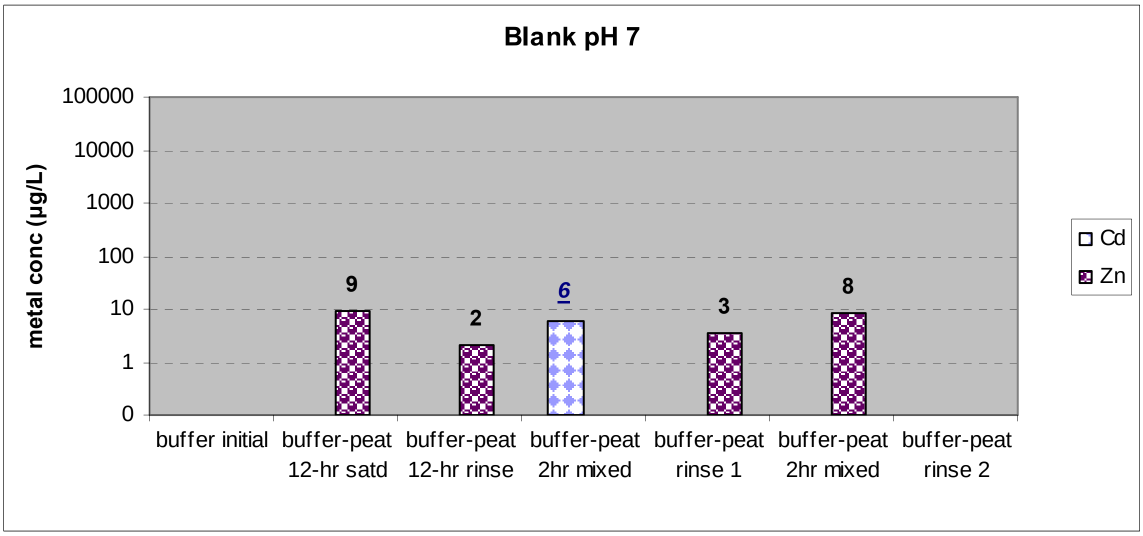
Rinse period	A	B	C	B+C	Difference/Notes
Pb/Zn	In column, before rinse	In column, after rinse	In collected rinse buffer		***A = B+C?***
pH 4					
12-hour	160	44	47	91	A > B+C; 69 µg lost during rinse (unaccounted for)
Rinse 3	54	42	49	91	A < B+C by 36 µg; excessive amount in collected rinse
pH 5.6					
12-hour	204	19	80	100	A > B+C; 105 µg lost during rinse (unaccounted for)
Rinse 3	91	6	0	6	A > B+C; 85 µg lost during rinse (unaccounted for)
pH 7					
12-hour	5117	667	2669	3336	A > B+C; 1781 µg lost during rinse (unaccounted for)
Rinse 3	115	50	82	132	A < B+C by 17 µg; excessive amount in collected rinse

APPENDIX J: Blank test results

This section graphically presents the results obtained from the blank tests conducted at pH 4, pH 5.6, and pH 7. The treatment of peat in the blank columns was exactly like that for the experimental columns, except that no metal solutions were added. The black test was conducted to check for natural metal releases from peat, as well as possible occurrence of contamination from the apparatus and equipment.







APPENDIX K: Considerations on methodology and analysis of results

This section contains information that will be helpful for those who wish to conduct the experiments made in this study. Some laboratory notes on the development of the experimental methodology are discussed. There are also considerations on the analysis of the experimental results that need to be taken in account, which serve as motivation for the way the results were assessed in the study.

1. On ICP-MS measurements

On standard deviation: each sample is "read" multiple times by the ICP-MS, and the result is actually an average of these readings. The magnitude of the standard deviations of the individual measurements was not analysed in this study.

On detection limits: a number of results obtained in the experiments were negative values. These were construed as levels which are below the detection limit of the instrument.

On dilution effects: as the experiments worked with metal solutions at ppm levels (mg/L), aliquots of samples were taken and diluted to ppb level (μg/L). The actual concentration was then derived by multiplying the result by the dilution factor (x 100). With the analysis of aliquots, instead of the entire sample, there is always the possibility of some error in measurement. However, the aqueous samples taken from the experiment columns were assumed to be fairly homogeneous, as the solutions were continuously stirred. The aliquots are then considered to be adequate representative samples.

On ICP-MS calibration: there may be a slightly different context in the measurement of metals for each batch of samples, as calibration curves are created for each analysis run. This means that, although ICP-MS is a reliable analytical instrument, there is still a degree of approximation in the measurement. The best scenario would be to analyse all the samples using only one set of standards. As this was not possible due to the large amount of samples, the careful preparation of standards is important in order to maintain consistency as much as possible in calibration.

2. Sources of error

There are a number of sources of error in the experiment that the analyst needs to be aware of. These errors can be systematic, analytical, or random.

- Despite the use of the same settings on the peristaltic pump, there are differences in the volume of buffer passing through the columns due to the irregularity of the pump mechanism, especially for the 12-hour rinse, and due to peat particle clogs in the outlet filter.

- The column is an open set-up and evaporation effects, facilitated by the nearby ventilation shaft, may account for some increase in the aqueous concentration.

- There were differences in rotation speed of overhead motors. Only one motor had a digital display of speed as revolutions per minute (min^{-1}). Speed of stirring was set at 58 rpm for that motor, which served as the basis of visual comparison for the other three. Speed of stirring can be in the range of 60 ± 5 rpm. A moderate speed is advisable for the mixing of peat, in order for the adsorbent to remain homogeneously suspended in solution. High-speed mixing tends to make peat adhere to the sides of the column.

- Small particles were observed to pass through the outlet filter, adhering to pump tubes and settling in the buffer collection containers. Losses of adsorbent from the column results in errors in the approximation of adsorbed vs. aqueous metal concentrations. Particles in the column samples collected for ICP-MS are also a concern; the column sample is allowed to settle and the aliquot for dilution is taken from the clear supernatant liquid.

- Turbidity and brownish precipitation, which may be due to humic acids, were also observed in some column samples. The precipitation of Pb at pH 7 is also something that needs to be noted. Some samples yield clear supernatant liquid after letting the particles settle; in some samples, suspended turbidity remains. These occurrences can introduce error in the measurement of the aqueous concentration (i.e., the unadsorbed metal fraction).

3. The buffer rinse

The buffer rinse is one of the most important features of the experiment. Its purpose is to wash away excess aqueous metal, while maintaining constant volume, in order for the system to be stable enough such that the desorption of metals attached to peat is minimised. In principle, a proper execution of the buffer rinse ensures that additional metals in aqueous solution are results of displacement from peat.

The buffer rinse is also the experimental stage with the most complications. Despite preliminary testing, selection of the appropriate tubing diameter and adjustment of flow rates, there was irregularity and unpredictability in the buffer rinse, especially during long hours of operation. A drastic malfunction in the 12-hour rinse can lead to cancellation of the experiment, which means wasted time, effort and reagents.

Flow in = Flow out: the gradient differences associated with the positioning of the inflow and outflow ports make constant volume in the column difficult to achieve. During the experimental runs, balance between inflow and outflow was not always attained and the column volumes fluctuated above and below 500 mL. This imbalance in flow rates is a very significant factor in the 12-hour rinses, as there runs the risk of column overflow if the inflow rate is too high, or the draining out of solution if the inflow rate is too low.

Manual adjustment: during the shorter 1-hour rinses, it is possible (and often necessary) for the analyst to make manual adjustments in order to maintain constant volume in the column. This entails adjustments on the pumping wheel by tightening / loosening the tube attachments, or even attaching / detaching the tubes from the column. The goal is to keep the volume at 500 ± 25 mL, as much as possible. This can be rather tedious for the analyst, as samples taken from the column also have to be treated immediately after extraction, and good time management is essential. As for the 12-hour rinses, manual adjustment is hardly an option.

Clogging of filters: the clogging of peat particles in the outlet filters also adds complications to the buffer rinse, as this slows down the outflow rate. Glass filters need to be periodically acid washed and replaced.

4. On the 12-hour buffer rinse in the kinetic experiment

The 12-hour buffer rinse in the kinetic experiment was done in order to minimise, as much as possible, the background levels of unadsorbed aqueous Cd prior to the addition of Pb. After the 12-hour rinse, an 86 % removal of excess aqueous Cd was observed. This is considered as an assumed value, as the rinsed buffer was not collected in order to verify the Cd removal. Confirmation would have been obtained by doing mass balance calculations in order to determine the distribution of Cd among the different compartments of the experimental set-up.

Although 86 % excess Cd removal was sufficient for the purpose of the kinetic experiment, it is, of course, advantageous to improve on this efficiency in future experimental runs.

5. On the Cd displacement results at pH 5.6

There was unusual behaviour observed in the Cd/Ni, Cd/Pb, and Cd/Zn columns at pH 5.6, wherein aqueous Cd concentrations stayed at levels > 4 000 µg/L from the time of the 12-hour Cd saturation, all the way to Rinse 1 the next day. This occurrence was due to a malfunction in the pumping mechanism that resulted in ineffective “washing” by buffer. The 12-hour rinse is designed such that the peat-metal suspension is rinsed to at least 4x the original solution volume (approx. 2L in total). In the case of these three experimental columns, which were performed at the same time, the pump tubes became loosened from the wheel at some point in the overnight rinse. This resulted in a buffer rinse that was < 2x the original volume. The malfunction was remedied by tightening the attachment of the tubes. However, some adverse effect on the experimental results was anticipated, and it was observed in the very similarly absurd measurements for all three columns.

Nevertheless, the pH 5.6 experiments were continued and the systems appeared to have attained some stability after the second addition of competing metal (+1 000 µg/L). Thus, the measurements obtained from this point onwards were considered in the analysis. It needs to be noted though, that the use of three data points, instead of 4, brings more uncertainty to the analysis. In order for more conclusive results to be obtained, a repetition of the Cd displacement experiments at pH 5.6 is advisable.

6. Mass balance analysis on Pb displacement experiments

When it was decided that the mass balance calculations were to be performed using the experiments on Pb displacement, background information on pH-dependent Pb speciation had yet to be obtained. It was subsequently discovered that, due to the precipitation of Pb at pH 7, a proper mass balance calculation cannot be done for all three pH levels, using the current experimental set-up. Lead was not the best choice for mass balance determination, as its speciation behaviour makes it difficult to track the distribution of Pb using only aqueous concentrations. In retrospect, mass balance would have been better accounted for by using the Cd experiments. Unfortunately, the buffer rinses weren't collected separately according to column, at the time when the Cd experiments were conducted.

7. Limitations of the experiment and other considerations in methodology development

As this was a pilot study that involved both analysis and methodology development, there was a great deal of "trial-and-error" in the first stages of the experimental design. Although there was some success in the results obtained from the experiments, there are limitations and areas of improvement that need to be addressed, in order to come up with a highly reliable experimental methodology for metal displacement analysis.

The porosity of the glass filters is a concern, particularly for the outlet filters. The passage of small peat particles through the filter can be a source of error in measurements. This may be remedied either by using glass filters of a different porosity (additional cost), or by secondary filtration of column samples (additional analysis time).

Improvements need to be made in the buffer rinse as well. It may be good to consider shortening the 12-hour rinse period and correspondingly increasing the flow rates, as higher flow rates were used anyway in the short 1-hour rinses. The decision will be a balance of time management considerations and the minimisation of system instability.

Additional testing is necessary to validate the efficiency of the experimental set-up and to assess the precision of the method. In this study, each binary metal system was run only once. It is advisable to select one metal pair at one pH level and run the same conditions in at least three columns, in order to statistically analyse for method precision.

Lastly, the development of procedures involving the sampling and direct measurement of metals on the solid adsorbent would be very advantageous in conclusively determining the occurrence of metal desorption by competitive displacement. This is, however, a significant challenge area in terms of logistics and feasibility.

APPENDIX L: Statistical formulas

This section lists the statistical formulas used in the correlation and linear estimate of experimental results. The actual calculations were performed on Excel.

Slope of the linear estimate, *m*:

$$m = \frac{n\left(\sum xy\right)\left(\sum x\right)\left(\sum y\right)}{n\left(\sum \left[x^2\right]\right) - \left(\sum x\right)^2}$$

Where: y = concentration of aqueous Cd or aqueous Pb
x = added concentration of competing metal

Correlation coefficient, *r*:

$$r = \frac{Cov\left(X, Y\right)}{\sigma_x \cdot \sigma_y}$$

Where: $-1 \leq r \leq 1$

$$Cov(X, Y) = \frac{1}{n} \sum_{i=1}^{n} \left(x_i - \mu_x\right)\left(y_i - \mu_y\right)$$

Coefficient of determination, R^2:

$$R^2 = 1 - \frac{\sum \left(y_i - \hat{y}\right)^2}{\sum \left(y_i - \bar{y}\right)^2}$$

Where: $\sum \left(y_i - \hat{y}\right)^2$ is the residual sum of squares for the linear estimate

$\sum \left(y_i - \bar{y}\right)^2$ is the residual sum of squares for the reference line, the null model (i.e., the horizontal line at the level of the mean of the *y*-values)

APPENDIX M: Degree of peat decomposition (Von Post)

Von Post (1922) used ten classes to grade peat by degree of decomposition (Day, 1979).

H_1	Completely unhumified and muck-free peat; upon pressing in the hand, gives off only colourless, clear water.
H_2	Almost completely unhumified and muck-free peat; upon pressing, gives off almost clear but yellow-brown water.
H_3	Little humified and little muck-containing peat; upon pressing, gives off distinctly turbid water, no peat substances pass between the fingers and the residue is not mushy.
H_4	Poorly humified or some muck-containing peat; upon pressing, gives off strongly turbid water. The residue is somewhat mushy.
H_5	Peat partially humified or with considerable muck content. The plant remains are recognizable but not distinct. Upon pressing, some of the substance passes between the fingers together with mucky water. The residue in the hand is strongly mushy.
H_6	Peat partially humified or with considerable muck-content. The plant remains are not distinct. Upon pressing, at the most, one third of the peat passes between the fingers. The residue is strongly mushy but the plant residue stands out more distinctly than in the unpressed peat.
H_7	Peat quite well humified or with considerable muck-content, in which much of the plant remains can still be seen. Upon pressing, about half of the peat passes between the fingers. If water separates it is soupy and very dark in colour.
H_8	Peat well humified or with considerable muck-content. The plant remains are not recognizable. Upon pressing, about two-thirds of the peat passes between the fingers. If it gives off water at all, it is soupy. The remains consist mainly of more resistant root fibres, etc.
H_9	Peat, very well humified or muck-like in which hardly any plant remains are apparent. Upon pressing, nearly all of the peat passes between the fingers like a homogeneous mush.
H_{10}	Peat completely humified or muck-like in which no plant remains are apparent. Upon pressing all of the peat passes between the fingers.

Reference:

Day, J. H., P.J.Rennie , W.Stanek and G.P. Raymond, Ed. (1979). Peat testing manual. Ottawa, National Research Council Canada.