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The Uptake of Pentachlorophenol, Chromated Copper Arsenate and Copper Naphthenate by Soils

by

Susan Janet Morante

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ABSTRACT

The Uptake of Pentachlorophenol, Chromated Copper Arsenate and Copper Naphthenate by Soil

Susan Janet Morante, M.Sc.

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Uptake of the wood preservatives pentachlorophenol, chromated copper arsenate and copper naphthenate by soil was studied using a recently introduced batch technique capable of following the long-term kinetics of sorption. This method utilises microfiltration in conjunction with high performance liquid chromatography (HPLC). Substituting inductively coupled plasma spectrometry (ICP) and solid-phase microextraction/gas chromatography (SPME/GC) for the HPLC modified this analytical method in two phases of the study. Method development was an important part of this project since many of the techniques had to be modified for these applications. SPME, a relatively new technique that allows trace contaminants to be analysed in an aqueous environment, requires further studies to be carried out to demonstrate its complete usefulness, although preliminary studies are encouraging. While all three compounds studied showed the expected two-stage uptake, initial rapid sorption followed by a slower phase, it was interesting to note that the sorption of copper, in copper naphthenate, was delayed in the presence of the organic acid to which it was bound initially.

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I dedicate this thesis to my children:

To Becky, who had to suffer through high school chemistry class without much help from a mother who was busy writing her thesis,

To Lizzy, who just wants this over with so we can have fun again,

To Carlos, who would never let me give up,

To Tommy, who has more questions about polymers than I have answers,

And

To Ricky, who wants to be a chemist when he grows up,

Here it is guys – I hope you still think it was worth all the work.

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1 INTRODUCTION

Throughout history, wood has been a popular construction material due to its ability to resist oxidation, corrosion, fatigue, and crumbling. When wood is kept dry and free from attack by various organisms, it can last indefinitely. Thus, the impregnation of wood with substance toxic to living organisms is the best method, to date, for rendering it resistant to decay and insect penetration. Although the history of wood treatment predates Noah and his use of pitch on the Ark (1), modern pressure treating had its beginnings with the work of Bethel in 1838 (2). By the early part of this century wood treated with creosote or pentachlorophenol (PCP) was in great demand for railroad ties and timbers (3). After World War II, chromated copper arsenate (CCA) began to be used more frequently and by the 1960's had come to dominate the market (2). The four major wood preservatives in use today are creosote (13% of all utility poles), PCP (43% of all utility poles), CCA (42% of all utility poles), and copper naphthenate (2% of utility poles) (2,4). As well as utility poles, treated wood is used in decking, fencing, retaining walls, various marine structures such as piers and boardwalks, wood foundations for houses, and playground equipment (5).

To be effective, wood preservatives must have broad-spectrum toxicity characteristics but they must also be highly resistant to depletion by leaching, photodecomposition, and biological degradation (3). Since treated wood products are used widely in modern society, the potential environmental impact of this usage is an area of increasing investigation. There is a need for a deeper

understanding of the interactions of xenobiotics with the environment. Indeed, insight into the dynamics of the sorption of xenobiotics by soil allows better prediction of their bioavailability, biodegradation and potential mobility.

Studies of the kinetics of soil sorption show an initial rapid uptake (hours to days) of xenobiotics by soil, followed by a slower but continuous uptake (weeks to years) (6,7,8,9). While some authors suggest equilibrium is reached relatively quickly, i.e. within 48 hours (10,11), others question whether this assessment takes into account slow sorption processes that occur in the soil (6,12,13). Data collected from investigations of the extractability of xenobiotics aged in the soil and the kinetics of their sorption and desorption suggest that they become slowly sequestered within the soil matrix, and thus increasingly unavailable to degradation and leaching processes (6,8,12,14,15,16,17). Slow sorption processes appear to reduce the impact of xenobiotics on the environment. That is, the xenobiotics do not leach out to contaminate the underlying aquifers to the extent predicted (8,18,19). However, the slow kinetics also appears to increase the time required to achieve clean up of a contaminated site (8). This has great relevance in determining the environmental risk associated with xenobiotics.

This chapter will give an overview of: soil characteristics and classification; soil sorption phenomena; the known interactions of several wood preservatives with soil; and techniques used to study soil sorption processes.

1.1 SOIL CLASSIFICATION

Agriculture Canada defines soil as "that collection of natural bodies on the earth's surface supporting or capable of supporting biological activity" (20, p.15). As can be seen while driving across Canada, soils vary widely in colour and in the type of vegetation they support. The Russian soil scientist, Dokochaiev, in 1870, proposed that soils should be viewed as individuals. That is, as independent natural bodies with unique characteristics developed by the influence of climate, flora, fauna and time (21,22,23). These soil development processes alter the underlying rock materials, and together with added organic matter, form layers called soil horizons (24).

The succession of horizons, which are exposed when a vertical cut is made through the soil to the parent material, comprise the soil profile (22). Soil horizon sequences vary widely from one type of soil to another. In general a soil profile shows a layer of plant residue designated by the letters O, L, F or H, a humus enriched A horizon followed by a leached E horizon, sub-surface B horizons (often clay) and the parent (or underlying, unconsolidated) material designated by the letter C. If bedrock is within a few feet of the surface, it is called the R horizon. These categories are further subdivided, shown by the addition of small letters and numbers to the symbols above, because of the diverse nature of soil (20, 22,24).

A particular soil is classified by identifying the various layers or horizons that make up its profile. Agriculture Canada has developed the Soil Classification System for Canada (23) and has carried out extensive mapping of

soils in all areas of Canada (25,26). Of particular concern to this study were soils collected from Canmore and Brooks, Alberta. Soils from the area of Canmore, Alberta have been classified as Eutric Brunisolic (25). Soils from Brooks, Alberta are classified as Brown Chernozemic with inclusions of Brown Solonetzic (25,26).

Eutric Brunisolic soils are well to imperfectly drained mineral soils developed under varying types of forest, alpine or tundra conditions. Their textures range from sandy loams to clays. They occur under climatic conditions ranging from Boreal to Arctic in temperature and from perhumid to semiarid in moisture regime. These soils have a thin Ah horizon[1] and a pH greater than 5.5 (23) but they are identified by their prominent brownish Bm horizon[2] (20). The usual order of the horizons in Eutric Brunisolic soils is Ah/Bm/Ck with the Ck horizon[3] being quite calcareous[4] (23). Due to weakly developed leaching and weathering processes, Eutric Brunisols tend to have similar chemical characteristics to the parent materials from which they derive (20).

Brown Chernozemic soils are well to imperfectly drained mineral soils of good structure. The soils in Brooks, Alberta occur within an area of cool Boreal semiarid climate that is characterised by severe moisture deficits during the

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[1] The Ah horizon is enriched with organic matter but contains less than 17% organic carbon by mass (20).
[2] The Bm horizon has a relatively strong colour and has been altered by hydrolysis, oxidation, or solution so as to produce significant changes in colour, structure, and composition from those of an A or C horizon (20).
[3] Ck denotes a horizon relatively unaffected by the pedogenic process, except for the accumulation of calcium and magnesium carbonates. Their presence is indicated by visible effervescence when dilute HCl is added (20).
[4] A soil containing enough free calcium and/or magnesium carbonate to show effervescence with acid (24, p. 194).

growing season (20,23). They have developed mainly on glacial till[5], and lacustrine[6] and fluvial[7] deposits (23). Brown Chernozemic soils have a greyish brown A horizon (usually Ah), which is generally lower in organic matter content than those of other Chernozemic groups and very dark brown, alkaline, B (usually Bm) and C (usually Ck or Cca) horizons (20). The deposits are moderately calcareous, dominantly loam in texture but with significant occurrences of sandy and clayey areas. It is a medium to coarse-textured soil (26) consisting of blocky aggregates usually covered with a thin clay coating (23). Minor inclusions of brown Solonetzic[8] soils are often found. The humus-enriched A horizon is developed and maintained by the growth, accumulation, and decomposition of grasses and other plants typical of drier regions of the Canadian Prairie (20). Soils of this type are used for agricultural activities ranging from field cropping, mainly for wheat and other small grains, to raising livestock. Although this soil has good fertility, its productivity is significantly limited by severe moisture deficits during the growing season and by the probability of disastrous droughts in some years. (20)

There are four main constituents of soil: mineral matter, organic matter, air and water. The mineral matter, in the form of sand, silt, and clay, includes all those minerals weathered from the parent material as well as those formed by reaction with other soil constituents. The organic matter is derived mostly from

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[5] Unsorted debris left by a glacier (24, p. 196).
[6] Sediment, beach or nearshore materials that have settled in a lakebed from fresh water (23, p. 142).
[7] Sediment deposited by streams and rivers (23, p.142).
[8] Brown Solonetzic soils are distinguished by the high saline content in the B horizon. They occur on saline parent materials and are sparsely covered with vegetation (23 p. 107).

decaying vegetable matter. Air and water occupy the spaces between particles of the soil, but if a soil is saturated with water most of the air is driven out. Even in fairly "dry" soil, water is still present in the form of thin films around the mineral particles (24).

The mineral portion of soil consists of particles ranging in size from 0.002 mm (clay) to 2 mm (sand) in diameter (27). Larger particles or stones (diameter greater than 2 mm) are considered to be inert but contribute to the soil by breaking up the continuity of the clay material. Sand (2 mm to 0.05 mm) forms the framework of the soil and gives it stability when in a mixture with finer particles. However, sand contributes very little to plant nutrition. The most common mineral in sand is quartz, but feldspar and other minerals are also found. Each spherical sand particle is coated with a film of tiny clay particles (24). Silt (0.050 mm to 0.002 mm) is mineralogically similar to sand, but the particles are smaller (27). Clay (<0.002 mm) is much different from sand or silt because it is made up of secondary minerals formed by the alteration of the original materials, often due to the recrystallization of the products of mineral weathering (24).

Clay minerals are characterised by a layered, crystalline structure; in fact, clay particles look like a tiny stack of very thin sheets (27). The three main clays are kaolinite, montmorillonite and hydrous mica (24). All clay minerals are built up from layers of silica and aluminium atoms, with their associated oxygen atoms, arranged like a sandwich. The layers of the sandwich are held together by chemical bonds (22). Clay particles are so small that the minute electrical

forces of any molecules present on the surface confer upon the particles a colloidal status. In the colloidal state particles gain the properties of plasticity, cohesion, shrinkage, swelling, flocculation and dispersion. (22)

The major portion of organic matter in soils is made up of the remains of woody terrestrial plants (28), which are broken down both physically and chemically, often through animal and microbial action. This soil organic material, known as humus, has lost all the visible features of the organic matter from which it formed. It is a high surface area material responsible for many of the chemical and physical properties of soils (29). Humus can be subdivided into recognisable biopolymers like proteins, lignins, cellulose, polysaccharides, and polypeptides (30), and a group of brown-coloured amorphous heteropolycondensates (31). These amorphous macromolecules are typically referred to as humic substances if they are soluble or extractable in aqueous base, and humin or kerogen if they are not (32). They are thought to arise from the partial degradation and crosslinking of various organic residues (33) and exist as polydisperse polyelectrolytes with charge dependant on pH. The main sources of charge are the carboxyl and amine groups. Because of the opposing behaviour of these functionalities at different pH's, humic substances are species of variable charge (34). Humic substances are subdivided into fulvic acids, which are soluble in both acidic and basic solutions, and humic acids which are soluble only at high pHs (34,35). Humins, a third type of humic substance composed in part of lignins, are insoluble (32). The specific composition of humic substances varies widely. Although they are predominantly made of carbon (40-60% by weight),

some humics have nearly as much oxygen as carbon in their structure (34,36, 37). Humic acids contain 35 to 92% aromatic carbons (38). Fulvic acids, in contrast, contain only 25% aromatic carbons or less (34). Both contain large numbers of repeating aliphatic structural units (32). Humus occurs in a very broad spectrum of molecular sizes from the smallest fulvic acids (spheres of about 2-nm diameter) to the huge complexes of solid kerogen (35). Humus exists generally as organic chains coiled into globular units, similar to globular proteins, and occurs in isolated patches coating mineral solids (34). The coiling occurs because the humus tries to minimise the hydrophobic surface area exposed to the aqueous solution (35).

1.2 SOIL SORPTION PROCESSES

The process whereby chemical compounds become associated with soil is generally referred to as sorption. Sorption is extremely important because it may dramatically affect the fate and impact of xenobiotics in the environment (35). Identical molecules behave very differently if they are dissolved in aqueous solution and thus surrounded by water molecules and ions, or sorbed to the exterior of solids, or buried within a solid matrix (39). For example, structurally identical molecules react at different rates in acid/base reactions if they are in the thin layer of water surrounding a silicate surface than if they are in the bulk water. This is because of a difference in acidity of the two locations (35). Another crucial difference is in biodegradation where molecular transfer into microorganisms is frequently a prerequisite. The greater ease of chemical movement from solution,

versus from within solids to bacteria, generally causes the biological decomposition of the sorbed form of the chemical to be slower than its dissolved counterpart (8,35).

1.2.1 Sorption of Inorganic Chemicals by Soil

Sorption of inorganic ions in soil is known to occur via three processes (40):

a) Ion exchange reactions, which involve sorption of ions to the soil via low-energy, long-range, non-specific electrostatic attractions. There is a retention of the hydration sphere of the ion. The reaction tends to be fairly reversible leading to what might be termed a "labile fraction".

b) Chemisorption is the sorption of ions to the soil via covalent or high-energy, short-range, specific electrostatic bonds. Often, this takes the form of a ligand exchange reaction and in the case of multidentate ligands is referred to as chelation. The hydration sphere is not usually retained and thus these are sometimes referred to as inner-sphere complexes. Chemisorption is considered to be a less reversible process leading to a "nonlabile fraction".

c) Precipitation reactions are significant only at ion solution concentrations close to the saturation point. For most trace elements, precipitation is likely only when solids become heavily loaded with these metals. There will be no further discussion of precipitation reactions of inorganic ions in this paper as it is not relevant.

Chemisorption differs from ion exchange in that: there is a high degree of specificity toward particular trace metals (or anions); the measured surface charge becomes more positive (or more negative); there is a release of H^+ (or OH^-); the bonding is irreversible (or at least the desorption rate is orders of magnitude lower than the sorption rate) (29).

Sorption processes of inorganic ions are made somewhat complex by the fact that one must consider both cationic and anionic sorption to both clay and organic matter separately.

1.2.1.1 Cation exchange on clay

Most silicate clays (properly called aluminosilicates) possess a structural (or permanent) negative charge (29). The faces of these plate-like particles exhibit a charge due to cation substitution for the aluminium or silicon atoms within the internal structure (24). This isomorphic substitution often involves cations of lower total positive charge (e.g., Mg^{2+} for Al^{3+}) resulting in a fixed and permanent charge deficiency that looks like a negative surface charge to the surrounding solution (35). The negative surface charge, often referred to as the cation exchange capacity (CEC) and defined as moles of positive charge sorbed per unit mass of clay, varies from near zero to 0.150 moles/kg (29) depending on the type of clay.

The CEC is also dependent on the specific surface area (area per unit mass of clay). Some charged sites may be physically inaccessible to solution, and thus to exchange, in clays with reduced surface area. The bonds formed

and broken in the exchange process are long-range electrostatic bonds and the cation retains its hydration sphere. In accordance with a strictly electrostatic process, it is generally the cations with higher valence state, largest ionic radii and lowest hydration energies that sorb most strongly on the permanent charge sites. These sites occur both on the clay surface and the interlayer region (29).

Cation exchange rates at clay surface sites appear to be almost instantaneous. That is, they are not easily measured by conventional means (29). On the other hand, exchange at sites in the interlayer region is much slower (sometimes taking many hours), limited by the rate of cation diffusion to the sites. This leads to an initial rapid uptake of cation followed by a slower, more gradual uptake of cation from solution as seen in kinetic studies of cation exchange (41,42).

It is also possible to have cation exchange at the "edge" sites of most minerals. "Edge" sites consist of terminal hydroxyl groups (in iron and aluminium oxides and layer silicate edges) or terminal silanols (in silica, allophane and layer silicate edges). Silanol groups sorb cations at pH $\approx$ 7, by dissociating and then attracting metal ions electrostatically. Other common edge sites, such as iron hydroxides, only dissociate to form cation exchange sites at high pH (29).

Desorption of a cation from a clay particle occurs at a rate determined by the competition between the cation of interest and any other cation in the vicinity (29). Sorption and desorption, therefore, often proceed at different rates. This leads to hysteresis (the existence of two different equilibrium states in the same system) (10).

1.2.1.2 Anion exchange on clay

Clays high in oxides and hydroxides of iron, aluminium and manganese and "edge" sites of many clays possess little or no permanent surface charge. They are in fact amphoteric since they support both cation and anion exchange, depending on pH (29). The consequent anion exchange capacity (AEC) observed for most clays is near 0.1 mole/kg (35). However, this value changes with solution pH and ionic strength. Generally, anion exchange capacity is increased at low pH. This allows uptake of such anions as phosphate and nitrate. Chromate and arsenate appear to form directional bonds at these sites and in fact alter the surface charge in the process. Thus their bonding is classified as chemisorption (29) and will be discussed in later sections.

1.2.1.3 Ion exchange in organic matter

The main functional groups of soil organic matter contain oxygen atoms. Carboxylic acid and phenolic groups have been found to occur at concentrations of 1-10 mmol/g of organic matter (35). In the presence of base, these acid functional groups dissociate to form carboxylate and phenolate anions, creating negative charge at the organic surface, which is then balanced by cations. Thus CEC increases with increasing pH (29). Humic substances in soil become more soluble at higher pH (32). This is partially because of a general increased solubility of salts compared to their conjugate acids. It is also because the rise in pH causes an increased surface negative charge, which in turn causes an increase in the intermolecular and intramolecular electrostatic repulsions. This

promotes an unfolding, and expansion of the humic substances. Thus a greater number of surface sites become available (34). When the fraction of unprotonated carboxyl groups becomes sufficiently great the humic molecules go into solution (43).

In the ion exchange process, the charge and radius of the metal ion control selectivity. Trivalent cations form more stable complexes than mono or divalent cations because they are able to bond to two or more functional groups (29). Large cations preferentially displace small cations and strongly hydrating cations retain their hydration shells when sorbed at the organic sites. It has been found that in sandy soil, at acid pH's, organic matter is one of the most important solid phases sorbing heavy metals such as copper (41).

Anion exchange on organic matter does not appear to be a reaction of significance (29).

1.2.1.4 Chemisorption of cations on clays

Noncrystalline aluminosilicates and oxides or hydroxides of iron, aluminium and manganese provide surface sites for the chemisorption of transition and heavy metals. All of these minerals present a similar type of sorptive site, an OH^- or H_2O ligand bound to a metal ion (Fe^{3+}, Al^{3+} or Mn^{3+}). The bonding that occurs is a replacement of the H^+ from the hydroxide or water ligand with the metal cation, giving a metal-oxygen-metal bond. These minerals absorb Pb^{2+} and Cu^{2+} more strongly than any other divalent metal cation. This is

because unlike the cation exchange reaction, chemisorption seems to be favoured by high charge, small radius and good polarisability of the cation (29).

Chemisorption of metal cations on clays is slower than cation exchange. The cations lose much of their initial lability (as measured by diminishing self-exchange rates) over a period of days (44,45) as they are slowly sorbed. Thus, chemisorption of cations on mineral surfaces is considered to be highly nonreversible. On the other hand, at least one study has shown that it is possible to desorb Cu^{2+} almost completely at low pH's (44). This suggests that the "nonreversibility" of metal cations on clay may simply be the result of the long time period required for desorption to be complete. Some studies suggest a desorption rate three orders of magnitude slower than the sorption rate (29).

1.2.1.5 Chemisorption of anions on clay

Anion chemisorption occurs on the same types of clays that support anion exchange reactions, that is, clays that possess surface hydroxyl groups. Generally the reaction proceeds as a ligand exchange process. Anions, such as arsenate or chromate, displace the H_2O and OH^- ligands bound to the surface metal ions from the co-ordination position. This process is favoured at low pH when much of the OH^- is converted to H_2O, an easier ligand to displace. In deciding which anions (usually oxyanions) will most effectively compete for the ligand position it has been found that the greater the effective negative charge on the oxygen atoms of the anion, the stronger the metal-oxyanion ionic bond

formed. Thus anions such as borate and arsenate have a stronger affinity for oxides and aluminosilicates than do nitrate and chromate (29).

In general, chemisorbed anions retain higher lability than chemisorbed cations. This is probably due to the fact that the ligand exchange reaction of anions is a low energy process (35), since the replacement of one oxygen ligand by another requires less energy than the replacement of a proton by a metal cation. However, some oxyanions bond to clay surfaces in an apparently irreversible manner. For example, arsenate chemisorbs onto oxides by a binuclear bridging process. This association is stabilised both energetically, it is a high-energy reaction, and by entropy, since two bonds would need to be broken simultaneously in order to desorb (29).

1.2.1.6 Chemisorption of cations on organic matter

Chemisorption of cations onto organic matter, as with chemisorption onto clays, can be viewed as a cation exchange process between H^+ and the metal cation at the acidic functional groups. The difference between this process and proper cation exchange is that chemisorption shows a high degree of selectivity. Also the metals co-ordinate directly with the functional groups, forming strong ionic and covalent bonds. Metals with a smaller radius and high electronegativity tend to form the strongest bonds. To some degree the selectivity of this process also depends on the type of functional group, with a much more varied selection available than on clays. If the metal bonds to two or more functional groups (acting as a bidentate ligand) there is increased stability due to the "chelating

effect". For example, Cu^{2+} complexes with a high degree of selectivity to the polyphenolic groups in humus which act as a bidentate ligand. In general, the complexing process is favoured at intermediate pH. This is because at high pH there is a tendency to precipitate out metal hydroxides and at low pH the ligands more easily associate with protons than metal cations.

Since a large activation energy is required to break the ligand-metal bond of strongly sorbed cations such as Cu^{2+}, the rate of desorption tends to be very slow. That is, metal cations tend to be "non-labile" on soil organic matter (29).

1.2.1.7 Chemisorption of anions on organic matter

Certain anions such as borate are known to bond to soil organic matter as shown in Figure 1.2.1 below, where the carbons can be aromatic or aliphatic (29). Some anions bond indirectly to organic groups through a bridging metal ion such as Al^{3+} or Fe^{3+}. Most anions sorb very little to humus, other than through the formation of ternary complexes, discussed below, and thus anion retention in soils is primarily due to chemisorption on clay.

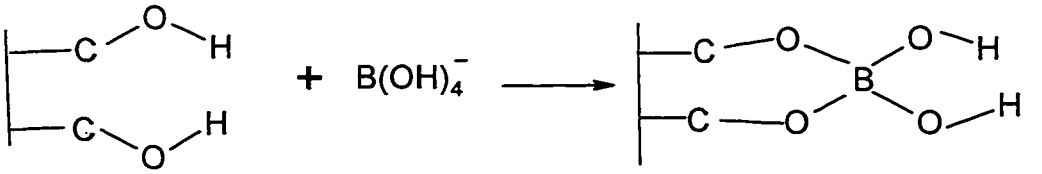


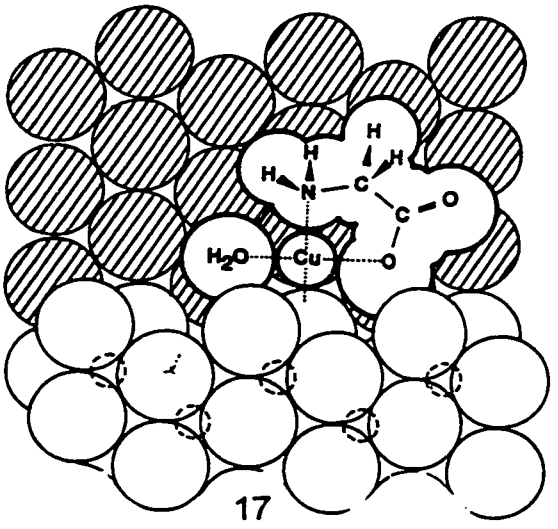
Figure 1.2.1 Bonding of Borate to Organic Matter

1.2.1.8 Ternary complexes

Since the same type of hydroxyl group can be involved in both cation and anion sorption on variable-charge surfaces, competition for these sites is

expected. However, what is found appears to be a synergistic process in which sorption is enhanced by the presence of both anions and cations. The synergism arises from formation of a ternary complex, of which there are two types. In Type A, the metal cation forms a bridge between the surface and the anion by replacing the hydrogen of the surface hydroxyl group. In Type B, the anion forms a bridge between the surface and the cation by replacing the hydroxyl group completely. In Figure 1.2.2 below is shown a Type A ternary complex (29 p.153). The metal ion, Cu^{2+}, bonds simultaneously with the organic ligand, glycine, and surface oxygens on the soil, in this case present as $Al(OH)_3$. (The large circles represent hydroxyl groups and the smaller circles represent Al^{3+} ions.) Type A complex formation is more commonly encountered than is Type B (29). Usually the Type A complex forms with Al^{3+} or Fe^{3+} bonding to humus and simultaneously to an anion such as phosphate. Ternary complexes form only between soil, multivalent cations and bidentate anions. Multidentate anions tend to cause the cation to release the soil particle to maximise the bonding with the ligand. As a consequence of ternary complex formation, binding of inorganic soil contaminants (particularly anions) to the solid phase increases.

Figure 1.2.2 Depiction of a Type A Ternary Complex



1.2.2 Sorption of Organic Compounds by Soil

Organic compounds often persist in soils for years despite being biodegradable by bacteria found in soils (12,46,47). The transfer of xenobiotics into the microorganism appears necessary for biodegradation to occur (35,48), and desorption into the aqueous phase may be a necessary prerequisite for this molecular transfer (49). Thus, if the kinetics of desorption are sufficiently slow, desorption from the solid-bound state may limit the rate and extent of biodegradation (19). In addition, it appears that the ageing of organic compounds in soil is extremely important in determining the kinetics of desorption. This is because, with time, these molecules occupy increasingly remote sites inside soil aggregates, accounting for their extremely slow release times, and possibly for their persistence (48). For example, in separate experiments, aged 1,2-dibromoethane and picloram were shown to be completely resistant to biodegradation. However, when an additional aliquot of compound was added to the original soil sample it was rapidly biodegraded (12,50). Undoubtedly, contaminant-ageing results in slower desorption kinetics and lower bioavailability (48).

Sorption is not always a single process, but rather a combination of interactions that govern the association of any particular sorbate with any particular sorbent. An organic substance may penetrate organic matter in the particulate phase or it may displace water molecules from the region near the mineral surface. In either case, it associates with these surfaces via van der Waals, dipole-dipole, and other weak intermolecular forces. If the sorbate is

ionisable, additional attractions to specific surface sites exhibiting the opposite charge will promote sorption of the ionic species. Additionally, the sorbate and sorbent may be capable of covalent bonding and so some portion of the sorbate may actually become bonded to the solid. All of these interaction mechanisms operate simultaneously, and the combination that dominates depends on the properties of the organic substance and the soil particle (35).

1.2.2.1 Sorption of neutral organic compounds to organic matter

Nonpolar compounds do not dissolve well in water. Nor do they interact well with the mineral fractions of soil (8). Most minerals are polar due to the combination of oxides and hydroxides on their exterior surfaces. These polar surfaces strongly favour interactions that allow them to form hydrogen bonds, usually with water. As a result, replacing the water molecules at such a mineral surface by nonpolar organic compounds is difficult (35).

On the other hand, penetration of neutral organic compounds into any humus included in the solid phase does not require displacement of tightly bound water molecules since humic substances can only be involved in H-bonding at limited points on their structures (e.g., carboxy, phenoxy, hydroxy, and carbonyl substituents). Humus associated with soil particles offers a relatively nonpolar environment into which a hydrophobic compound may escape (8). Interactions include van der Waals attractions, dipole-dipole interactions and H-bonding. In addition highly conjugated or aromatic compounds participate in π-π interactions, such as π-stacking, between surface and sorbate aromatic rings (51). The

porous nature of humus allows a nonpolar sorbate to physically penetrate between its coils and find itself "dissolved" in a nonaqueous medium. Not surprisingly, neutral organic compounds show greater affinity for soils that contain high amounts of humus (52) and are only limited in their ability to sorb to humus by the degree to which they interact with water (35). Thus, as long as the fraction of humus in the soil is sufficiently high, the sorption of neutral nonpolar organic compounds to humus is the primary sorption process.

This bonding process has been demonstrated to be reversible for many nonpolar compounds (10,53). Studies have also found that solvated inorganic ions increase the sorption of nonpolar organic compounds into organic matter. In contrast, the presence of substantial concentrations of organic solvents in the aqueous phase decreases the sorption of neutral organic compounds to soils (54). This is because the nonpolar organics partition into the organic solvent.

Another area of concern in the sorption of nonpolar organic molecules to soil is sorption onto colloidal particles. Soil colloidal structures are irregular and complex. Little compositional information is available for these colloidal structures (34). They include humic substances and proteins, viruses and nonmotile bacteria, and organic coatings on very small clay particles. Colloids range in size from a few nanometers to a few micrometers in dimension, and are not separable from water. This is important when trying to measure concentrations of xenobiotics in the dissolved versus sorbed phases, since the compound would occur in the water both as a dissolved species and sorbed to the colloidal particles. This would increase the apparent solubility of organic

compounds in solutions containing a colloidal phase (55). The association of nonpolar compounds with colloidal particles diminishes the tendency of these compounds to bioaccumulate in aquatic organisms (56), and can also change some of their other properties, such as how they interact with light (57).

1.2.2.2 Sorption of neutral organic chemicals to mineral surfaces

Some solids do not include appreciable amounts of organic matter. In these cases, association of hydrophobic organic solutes with mineral surfaces, as difficult as it may be, becomes significant (8). Laboratory glass surfaces and sampling vessels, frequently made of silicates, may sorb hydrophobic compounds from aqueous solutions, confusing subsequent data interpretation. Generally, coarser particles (e.g., silica sand) exhibit less binding than corresponding finer particles made of the same material (e.g., porous silica) presumably due to the difference in surface area (51). Binding seems to vary as a function of the sorbate's hydrophobicity (35) but strong molecule surface interactions are not involved (58). Nonpolar binding to minerals may involve an exchange of organic sorbate with water molecules at the surface, similar to the ligand exchange in anion binding to mineral surfaces (59).

1.2.2.3 Sorption of ionisable organic chemicals to mineral surfaces

Organic species with at least one ionisable group in their structure, such as PCP or naphthenic acids, are amphiphilic. Such amphiphilic compounds

interact with mineral surfaces through electrostatic interactions of charged molecules with charged sites on the sorbent; exchange reactions with ligands previously bound to the solid and other chemical reactions.

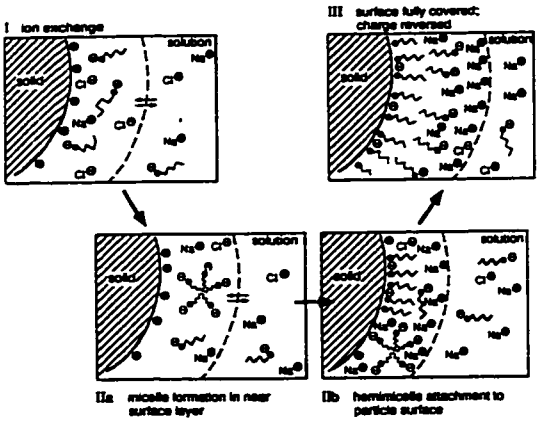
In a case where the solution contains two (or more) organic species, for example, a neutral compound and its conjugate acid or base, each of the species will be independently involved in its own sorptive exchange phenomena.

In aluminosilicates, possessing a permanent negative charge independent of pH, an ion exchange reaction occurs allowing positively charged organic species to exchange with sodium ions held near the solid surface (60). Electrostatic attraction to a surface is fairly non-selective, but the hydrophobicity of the nonpolar portion of the molecule appears to account for the apparent preference in ion exchange for organic ions over inorganic ones of the same valence. Some studies have suggested a further exchange process (59) that would maintain electroneutrality near the surface of the solid. This involves ion pair formation in solution followed by sorption to the surface. The surface need not be charged in order to act as a sorbent in this process. Similar to the ion exchange mechanism, this electroneutral sorption is ultimately limited by the capacity of the solid surface available to sorb the amphiphile. These two processes, ion exchange and non-ion exchange, taken together provide an explanation as to how the sorbed concentration can exceed the cation (or anion) exchange capacity for amphiphilic sorbates.

Amphiphilic sorption to minerals includes a special phenomenon called hemimicelle formation (60, 61). This can occur when organic ions are present at

0.001-0.01% of their critical micelle concentrations (CMC), the level at which they self-associate in the bulk solution. Amphiphile molecules accumulate to the CMC in the water adjacent to the mineral surface, even though the concentration of amphiphile in the bulk solution is well below this level. The aggregated amphiphiles coagulate with the oppositely charged particle surface, smothering that area of the particle's surface with hemimicelles. Continued increase in amphiphile concentration results in the surface becoming increasingly coated by hemimicelles, until the entire particle surface is covered with a bilayer of amphiphile molecules. Once the bilayer has formed there is an apparent charge reversal, as shown in Figure 1.2.3 below (35 p.318). The addition of more amphiphile to the solution does not effect further change.

Figure 1.2.3 Depiction of Hemimicellar Formation



1.2.2.4 Sorption of ionisable organic compounds to organic matter

Ionisable organic compounds sorb to organic matter just as described for nonpolar organic sorbates. For example, organic bases such as anilines have low pKa's, and so are not protonated at the normal pH of soil. When mixed with sediment, they become irretrievable by organic solvents or salt solutions, but can

be released by hydrolysis reactions. This suggests bond formation between the aniline and a carbonyl functional group (62).

In addition ligand exchange can occur between the organic sorbate and hydroxyl groups bound to metals in the solid. Generally, bidentate organic ligands displace these hydroxyl ligands better than monodentate organic ligands. Even so, pentachlorophenolate anion[9], a monodentate ligand, exhibits high levels of sorption to the soil that appear to be due to a ligand exchange process (64).

1.2.3 Sorption Kinetics

The time required to reach equilibrium in soil-water-xenobiotic systems is an area of intense investigation. Several processes could act to inhibit sorptive equilibrium. The sorbate molecules need enough time to move to all the possible sorption sites. Charged sorbate molecules need time to diffuse into a clay particle before they can associate with oppositely charged surface sites in the interior. The natural organic matter that absorbs nonpolar compounds may be located at inaccessible positions within silty aggregates. Finally, there may be slow diffusion into porous alumina particles where ligand exchange can occur. Since sorptive equilibrium is reached only when every part of the solid has reached equilibrium, simply delivering molecules to all the internal binding sites takes time. If the time spent in arriving at these binding sites is long compared to the

[9] Much of the published data on sodium pentachlorophenolate (NaPCP) is relevant to PCP and vice versa because PCP is largely in its dissociated form at pHs greater than 6 (63).

time required to bind to the site, the rate of molecular movement to the binding sites dominates the overall sorption kinetics. There may also be other processes occurring such as reactions between sorbate and sorbent that slow the equilibrium process (65).

1.3 WOOD PRESERVATION AND WOOD PRESERVATIVES

1.3.1 Pentachlorophenol

2,3,4,5,6-pentachlorophenol (molar mass 266.34 g/mL) is one of the most widely used pesticides in North America (66,67). It is a white, monoclinic, crystalline, non-combustible solid with a phenolic odour, pungent taste and a melting point of 188°C (68,69). In its impure form the solid may range in colour from grey to brown (67). Pentachlorophenol (PCP) is sparingly soluble in water (0.002% or 14 ppm at 20°C), with increased dissolution occurring in direct proportion to pH and temperature (5,69). It is highly soluble in organic solvents, which enhances its ability to penetrate skin following dermal contact (4,67) and sorb to organic solids such as cellulose in wood (5). PCP is classified as a poison (WHMIS class 6.1) to humans (68) and may be teratogenic (70).

PCP has been used in Canada as a wood preservative since 1936 (71). It is an effective wood preserving agent because it is a biocide (66) and survives a long time in the treated material (72). Once popular for home use, it is no longer available for over-the-counter-sale (68) and is not recommended for marine use (5,66). It is sold instead, for commercial use as a preservative of utility poles,

fence posts and railway ties (5,67). The commercial form of PCP, Penta, contains 86% pure PCP, with other chlorinated phenols, polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans making up the remainder. It is usually applied to wood as a 3-6% solution in petroleum oil or other solvent (5). Currently, 2000 metric tonnes of PCP are used in Canada annually (72, 73) and 140 million litres of PCP solution were used in the USA in 1995 (74). PCP is banned in 26 countries in the world (2,4). In Canada, reduced demand has led to the closure of many treatment facilities over the last 15 years (2).

PCP does not occur naturally but is now ubiquitous in the environment (75,76). Many sources of PCP release are suspected such as: spills at wood treatment sites; old waste chemical disposal areas; wastewaters from pulp and paper mills; and, to a lesser degree, leaching from treated wood (63). Total releases of PCP in the United States in 1988 were 1600 tonnes, of which 1400 tonnes were waste disposal on land (66).

Once PCP enters the environment it is subject to photolysis, sorption to particulates, covalent coupling to large or small molecules, volatilisation, and biodegradation (72). Biodegradation is the predominant mechanism for breakdown of PCP in soil (68). Soil-water partition coefficients, K_{oc}, for PCP range from about 10 to 1000 depending on the soil type (77); thus, PCP tends to bind to the organic matter in soils, which greatly reduces its water availability and subsequent mobility (66). PCP sorbs to soil in several different ways with about 20 – 50% being irreversibly sorbed, depending on soil type (77). If PCP dissociates in soil, which is dependant on the pH of the soil, little volatilisation will

occur, but leaching to ground water is possible. For example, survey of several wood treatment facilities in Canada showed, in all cases, ground water contamination extending down 6-18 m (5). Since anion exchange on organic components is promoted at low pH's, PCP is more mobile in alkaline soils than acidic soils. In contrast, at higher pH's, increased clay content increases sorption (65), primarily by sorption of ion or ion pairs. Hydrolysis of PCP does not appear to be a significant process in soil at any pH. PCP released to soil will eventually biodegrade to carbon dioxide and HCl. Some researchers report half-lives of 63-200 days for this biodegradation process (66,78,79,80). Others report that degradation does not take place in soils that have been sterilised, indicating that the activity is of biological origin (72). Soil type, organic matter content and moisture levels are some of the factors that can influence the rate of degradation in soil (47,80). Also important is the presence of adequate concentrations of the appropriate microorganisms. Photolysis, another degradation process, occurs to some extent in soil, with some of the photodegradation products being other chlorinated phenols, tetrachlorodihydroxybenzenes and dichloromaleic acid (66,81).

An occupational hazard associated with PCP is exposure via inhalation or dermal contact when using this preservative or when in contact with treated wood product (82). The general population risks exposure primarily from eating food contaminated with PCP. Brief exposure can irritate eyes, nose and throat and cause breathing trouble (66). Long-term exposure may cause genetic mutations

and teratogenic effects (70). Chronic poisoning may cause weight loss, weakness and chloracne (66).

Dioxin contaminants produced in the manufacture of commercial grade PCP are an additional concern. Conventional synthesis techniques result in about 15 ppm of various isomers of hexachlorodibenzo-p-dioxins (HxCDD) in PCP. Dioxins such as 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) are known to be highly toxic and carcinogenic. The dioxins found in PCP are less toxic, but they are still a major concern to regulatory agencies (3).

1.3.2 Chromated Copper Arsenate

Chromated copper arsenate (CCA) is prepared as a mixture of chromium, arsenic, and copper salts in a variety of different ratios. The most common formulation in North America is Type C, sold as a 50% concentrate by weight. Type C contains 9.25% copper (II) oxide, 23.75% chromium (VI) oxide and 17.0% arsenic pentoxide[10] (83,84). This dark brown liquid concentrate is strongly acidic (pH 1.6-3.0), non-volatile, and has a freezing point of –30°C. It is odourless and not flammable. Upon contact with reducing agents such as aluminium or zinc, CCA may liberate arsine gas or undergo violent explosions due to chromic acid reactions. Contact with combustible materials such as ammonia, naphthalene or glycerol may also result in violent reactions and subsequent explosions (83). CCA has been in use as a wood preservative since

[10] Arsenites derived from arsenic trioxide, As_2O_3, are less stable and far less soluble than arsenates derived from arsenic pentoxide, As_2O_5. (85)

1933 (85). Major CCA treated products include: fence posts, lumber for patios and landscaping, foundation lumber and plywood (84). In 1984 about 5000 tonnes of the 50% concentrate were used in Canada (84), with usage in the USA in 1995 of about 63 thousand tonnes (74). It is the most highly utilised water based preservative in use today. It is very soluble in water and thus mixes easily with wood stains for production of prestained-treated wood (2). It is possible to paint CCA-treated wood, unlike wood treated with other preservatives such as PCP or creosote. The advantages of CCA are that it is toxic to wood destroying organisms, clean, odourless and readily available at a reasonable cost. The disadvantages are that it does not prevent the weathering of wood, it can cause the wood to become more brittle than other treatments and it is more corrosive on metal parts in contact with the wood (2).

The treatment of wood with CCA (known as CCA fixation) is a complex process and the reactions involved depend upon the specific CCA formulation, concentration, wood species, pressure and temperature (85,86). Reaction products include insoluble chromates and insoluble arsenates of copper and chromium (87). During CCA fixation copper reacts with water-soluble wood components, forming complexes such as a copper cellulose complex (85). Any remaining copper reacts with chromium to produce mixed copper chromates (87). Since not all the chromium is required for reaction with copper, the rest of the chromium is reduced from hexavalent chromium to trivalent chromium, which then reacts with any arsenic present (85). Arsenic is fixed principally by trivalent chromium, probably as $CrAsO_4$, although some arsenic may be precipitated as

copper arsenate and some may be absorbed by the wood (87). Reactions are complex and time dependent (88,89). The pH changes as the reactions proceed, and in turn the pH governs the reaction rate (87,89,90). Since the reaction involves ions in solution, and the sorptive ability of chromium depends on the amount of water in the wood, the presence of water over the time period where reactions are occurring is important for maximum fixation (85).

Copper, chromium and arsenic all occur naturally, but at normal background concentrations they do not have discernible adverse effects on biota (84). There is considerable variation in natural concentrations of copper (2-100 ppm), chromium (5-1000 ppm), and arsenic (1-50 ppm) in Canadian soils (9,84).

Studies of CCA releases from wood preservation facilities to the adjacent environment show groundwaters in the immediate vicinity of some facilities to be contaminated to unsafe levels (85). The ratios of the three metals within these waters often differ from the ratios used in the wood preservation facilities (84). The inconsistency may be due to differences in the ability of the components to bind to soils. Valence changes of arsenic, chromium or copper occur within the environment, and those changes may reduce or enhance the toxicity of these elements and their sorption.

The form of chromium used in CCA facilities is Cr (VI), which is not found as commonly in nature as Cr (III), but is of far greater concern since it easily crosses biological membranes, is a strong oxidising agent and is highly toxic (84). Cr (VI) is water-soluble and reacts very slowly with soil constituents. Thus it is much more mobile in the soil water system than Cr (III) (45). Trivalent

chromium on the other hand is highly partitioned to the soil particles. Fortunately Cr (VI) is reduced to the less toxic Cr (III) during the CCA fixation process. However, it has been hypothesised that some of the fixed chromium remains in the hexavalent state (3). Cr (VI) is also reduced by organic components of the soil (3, 42) and by iron sulphide, which is often found in the mineral portion of soil (45). Organo-chromium (III) complexes tend to be stable and soluble even at pHs where Cr (III) normally precipitates (42). The most common manifestation of Cr (VI) poisoning is kidney damage, but levels in air of <0.05 mg/m^3 will injure nasal tissues, and 3-10% solutions containing Cr (VI) will cause slow-to-heal ulcers (4). This is a hazard to workers in the wood preservation industry, especially where plant hygiene is poor. Workers operating without proper protective clothing often suffer from these ulcers (4). The lethal oral dose for humans, LD_{50}, is 10-mg/kg body weight (91). Hexavalent chromium is toxic to plants at 1-5 ppm in solution cultures or sand, but at 500 ppm in compost soils (44). Trivalent chromium is less toxic by a factor of about 10 (3).

An average background level for copper in soil in Canada is 22 ppm (92). Copper is retained well in soil due to its high affinity for oxides and organic matter (9, 41). It is usually retained in the first 20-30 cm of soil with no evidence of leaching even after long periods of equilibration (9). Decreasing the pH (41) can increase copper mobility in soil. Copper (occurring as the divalent ion) is present in most living organisms and most people are essentially immune to copper poisoning unless a gram or more is ingested, resulting in nausea, vomiting and death (93). However, many other species, such as brook trout, are very sensitive

to copper (94). For example, *Gammarus pseudolimnaeus* has an LD_{50} of 0.0046-mg copper/L (84).

Arsenic is a natural, low-level constituent of most human tissues (95) but there is no general agreement on what levels reflect normal or excessive exposure to arsenic. The World Health Organisation suggests urine background levels of <80 μg/L (84,96). Since they are more toxic to humans than pentavalent arsenical substances, trivalent arsenical compounds bind readily to biological tissues (97). It is also believed inorganic forms are more toxic than organic, because the organic forms are rapidly excreted (95,96).

The toxicity database for As (V) is poor (84). Some studies suggest that As (V): is non-toxic at low doses (98); does not accumulate in human tissues but rather it is excreted within 24 hours; and is not reduced by the body to the trivalent state (85). Other studies show that inorganic arsenic compounds are carcinogenic in humans (84) and can cause a variety of problems involving heart, liver, lungs, and skin if there is a chronic exposure of 22-63 μg per day.

Although small amounts of arsenic stimulate growth in most plants, arsenic toxicity occurs at tissue levels of 1-9 ppm, depending on the plant. Soils treated with pesticides such as lead arsenate ($PbHAsO_4$) and sodium arsenite ($NaAsO_2$) average about 160 ppm As while untreated soils average 6.5 ppm As (9,99). Plant growth in arsenic contaminated soil is greatly affected by the soil chemistry and its ability to bind arsenic. For example, in soils high in aluminium, plants are tolerant to soil arsenic levels as great as 670 ppm (100). Elements in the soil such as aluminium, iron, and calcium bind the arsenic in place and

prevent its leaching (3). Sandy soils, low in reactive Fe, Al and exchangeable Ca, may permit leaching. Arsenic is primarily sorbed on iron oxides (97) and, to a lesser extent, on aluminium oxides and aluminosilicates (99). Various studies (85,100) show that arsenates (AsO_4^{3-}) are better sorbed by all soils than arsenites (AsO_2^-) (7). After sorption, the arsenate ion, which is the more stable form, will not convert to arsenite (100); rather As (III) appears to be slowly oxidised to As (V) (99). Since the pentavalent ion is less mobile and less toxic than the trivalent ion, this is an important factor in reducing mobility and toxicity.

Arsenic in wood preserved with CCA is in the form of chromium arsenate and copper arsenate, both insoluble compounds of pentavalent arsenic (85). Some studies suggest both valence states may be present on treated wood, with the concentration of trivalent arsenic increasing with the age of the wood (3), contrary to the behaviour observed in soil. The interconversion of the two valance states justifies the regulation and study of both species as one entity rather than separately.

Chromium, copper and arsenic generally sorb well to soil. Sandy soils with little cation or anion exchange capacity, low organic matter, and low pH will bind less of these components than other soils (3). Organic compounds with at least two carboxylic acid groups are capable of chelating copper and other metals thereby rendering them soluble (29) in the soil solution. In fact, copper complexes so well with humic acids (29) that dissolved humic materials can extract copper from sediment by formation of these complexes (41). It is also possible to reduce the leachable arsenic content of ore refining sludges by

extracting them with humic acids (3). Finally, trivalent chromium can be mobilised by complexing with components of composting organic matter in poorly drained soils (42).

There appears to be a synergistic effect in the CCA formulation, in that lower concentrations of each metal result in higher toxicity effects than any of the ingredients acting alone (101). This is an important advantage in the biocidal activity of CCA.

1.3.3 Copper Naphthenate

Copper naphthenate (CUNAP) has been in use as a wood preservative since about 1947 (102). Copper naphthenate is a name applied to a group of compounds that are copper salts of naphthenic acids (103). Naphthenic acids, sometimes referred to as petroleum acids (81), are the carboxylic acids derived from petroleum during the refining of the various distilled fractions. They are natural components of crude oil, not formed during the refining (103), and they are predominately monocarboxylic acids (81). Despite intensive investigation by a variety of chemists (104), the number of component acids that have been identified remains small (105). The simplest of these acids is cyclopentylethanoic acid but structures can include many more methylene groups between the ring and the carboxyl group and may include several fused rings (81). The exact composition of naphthenic acids depends on the crude oil from which they are derived and is usually quite complex (103). Commercial

naphthenic acid contains all the acidic components of crude oil, and varying amounts, usually less than 10%, of hydrocarbons (4).

CUNAP is manufactured either from copper sulphate and naphthenic acid in combination with a strong base or by heating naphthenic acid and copper oxide (106). Commercial grade CUNAP usually contains between 8-19% copper naphthenate in petroleum distillate, giving a maximum copper content of about 2% (103,107). This mixture is a green-blue waxy solid or very viscous liquid with a mild odour but practically no inhalation hazard from the vapour (103). Most of the health hazards associated with the use of CUNAP are due to the solvent. If ingested, excess copper is excreted and naphthenic acids, like other carboxylic acids, are quickly broken down by the body (108). Melting and boiling points vary with the composition of the naphthenic acids. CUNAP is insoluble in water but miscible with most organic solvents (103). The LD_{50} is >6 g CUNAP/kg body weight (103) and no teratogenic effects have been observed (108). CUNAP is toxic to a wide variety of microorganisms, fungi, plants and aquatic life, including invertebrates, algae, and fish (94,109).

CUNAP is the only "over-the-counter" wood preservative in Canada and the USA (2). Its advantages are its non-toxicity to plants, non-irritability to the skin of the user, hardware store availability, and easy application. The disadvantages of CUNAP are its odour, the cost (higher than PCP) and its lower toxicity compared to other preservatives. Few treatment plants utilise this chemical and thus it is not readily available in the quantities required for commercial usage (2). For example, production in the USA in 1988 was only 1500 tonnes (4).

Copper naphthenate tends to hydrolyse after application to wood. The acid is lost by volatilisation comparatively rapidly, but the metal persists. While the acid is still present the activity is enhanced, suggesting a degree of activity which will be lacking in prolonged service (85).

Despite widespread industrial use of CUNAP, there are few reports of the effects of copper naphthenate on humans. In one report, health was compromised and serum copper levels were still elevated 4 years after contact with CUNAP as a fungicide (109).

No information was available on the binding of CUNAP to soil or its subsequent degradation.

1.4 TECHNIQUES TO STUDY SORPTION PROCESSES

An understanding of contaminant behaviour in soils requires several types of physical and chemical information including the kinetics and equilibria of sorption (110). An analytical methodology capable of measuring the distribution of contaminant species between solution and soil phases is essential (111). The monitoring of these variables throughout a kinetics experiment has not been practical until the recent introduction of the microfiltration/high performance liquid chromatography technique (MF-HPLC) by Gamble (110). This technique applied to analysis of a batch sample allows study of the labile and nonlabile sorption processes that occur between a contaminant and soil (111).

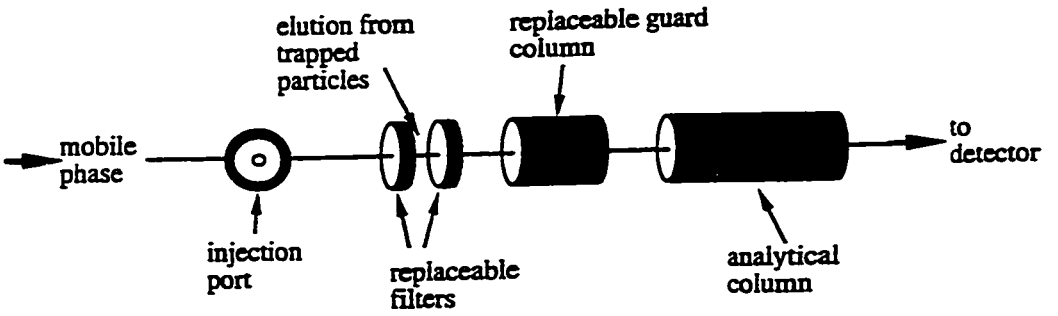
1.4.1 Microfiltration Techniques

The method developed by Gamble and co-workers (112, 113) describes pesticide-soil interactions by assuming at least two kinetically linked processes, a relatively fast labile surface sorption followed by slow intraparticle diffusion. The labile sorbed fraction is defined as the amount of sorbed species desorbed, during the microfiltration process[11], by extracting the soil with the HPLC mobile phase. The fraction of contaminant not extracted from the particles by the mobile phase is identified as the nonlabile fraction (111).

Gamble's method (110) involves a batch set-up with a reaction vessel containing water and soil (forming a slurry), a Teflon-coated stir bar and magnetic stirrer (to keep the soil samples suspended), and a thermostated circulating bath (to maintain constant slurry temperatures) (110). The MF-HPLC arrangement consists of an HPLC with a C-18 column and a C-18 guard column fitted with replaceable 2.0 μm and 0.5 μm stainless steel microfilters. The microfilters are used to trap solids and protect the main HPLC analytical column. In runs designed to determine solution phase contaminant only, the slurry is microfiltered prior to injection with a disposable Tuberculin syringe and a disposable, 0.45 μm pore size, nylon syringe filter. For direct injections of standards, filtrates and whole slurries Hamilton syringes with fixed needles are used (110). Figure 1.4.1 below shows the arrangement of filters for the Gamble method (129 p.12).

[11] The term microfiltration refers to the process of passing a solution through a filter with a mesh size of 2.0 μm or less, a "microfilter".

Figure 1.4.1 Schematic Representation of MF-HPLC On-Line Extraction



Post-injection filtration, on the HPLC, traps the solid particles on the stainless steel inline filter. There the solid particles are washed by the mobile phase. The quantity of a compound eluted by the mobile phase represents the sum of the amount of compound dissolved in solution (aqueous fraction) and the amount of compound reversibly sorbed to the soil (labile sorbed fraction). Pre-injection filtration with disposable syringe filters traps the solid particles and leaves only the filtrate to be injected into the HPLC. This gives a direct measurement of the aqueous fraction. Subtraction of the two values (post-injection and pre-injection) determines the concentration of the labile sorbed fraction. During the experiment, some of the compound may sorb onto sites for which the sorption and desorption rates are very slow. Any such sorption should be manifest as a loss of material and is labelled "nonlabile sorption". This makes it possible to monitor changes in the nonlabile sorption throughout the course of a heterogeneous kinetics experiment. The only complication is formation of degradation products, which should be monitored (110).

1.4.2 Inductively Coupled Plasma

A variety of traditional methods exist for the determination of copper, chromium and arsenic (40). Most commonly, concentrations of metals are determined using atomic absorption spectrophotometry (7, 9, 41, 42, 97, 99, 114, 115, 116). However, within the last few years, the development of standard methods using inductively coupled plasma technology have made the determination of multiple ions in solution relatively easy (114). This has led to an increased use of this technology by a variety of investigators (44, 45).

Emission spectroscopy using inductively coupled plasma (ICP) was developed in the mid-1960's as a rapid, sensitive, and convenient method for the determination of metals in water and wastewater samples (114). Dissolved metals are determined in filtered and acidified samples. Total metals are determined after appropriate digestion.

ICP permits effective multi-element determination of metals (114) but does not allow a determination of speciation. Estimated detection limits and upper limits are given in Table 1.4.1 below.

Table 1.4.1 Estimated limits for ICP determination of As, Cr and Cu (114)

Element	Detection Limit (μg/L or ppb)	Upper Limit (mg/L or ppm)	Calibration Concentration (mg/L or ppm)
Arsenic	50	100	10.0
Chromium	7	50	5.0
Copper	6	50	1.0

Of course, the real advantage to using ICP in the determination of CCA concentrations in soil-water slurries is that only one sample is needed to measure the concentrations of all three elements at once.

1.4.3 Solid-Phase Microextraction

Solid-phase microextraction (SPME) is an innovative approach to analysis of trace amounts of compounds (117). The analytical process typically consists of sample preparation (where the analyte is separated from the sample matrix and often purified and concentrated), sample analysis and finally data analysis. Problems associated with traditional sample preparation methods, such as toxic solvents, multistep procedures and loss of analyte, frequently made sample preparation the major source of error in an analysis. An ideal sample preparation technique should be solvent-free, simple, inexpensive, efficient, selective, and compatible with a wide range of separation methods (118). SPME has been developed as a solvent-free technique that can combine simultaneous separation and concentration of the analyte with sample introduction into a single step (119).

Since different types of sorbents can extract different groups of analytes, a variety of sorbents have been used for SPME. Polar coatings, such as polyacrylate and carbowax, extract polar compounds, such as phenols and carboxylic acids, very effectively. Nonpolar coatings, such as poly(dimethylsiloxane), are best for extracting hydrocarbons. SPME has been applied in sampling polyaromatic hydrocarbons (120) and phenols (121, 122) in aqueous samples with detection limits, precision and accuracy better than or equivalent to EPA method specifications (118).

SPME eliminates the use of solvent not only in extraction, but also during injection, which greatly improves chromatographic separation efficiency (118).

2 CHARACTERISATION OF SOIL

2.1 INTRODUCTION

Soils are complex materials, reflecting the variability of the parent rock material and organic residues from which they form. Their elemental composition, particle size, mineralogy and so on determine to a large extent how the soils will interact with their environment (29). Although soil maps and surveys (25, 26) classify the soils of each region very carefully, it is important to investigate the characteristics of a specific soil sample (27). This allows a clear understanding of how and why soils behave the way they do under the experimental conditions.

2.2 EXPERIMENTAL

Soil was obtained from Canmore and Brooks, Alberta. The Canmore soil (classified by Alberta Soil Survey as Eutric Brunisolic) was obtained at the crossing of the Spray Lake Road with Canmore Creek, at a distance of 50 meters from the creek, on the South Bank, in a wooded area. Samples were taken at depths of 20, 48, and 61 cm from two sites on the south bank, about 10-m apart. The samples from each site were combined to form one sample, but the different depths were maintained separate. The Brooks soil (Alberta Soil Survey: Brown Chernozemic) was obtained from a field at the Brooks Horticultural Research Station. Samples were taken at depths of 23, 37, and 61 cm from three sites 20-30 meters apart. As with the Canmore soil, the samples from the three sites

were combined but the depths were maintained separate. Prior to analysis all of the collected soil samples were air-dried for one week at 21°C, then passed through a standard 2 mm sieve. All soil samples were then placed in sealed glass jars and stored at -10°C until needed.

Richard Rogalski of the Department of Geography, University of Calgary, performed chemical analysis of the soils. Results obtained include organic carbon, percent organic matter, elemental analysis, particle size distribution, and cation exchange capacity. Tracey Henselwood, a graduate student in the Department of Chemistry, University of Calgary, performed soil surface area estimates. Areas were determined using the ethylene glycol monoethyl ether (EGME) method (123).

Particle sizes were determined by sieving and using hydrometer readings. Soil organic matter and organic carbon content were determined using a wet oxidation of the soil by potassium dichromate (124). Extractable phosphorus was determined using acid ammonium fluoride extraction (124). Other elemental analyses were performed on the barium chloride exchangeable elements, with and without washing pre-treatment, for calcium, magnesium and sodium, and without washing pre-treatment for iron, aluminium and manganese (125). Iron, aluminium, and manganese content were also determined by ammonium oxalate extraction (124). Cation exchange capacity (CEC) was estimated as the sum of the exchangeable elements using the barium chloride procedure without washing pre-treatment.

Soil pH values were also determined.

2.3 RESULTS and DISCUSSION

The results obtained from the analyses described in section 2.2 are summarised in Tables 2.3.1-2.3.5.

Particle size analysis (Table 2.3.1 & 2.3.2) of the soils, at all depths, suggests that the Brooks soil is a silty loam, using the Canadian System of Soil Classification (23), with finer particle sizes predominating (27). The Canmore soil is classified as a sandy loam based on particle size distribution, with over 60% of the particles fitting within the range defined for sand (24). The particle size distribution graphs derived from the data in Table 2.3.1 & 2.3.2 suggest that the Canmore soil contains a wider range of particle sizes than the Brooks soil. (See Figure 2.3.1 for two examples of these graphs or Appendix A (Figures A.1 – A.6) for the complete set of particle size distribution graphs.)

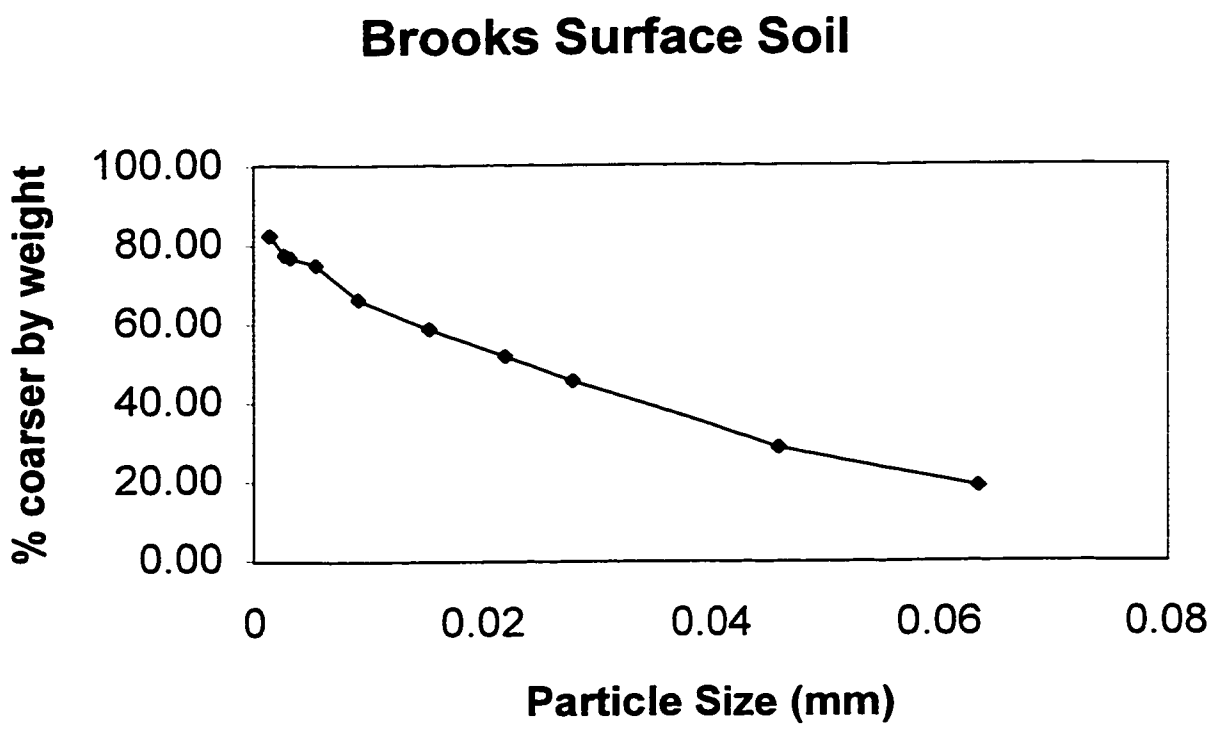
A comparison of the organic matter content of the soil samples, as given in Table 2.3.3, with the surface area of the soil samples, Table 2.3.4, shows that the Canmore soils contain about 45% more organic matter than the Brooks soils but about 51% less surface area. The diminished surface area correlates well to the dominantly sandy soil texture. Despite the lower surface area of the Canmore soils, the decrease after oxidation (Table 2.3.4) was 56% greater, on average, than the Brooks soils. It appears likely, from these data, that the organic matter present is responsible for a large proportion of the available surface area in the Canmore soil.

When the data from the chemical analyses (Table 2.3.3) is graphed, it becomes immediately apparent that Canmore surface soil contains more Fe, Al

TABLE 2.3.1 Particle Sizes of Brooks and Canmore Soils					
Brooks Surface			Brooks Deep		
Particle Size (mm)	% coarser by weight	% finer by weight	Particle Size (mm)	% coarser by weight	% finer by weight
0.0634	18.75	81.25	0.0637	20.00	80.00
0.04615	28.75	71.25	0.0463	30.00	70.00
0.0279	45.63	54.38	0.0311	46.88	53.13
0.02197	51.88	48.13	0.02202	52.50	47.50
0.0154	58.75	41.25	0.01575	58.75	41.25
0.0093	66.25	33.75	0.0093	66.25	33.75
0.0055	75.00	25.00	0.0054	73.13	26.88
0.0032	76.88	23.13	0.0032	75.63	24.38
0.00265	77.50	22.50	0.00264	76.25	23.75
0.00134	82.50	17.50	0.00137	81.25	18.75
% clay	17.50		% clay	18.75	
% sand	28.75		% sand	30.00	
% silt	53.75		% silt	51.25	
texture[1]	silty loam		texture[1]	silty loam	
Brooks Medium					
Particle Size (mm)	% coarser by weight	% finer by weight			
0.0631	17.50	82.50			
0.04585	26.25	73.75			
0.0278	42.50	57.50			
0.02202	52.50	47.50			
0.01565	56.25	43.75			
0.0093	65.63	34.38			
0.0054	71.25	28.75			
0.0032	76.25	23.75			
0.00266	78.75	21.25			
0.00138	83.75	16.25			
% clay	16.25				
% sand	26.25				
% silt	57.50				
texture[1]	silty loam				
[1]using chart pg 19 in Winegardner (27)					

TABLE 2.3.2 Particle Sizes of Brooks and Canmore Soils							
Canmore Surface				Canmore Medium			
Particle Size (mm)	Cumulative Soil (g)	% coarser by weight	% finer by weight	Particle Size (mm)	Cumulative Soil (g)	% coarser by weight	% finer by weight
1.41	0.65	2.60	97.40	1.41	0.14	0.90	99.10
0.71	2.73	10.90	89.10	0.71	0.69	4.42	95.58
0.59	3.46	13.84	86.16	0.59	0.89	5.71	94.29
0.42	5.33	21.32	78.68	0.42	1.54	9.88	90.12
0.25	8.24	32.96	67.04	0.25	2.90	18.61	81.39
0.21	9.24	36.96	63.04	0.21	3.43	22.02	77.98
0.088	14.76	55.04	44.96	0.088	8.16	52.37	47.63
0.044	15.57	78.28	21.72	0.07		54.38	45.63
0.02224		56.25	43.75	0.0503		61.25	38.75
0.016		63.13	36.88	0.044	12.62	81.00	19.00
0.0094		72.50	27.50	0.03015		76.25	23.75
0.0055		79.38	20.63	0.02346		78.75	21.25
0.0032		86.25	13.75	0.01665		81.88	18.13
0.0027		87.10	12.90	0.0097		87.50	12.50
0.00141	25.00	91.88	8.13	0.0057		90.63	9.38
% clay	8.13	% silt	36.83	0.0033		93.13	6.88
% sand	55.04	texture[1]	sandy loam	0.00274		93.75	6.25
Canmore Deep				0.00142	15.58	96.25	3.75
Particle Size (mm)	Cumulative Soil (g)	% coarser by weight	% finer by weight	% clay	3.75		
1.41	1.05	2.88	97.12	% sand	61.25		
0.71	3.35	5.15	94.85	% silt	35.00		
0.59	4.07	11.16	88.84	texture[1]	sandy loam		
0.42	6.10	16.73	83.27				
0.25	10.07	27.62	72.38				
0.21	11.66	31.98	68.02				
0.088	22.53	61.79	38.21				
0.02355		80.63	19.38				
0.01675		83.75	16.25				
0.0097		87.50	12.50				
0.0057		91.75	8.25				
0.0033		93.75	6.25				
0.00274		94.38	5.63				
0.00141	36.46	94.63	5.38				
% clay	5.38	% silt	32.83				
% sand	61.79	texture[1]	sandy loam				

Figure 2.3.1Particle Size Distribution Graphs for Two Soils



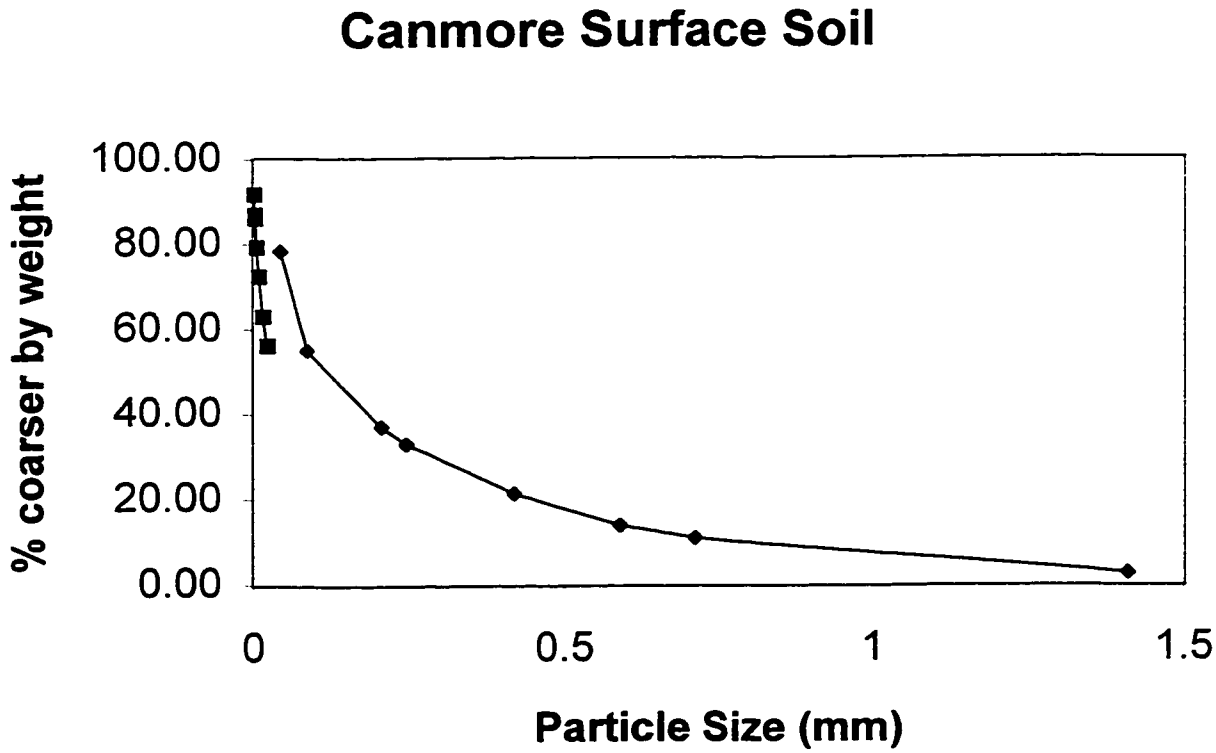


TABLE 2.3.3 Chemical Analysis of Brooks and Canmore Soils												
Analysis	Brooks Surface		Brooks Medium		Brooks Deep		Canmore Surface		Canmore Medium		Canmore Deep	
Barium Chloride Method	meq/100 g	RSD%	meq/100 g	RSD%	meq/100 g	RSD%	meq/100 g	RSD%	meq/100 g	RSD%	meq/100 g	RSD%
Ca	28.45	0.8	31.39	0.5	26.00	0.9	41.91	0.8	22.26	0.5	21.03	0.1
Ca with washing pre-treatment	26.30	0.9	25.64	0.5	19.51	0.6	39.44	0.5	21.68	1.0	19.60	1.5
Mg	2.05	0.3	9.23	0.3	10.52	0.2	2.84	0.1	1.76	0.8	1.72	0.5
Mg with washing pre-treatment	1.28	0.6	3.01	0.5	3.98	0.2	2.12	0.4	1.20	0.6	1.15	0.5
Na	0.25	0.5	2.72	0.5	4.64	0.1	0.20	0.6	0.13	0.0	0.13	0.9
Na with washing pre-treatment	0.12	0.2	0.18	0.2	0.20	0.5	0.11	1.0	0.09	0.0	0.10	0.9
K	0.69	0.2	0.55	0.1	0.47	0.0	0.58	0.4	0.12	2.7	0.23	0.3
K with washing pre-treatment	0.14		0.08	0.0	0.09	0.5	0.16	1.4	0.07	0.0	0.07	0.4
Fe	0.00		0.00		0.00		0.00		0.00		0.00	
Al	0.00		0.00		0.00		0.00		0.00		0.00	
Mn	0.00		0.00		0.00		0.00		0.00		0.00	
CEC	27.83		28.91		23.77		41.83		23.04		20.92	
Ammonium Fluoride Method	ppm	RSD %	ppm	RSD %	ppm	RSD %	ppm	RSD %	ppm	RSD %	ppm	RSD %
P	58.08	7.7	15.36	6.8	38.09	4.8	47.14	2.9	59.13	1.3	61.44	0.0
Oxalate Method	%	RSD %	%	RSD %	%	RSD %	%	RSD %	%	RSD %	%	RSD %
%Fe	0.17	0.4	0.17	1.4	0.19	1.0	0.34	0.2	0.15	0.1	0.15	0.4
%Al	0.08	3.2	0.08	2.2	0.04	19.2	0.35	1.3	0.12	4.5	0.11	5.7
%Mn	0.02		0.02		0.02		0.02		0.01		0.01	
Comparison of:	**Organic Matter Content**				**Organic Carbon Content**							
	OM	**avge**	**stdev**	**% diff.**	**OC**	**avge**	**stdev**	**%diff.**				
Brooks Surface	3.45				2.00							
Brooks Medium	4.30	3.60	0.64		2.49	2.09	0.37					
Brooks Deep	3.05			44.90	1.77			44.94				
Canmore Surface	7.50				4.35							
Canmore Medium	5.10	6.53	1.27		2.96	3.79	0.73					
Canmore Deep	7.00				4.06							

TABLE 2.3.4 Soil Surface Areas of Brooks and Canmore Soils		
Soil Pre-Treatment	**Specific Surface Area (m^2/g)**	**Standard Deviation**
Whole Brooks Surface	49.75	1.13
Oxidised Brooks Surface	40.25	0.55
whole Brooks Medium	48.64	1.27
Oxidised Brooks Medium	39.59	0.67
whole Brooks Deep	44.29	1.07
Oxidised Brooks Deep	41.54	0.95
whole Canmore Surface	41.05	1.56
Oxidised Canmore Surface	21.84	0.81
whole Canmore Medium	15.24	0.57
Oxidised Canmore Medium	9.07	0.20
whole Canmore Deep	14.33	1.69
Oxidised Canmore deep	15.80	0.41
	Average Surface Area	**Standard Deviation**
Brooks Soil	47.56	1.16
Oxidised Brooks Soil	40.46	0.72
Canmore Soil	23.54	1.27
Oxidised Canmore Soil	15.57	0.47
Percent Loss of Surface Area Due to Oxidation		
Brooks Soil	14.93	55.91
Canmore Soil	33.86	
% Difference in surface area (Brooks and Canmore)		50.50
% Difference in loss of surface area (Brooks and Canmore)		55.91

TABLE 2.3.5 pHs of Brooks and Canmore Soils		
Soil	pH	Average
Brooks Surface	7.50+/-0.10	
Brooks Medium	8.00+/-0.00	7.90+/-0.30
Brooks Deep	8.20+/-0.10	
Canmore Surface	7.25+/-0.05	
Canmore Medium	7.90+/-0.00	7.60+/-0.30
Canmore Deep	7.65+/-0.15	

and Ca (see Figures 2.3.2 and 2.3.3) than the other soils. It also has the largest cation exchange capacity. Thus, the Canmore surface soil may be expected to sorb copper ion more efficiently than the other soils. It is also noticeable (see Table 2.3.3) that Canmore surface soil has the highest organic matter content. This matches a recent study of several Alberta soils that showed a correlation between high organic matter content and higher levels of trace metals (44).

The pH measurement of the soils (see Table 2.3.5) shows that Canmore soils are more acidic (7.60 ± 0.30) than the Brooks soils (7.90 ± 0.30). This seems consistent with a soil developed in an area forested mostly with pine (pine needles tend to acidify soil) as opposed to open prairie. This may also have some effect on the sorption of the compounds to be studied.

Figure 2.3.2 Chemical Analysis of Brooks and Canmore Soils by Barium Chloride Method

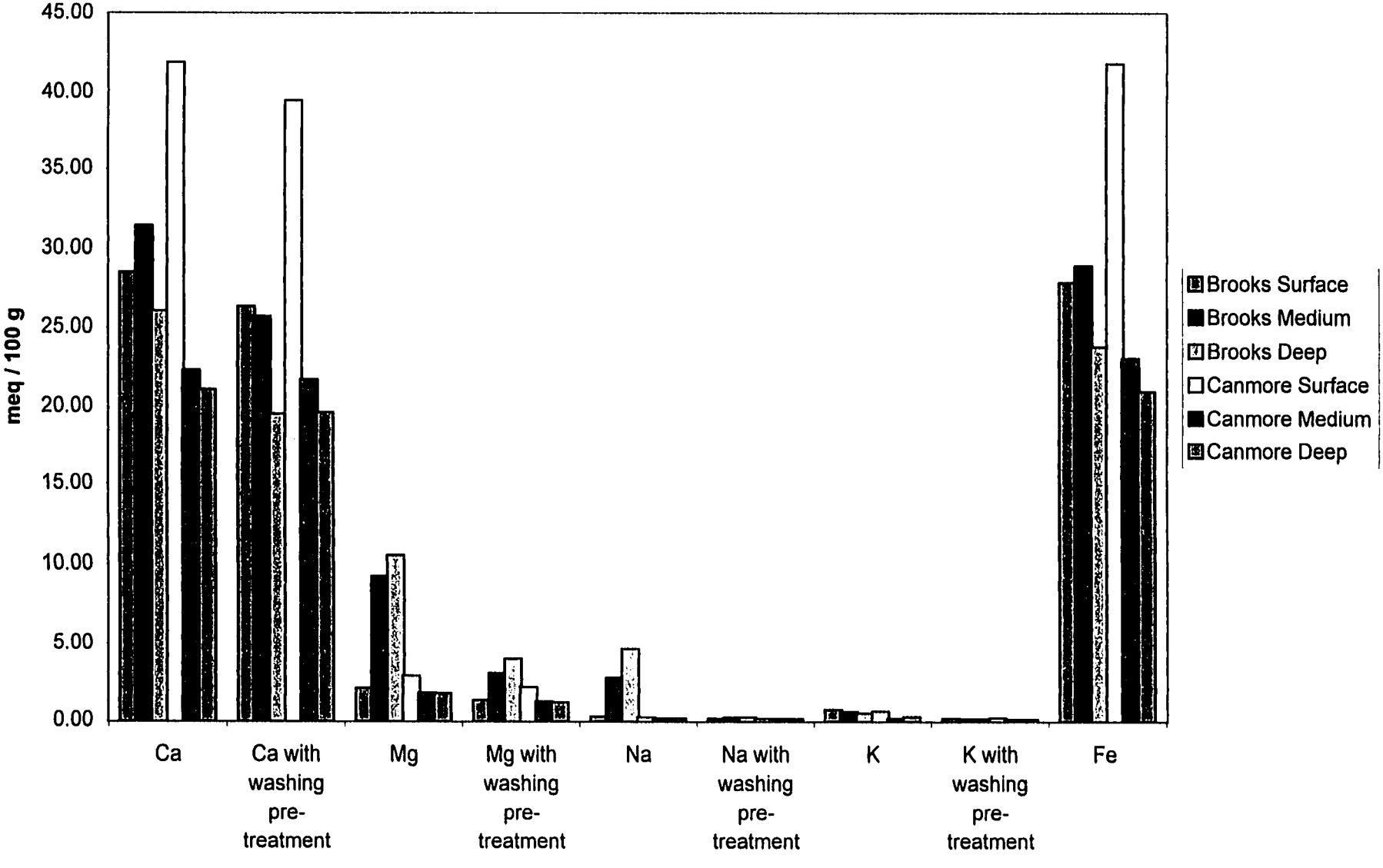
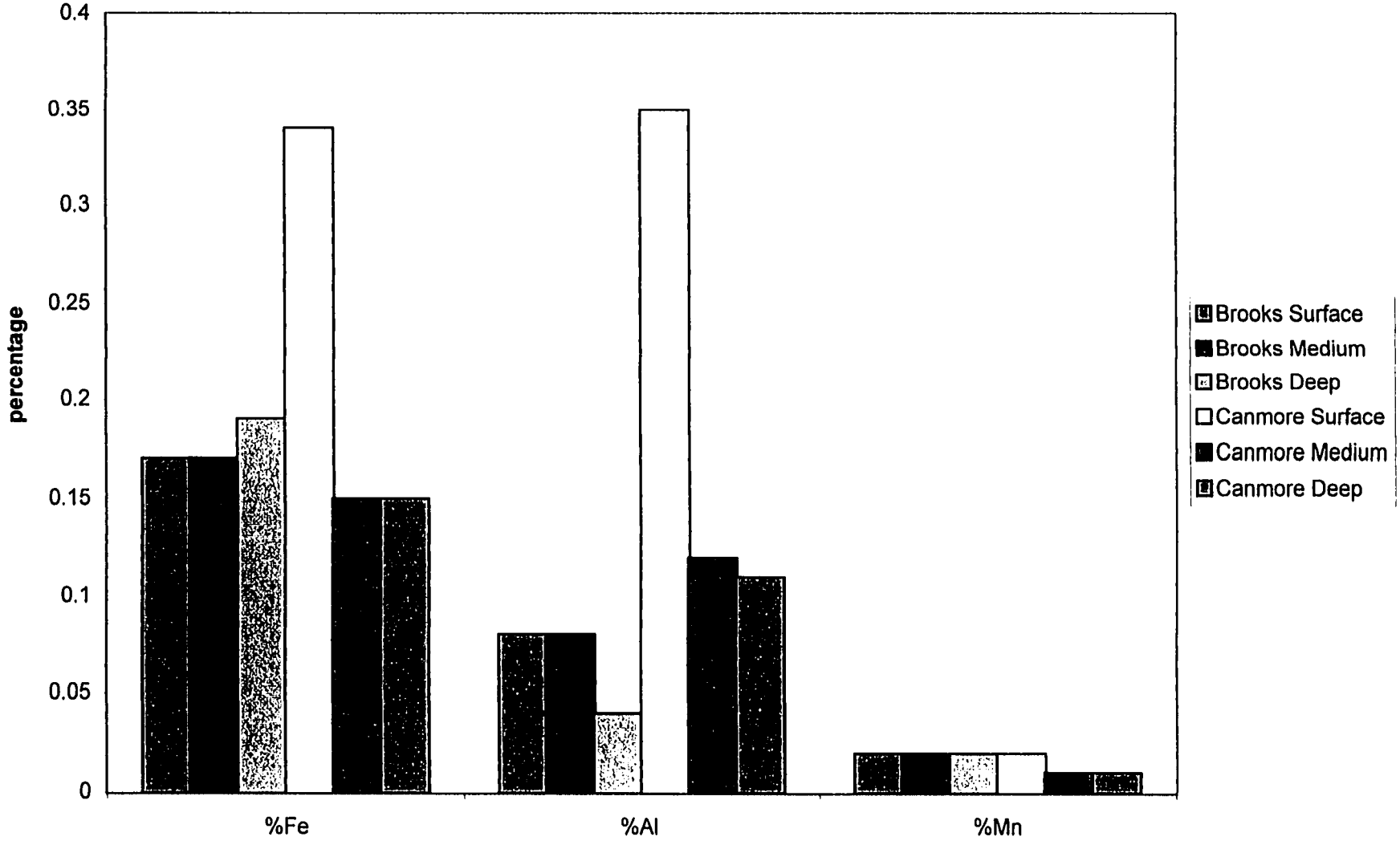


Figure 2.3.3 Chemical Analysis of Brooks and Canmore Soils by Oxalate Method



3 SOIL KINETIC INTERACTION STUDIES

3.1 PENTACHLOROPHENOL

3.1.1 Introduction

Determination of PCP can be done by a variety of methods. While some authors recommend the use of GC or GC/MS (6,77,114), decrease in UV absorbances (79), or the 4-amino antipyrine method (64), several studies of PCP sorption have been done using HPLC (126,127,128). Additionally the use of HPLC with UV detection allows a more direct comparison of the present work with that of other researchers using the MF-HPLC method (110,111,112,113, 128)

The method developed by Gamble (110) and Langford (111) offers a one step extraction and analysis of both the surface sorbed species (hereafter referred to as "labile") and solute that has penetrated into the soil interior (hereafter referred to as "nonlabile"). It also allows the determination of any degradation products that occur. This is the Gamble MF-HPLC method discussed in detail in Section 1.4 above.

The disadvantage of the Gamble method is that it involves direct injection of soil-water slurry onto the HPLC column, which is only feasible if a dedicated instrument is available. Since the instrument used in the present work was also being used for other purposes it was necessary to adapt the method. Modifications were made as needed. The final modified method is given in detail

in section 3.1.2. However, the changes made and the rationale for those changes are presented herein.

The pre-injection filtration was changed by the addition of a distilled water rinse of the same volume as the first aliquot of slurry. This was felt necessary to ensure that all PCP in the aqueous phase was removed. Rather than direct injection of a second aliquot of slurry onto the HPLC, the soil trapped in the syringe filter from the pre-injection filtration was rinsed with an extracting solution, such as methanol or acetonitrile. It was hoped that this would function in a fashion similar to injecting slurry onto the stainless steel filters and then passing HPLC eluent, such as an acetonitrile/water mix, through the slurry. To this end, two aliquots of extracting solution were pushed through the syringe filter to give a filtrate (tube B) with volume equal to the volume of the aqueous filtrate (tube A). This was far less than the volume of eluent used in a direct injection of slurry but it was hoped that the general trends of labile and nonlabile uptake would be seen. These modifications allow the microfiltration method to be used in the study of compounds that require separation and detection in systems other than HPLC/UV-Vis.

A further modification made was in the nature of the syringe filter. While a nylon syringe filter will work well with many compounds, including CCA and CUNAP, it was found that PCP could not be filtered acceptably using nylon. An investigation was carried out to determine the best filter material for PCP. After several trials, the syringe filter for PCP was changed to a Millex-FH_{13} syringe filter by Millipore. This new filter had the same dimensions and pore size as the

original nylon filter but was made of a modified PTFE material, Fluoropore®, that was inert to PCP. Further details of this search for an appropriate syringe filter are given in the discussion, section 3.1.3.

The changes to the method also necessitated a change in the calculations. That is, in the Gamble method the labile uptake was determined as the difference in peak area between slurry (post-injection filtration) and filtrate (pre-injection filtration) injections, whereas, in the adaptation, the labile uptake was determined as the peak area of the second, non-aqueous, filtrate. The peak area of the "water" filtrate was the aqueous or dissolved fraction. Nonlabile uptake was determined as the difference in the amount of PCP recovered (sum of aqueous and labile) and the original slurry concentration.

The HPLC column was a C-18 reversed phase cartridge with flow rate and eluent components as suggested by other investigators of PCP sorption (47,128). The UV/Vis wavelength settings were decided as a result of running a UV scan on PCP and other components of the system and by comparison with the literature (128). These settings were necessarily different from those of other investigators using the Gamble MF-HPLC method, since the majority of work done with this method has involved atrazine rather than PCP (110,111,112,113,129).

2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) is a contaminant of commercial grade PCP and a degradation product of PCP. The retention time of TCDD, under the experimental parameters, was determined using several

dilutions of TCDD. This allowed the detection of possible degradation during the experiment.

3.1.2 Experimental

Half-gram soil samples were weighed into 30 mL Wheaton vials using a Mettler analytical balance. Six samples of each of six soils were prepared, three to have PCP (Aldrich) added and three to act as blanks. There were also six vials, containing no soil, prepared as a method control, three to have PCP added and three to act as control blanks. Twenty-five millilitres of distilled water was added to each of the forty-two vials which were then sealed with plastic caps and placed in a 64 cm x 64 cm x 10 cm piece of Styrofoam (with bored-out holes). The Styrofoam holder was placed on a Khan shaker (Eberbach) and the vials were shaken for 48 hours, to allow the soil to wet. Although temperature control was attempted initially using a circulating water bath, this was subject to temperature fluctuations of over 10°C and was discontinued. It was found that room temperature stayed a fairly constant 22–23°C, which was considered acceptable. After 48 hours of shaking PCP was added as 500 μL of a 0.1752 g/100 ml PCP solution (pH 3.5) using a Finnpipet. This gave the soil slurry an initial concentration of 35 ppm PCP. The pH of the soil-water slurry was determined before and after adding the PCP solution.

Immediately after mixing, the first 0.3 mL aliquot was removed using a disposable Tuberculin BD-1 1-cc syringe. The slurry was filtered through a 13 mm diameter, 0.45 μm pore size, Millex-FH_{13} syringe filter (Millipore). After

removing the plunger, 0.3 mL of distilled water was added to the syringe barrel and pushed through the filter. The two filtrates, added together, became Sample A and were stored in 1 mL screwtop vials, as were all other samples. The soil trapped on the filter was then rinsed with two 0.3 mL aliquots of HPLC grade methanol (Aldrich) to give sample B. Beginning at Day 35 an addition was made to the method. This involved rinsing every third sample with two 0.3 mL aliquots of HPLC grade acetonitrile (Aldrich), instead of methanol, generating sample C.

HPLC analyses were performed using a Shimadzu SCL-6B system controller, a Shimadzu LC-6A pump and LC and a Shimadzu SPO-6AV UV-Vis detector. The injection valve was a Rheodyne Model 7010-084 with Model 7012 loop filler port. The analytical column was an ODS Hypersil, 5 μm x 12.5 cm x 4 mm i.d., cartridge (Shimadzu) which was replaced with a Spherisorb ODS-2, 5 μm x 12.5 cm x 4 mm i.d., cartridge column (Hewlett Packard) during experiment 2. The guard columns were Spherisorb ODS-2, 5 μm x 4 mm x 4 mm i.d. (Hewlett Packard). A filtrate sample of 80 µL was taken up into a 100 µL Hamilton syringe and injected into a 20 µL injection loop. The eluent was 1:1 acetonitrile and water with 5% acetic acid and 10 mM triethylamine at a flow rate of 1.2 mL/min. Detection was at 301.5 nm. The soils used have been discussed previously.

3.1.3 Results

To facilitate analysis of the results, data obtained from this experiment were tabulated (see Table 3.1.1) and then converted into a variety of graphs. The graphs show comparisons of all six soils with respect to change of concentration of PCP in the aqueous phase over time (Figure 3.1.1), and to change in PCP labile (Figure 3.1.2) and nonlabile PCP (Figure 3.1.3) uptake over time. The aqueous, labile and nonlabile concentrations of PCP were then shown for each soil. All of these figures are included in Appendix B (see Figures B.1-B.6).

The pH values of the slurry are given in Table 3.1.2 and show the pH before and after the addition of the PCP solution. As can be seen, the addition of the 500 μL of PCP solution to ~ 25 mL of slurry reduced the pH by about 0.4 pH units (on average). The effect this has on the soil is limited. What is of greater interest is that upon being added to the slurry the PCP is subjected to a dramatic change in pH (from 3.5 to an average value of 7.1). Since the pK_a of PCP is 4.75, this would indicate that a significant portion of the PCP is deprotonated and interacts with the soil as the pentachlorophenolate ion.

While a complete discussion of the results together with the results of the other two experiments will be conducted in section 4, it is important to assess these results with respect to the method and its suitability. Although only one set of results is presented in this section, three PCP trials were conducted. In the first trial an 1:1 ratio of acetonitrile:water with 5% acetic acid was employed as the HPLC eluent (47). After several runs peak broadening began to occur.

TABLE 3.1.1 Data Summary for Pentachlorophenol Experiment 3 (ppm PCP)					
Day	0	0.0021	3	7	35
soil type	aqueous phase	aqueous phase	aqueous phase	aqueous phase	aqueous phase
Brooks Surface	35	17.89	16.99	17.89	12.95
Brooks Medium	35	25.78	18.29	19.42	21.41
Brooks Deep	35	25.85	17.61	19.80	18.19
Canmore Surface	35	17.16	8.45	14.07	14.38
Canmore Medium	35	26.72	20.80	18.75	22.86
Canmore Deep	35	28.50	22.97	18.94	21.35
Control	35	26.54	13.28	16.39	16.26
soil type	labile bound	labile bound	labile bound	labile bound	labile bound
Brooks Surface	0	0.03	0.00	0.50	1.43
Brooks Medium	0	4.35	0.10	0.00	4.98
Brooks Deep	0	5.58	0.00	9.98	2.72
Canmore Surface	0	6.84	0.68	2.07	0.00
Canmore Medium	0	4.84	0.24	3.50	0.00
Canmore Deep	0	6.27	0.70	0.00	0.15
Control	0	3.71	1.09	0.58	0.00
soil type					acetonitrile labile
Brooks Surface					1.67
Brooks Medium					6.06
Brooks Deep					3.89
Canmore Surface					1.47
Canmore Medium					0.38
Canmore Deep					0.23
Control					0.00
soil type	non-labile bound	non-labile bound	non-labile bound	non-labile bound	non-labile bound
Brooks Surface	0	17.09	18.01	16.61	18.96
Brooks Medium	0	4.87	16.61	15.58	2.55
Brooks Deep	0	3.57	17.39	5.22	10.21
Canmore Surface	0	11.00	25.87	18.85	19.15
Canmore Medium	0	3.44	13.96	12.76	11.77
Canmore Deep	0	0.22	11.33	16.06	13.27
Control	0	4.75	20.63	18.03	18.74

Table 3.1.2 pH Values for Slurry with Addition of PCP				
Soil	pH before	pH after	pH change	
Brooks Surface	7.6	7.4	0.2	
Brooks Medium	8.0	7.4	0.6	
Brooks Deep	8.2	7.6	0.6	
Canmore Surface	7.3	7.0	0.3	
Canmore Medium	7.9	7.3	0.6	
Canmore Deep	7.7	7.4	0.3	
Water	6.0	5.5	0.5	
Average value	7.5	7.1	0.4	

Figure 3.1.1 PCP EXPERIMENT 3 Comparison of PCP levels in the aqueous phase

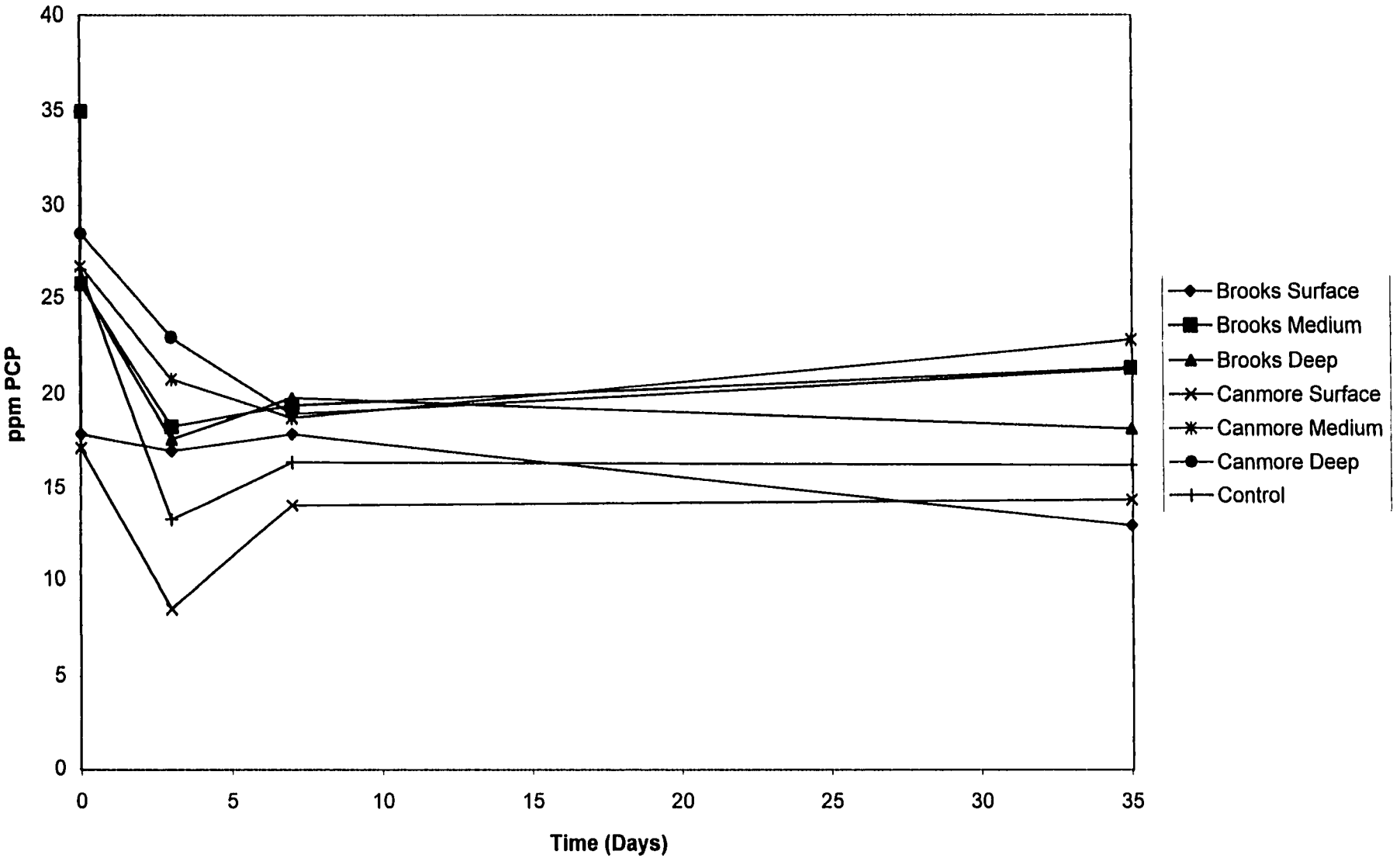


Figure 3.1.2 PCP EXPERIMENT 3 Comparison of PCP labile in methanol

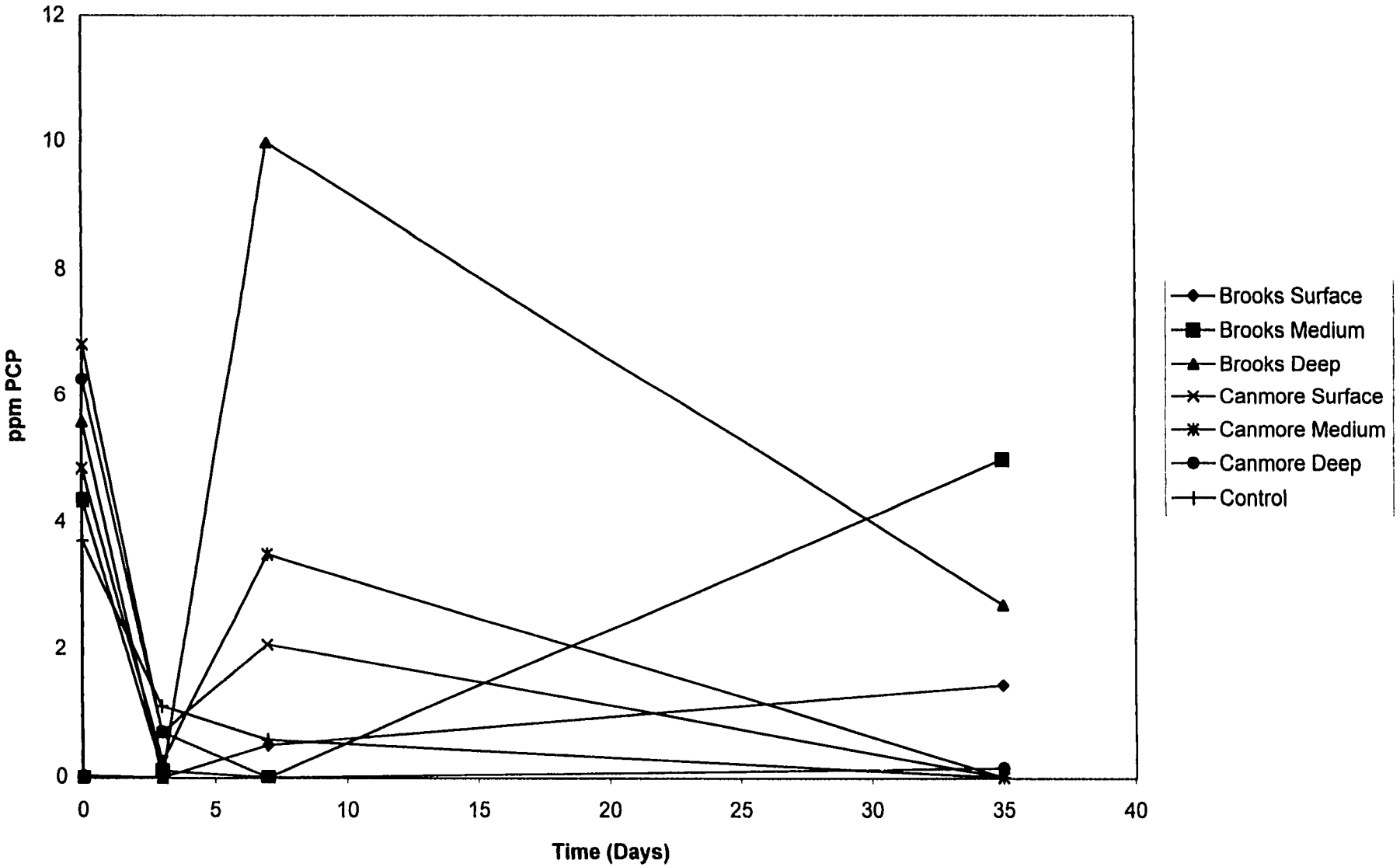
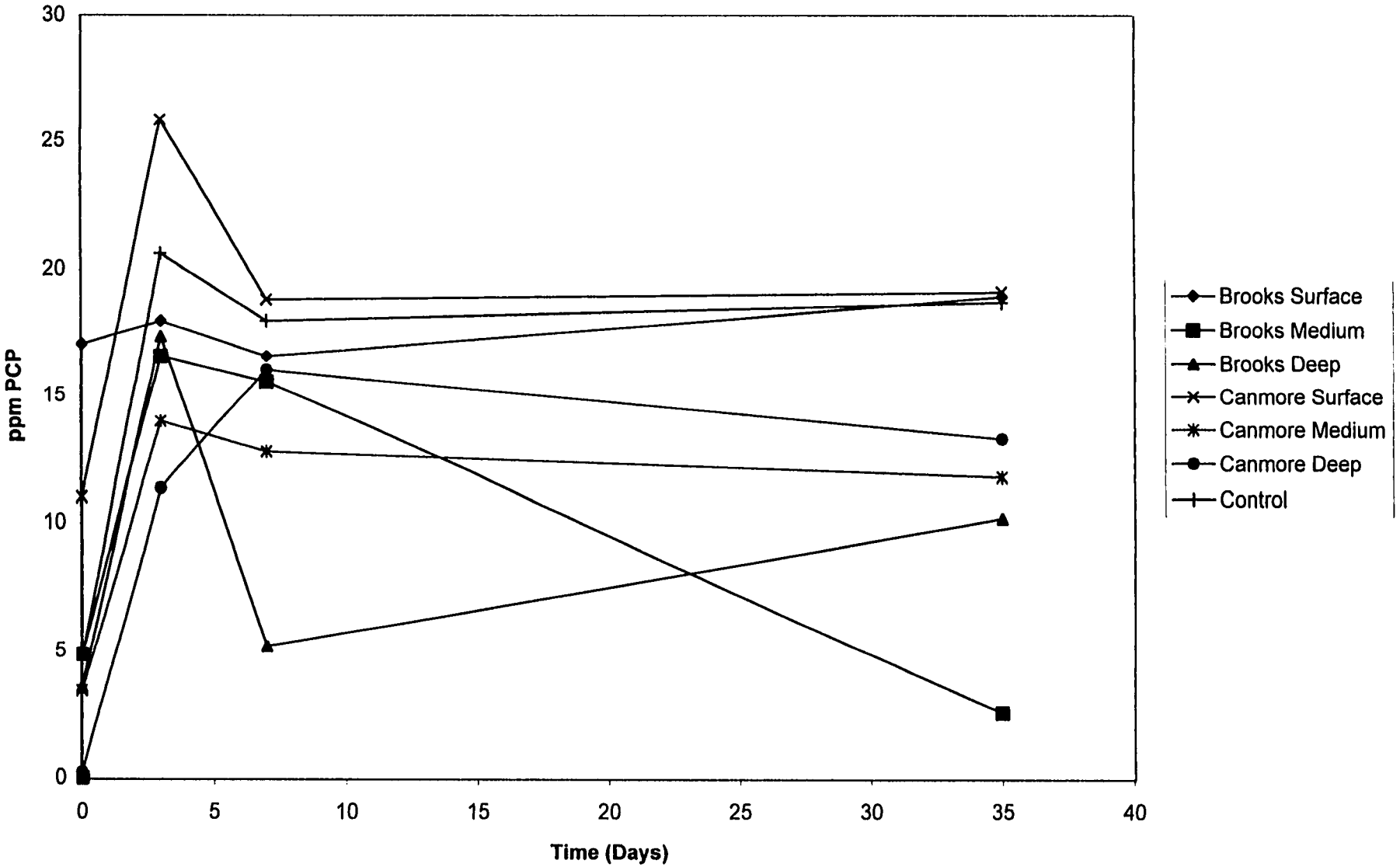


Figure 3.1.3 PCP EXPERIMENT 3 Comparison of PCP nonlabile to water or methanol



Several attempts were made to improve the chromatograms using varying ratios of acetonitrile and water and a variety of flow rates. Eventually it was realised that the problem was loss of endcapping of the silanols (-SiOH) on the HPLC column. Adding 10-mM triethylamine to the eluent solved this problem and a new trial began.

During the second trial, using an initial PCP concentration of 500 ppm, it was realised that the PCP concentration as recorded by the HPLC was a function of the volume of solution used to wash the slurry. In fact the syringe filters, originally nylon (110, 111), were retaining the PCP. After testing a variety of syringe filters the Millipore Millex-FH_{13}, a Fluoropore® membrane, was found to be inert to PCP. The other syringe filter membranes tested included nylon 66, nylon MA, cellulose acetate and PTFE.

The method for studying PCP sorption used in the third trial, and given in detail in Section 3.1.2, appears to give results similar to others reported in the literature (6), using different methods, and is thus felt to be acceptable. A direct comparison of the sorption of PCP using the modified method and the Gamble MF-HPLC method was not possible, due to lack of equipment. However, a comparison of results obtained for atrazine (43,110,112) and 2,4-dichlorophenoxyacetic acid (129), using the Gamble method, with the results obtained in the present work for PCP, do show great similarities in trends. Unfortunately none of the literature goes beyond 14 days, so it is not possible to see if other compounds have the same kinetics as PCP over the long-term.

The set of data points for the acetonitrile rinse on Day 35 appear to indicate that acetonitrile may be a better extracting solution for PCP than is methanol since the values are higher than the corresponding values for methanol. (See Table 3.1.1) This would require further investigation, as there is only one set of data thus far.

Minor peaks that were seen occasionally might have been TCDD. (The retention time for TCDD is 4.3 min. as compared to 9.6 min. for PCP.) However, there was no consistent pattern to these peaks and so it was assumed that degradation, if indeed that is what was occurring, was not occurring at any measurable levels.

A thorough discussion of the actual results, rather than the validity of the method are given in Section 4.

3.2 CHROMATED COPPER ARSENATE

3.2.1 Introduction

The method used for the CCA analyses was adapted from the PCP method, which was in turn adapted from the method of Langford and Gamble (110, 111). Microfiltration was done the same way as with PCP but using an extracting solution more suited to metal ions. The Inductively Coupled Plasma spectrophotometer (ICP) is an instrument and technique particularly well adapted to the study of multiple metal ions and was used to replace the High Performance Liquid Chromatography (as well as the UV/Vis detector) (99). Although hydride

generation has been found to be a sensitive technique for study of As (115, 123, 124, 126, 127), it was thought preferable to treat all three elements identically. As with PCP, the filtrate from the soil-water slurry plus a water rinse of equal volume gave rise to the aqueous phase data and two equivalent aliquots of an appropriate extracting solution (4M nitric acid) gave rise to the labile uptake values. Nonlabile uptake was again determined by subtracting these two values from the original slurry concentration of each of the metal ions.

The CCA stock solution used during this experiment was made in the lab as detailed below (section 3.2.2). A commercial preparation was not used because it contained unknown patented ingredients. It was felt that for a preliminary study a more simple solution containing known compounds was preferable.

3.2.2 Experiment

Five-gram soil samples were weighed into 250 mL Erlenmeyer flasks using a Mettler analytical balance. Six samples of each of six soils were prepared, three to have CCA stock solution[12] added and three to act as blanks. There were also six vials, containing no soil, prepared as a method control, three to have CCA added and three to act as control blanks. 200 mL of distilled water and a magnetic stir bar were added to each flask. The flask was then sealed with a rubber stopper and placed on a magnetic stirrer (a wide variety was used). The

[12]The CCA stock solution was made, using a recipe (83), by mixing together 1.28 g CuO, 1.35 g As_2O_3 and 1.99 g CrO_3. To this dry mixture was added 10 mL concentrated HNO_3. This was heated as water was gradually added. After cooling the solution was poured into a 500 mL volumetric flask and made up to the mark with water.

vials were stirred for 48 hours, to allow the soil to wet. It was found that room temperature stayed a fairly constant 22–23°C, which was considered acceptable. After 48 hours a one millilitre aliquot of CCA stock solution was added, using a Corex 7100-A one millilitre volumetric pipette, giving a final solution concentration of 10 ppm Cr and Cu, and 8 ppm As. The pH of the soil slurry was determined before and after adding the CCA stock solution.

Immediately after mixing, the first 3 mL aliquot was removed using a disposable Tuberculin BD 5 cc syringe. The slurry was filtered through a 25 mm diameter, 0.45 μm pore size, nylon syringe filter (Chromatographic Specialities). After removing the plunger, 3 mL of distilled water was added to the syringe barrel and pushed through the filter. The two filtrates added together became Sample A and were stored in a Pyrex culture tube (10 mL volume), as were all other samples. The soil trapped on the filter was rinsed twice with 3 mL of 4M nitric acid. The two nitric acid wash filtrates combined to give sample B.

The metal ion concentrations were checked using a Thermo Jarrell Ash Atom Scan 16 ICP controlled by Thermospec software. The ICP parameters were torch gas flow – high; auxiliary gas flow – 1.0L/min; flush pump rate – 200rpm; analysis pump rate –100 rpm; nebulizer pressure – 30 psi. Each element was analysed at three wavelengths. In each case the central line was a maximum. For arsenic the central wavelength was 189.0 nm, chromium was 267.7 nm and copper was 324.7 nm. The ICP was calibrated at the beginning of every session using a 10 ppm standard solution for each element and a blank (DI water). The instrument was recalibrated every two hours during the session as a standard

method. There was no evidence of drift at any time. An one/one-hundredth dilution of the CCA stock solution was run each day to compare between days. Again, there was no noticeable drift of values (correlation between days > 0.98). Atomic Absorption standards for Cu, Cr and As (Sigma) were used to make standards. The soils used have been discussed previously.

3.2.3 Results

The CCA experiment was repeated three times. Data obtained from the first experiment are not shown because the levels of copper, chromium and arsenic used were below the detection limits of the ICP once the sorption process had begun. Experiment 2 lacked the labile uptake determination and Experiment 3 was carried out as shown in Section 3.2.2. While Experiment 2 contained only data for the aqueous phase (see Table 3.2.1), this data together with that from Experiment 3 (see Tables 3.2.3-3.2.5) was tabulated and converted into a variety of graphs.

The pH values of the slurry are given in Table 3.2.2, which shows the pH values before and after the addition of CCA. The results do not show any clear trends other than to show that the soil acts almost like a buffer in reducing the effect of the addition of the CCA on the pH. There is a noticeable drop in the pH of the water control (~4.7 pH units) but the slurries themselves drop by less than one pH unit.

To assess these results with respect to the method, the reproducibility of the sorption trends from the aqueous phase were compared for Experiment 2

TABLE 3.2.1 RESULTS FROM CCA EXPERIMENT 2

Values for Arsenic (ppm/gram of soil)

Days	Brooks Surface	Brooks Medium	Brooks Deep	Canmore Surface	Canmore Medium	Canmore Deep	Control	Water
0	30	30	30	30	30	30	30	0.021
1	17.15	19.4	22.3	13.1	14.48	16.95	28.6	0.008
2	15.48	15.73	17.4	10.8	13.85	16.08	29.18	0.02
7	13.85	14.34	16.2	7.19	11.61	13.97	28.51	0.028
23	12.14	12.46	14.2	4.13	9.058	11.19	27.44	0.005
79	11.35	12.17	14.4	3.67	4.99	7.52	17.15	0.911

Values for Chromium (ppm/gram of soil)

Days	Brooks Surface	Brooks Medium	Brooks Deep	Canmore Surface	Canmore Medium	Canmore Deep	Control	Water
0	35	35	35	35	35	35	35	0.004
1	17.16	18.32	17.6	7.52	15.96	15.95	33.73	0.013
2	16.7	17.83	17.2	6.08	15.51	16.19	34.65	0.013
7	16.05	17.43	16.9	3.22	14.58	14.53	32.43	0.138
23	16.6	17.22	17.1	0.53	12.09	5.308	9.104	0.014
79	19.46	18.31	17.3	0.19	5.308	9.105	21.44	1.314

Values for Copper (ppm/gram of soil)

Days	Brooks Surface	Brooks Medium	Brooks Deep	Canmore Surface	Canmore Medium	Canmore Deep	Control	Water
0	30	30	30	30	30	30	30	0.03957
1	1.84357	0.56007	0.0561	0.1645	0.07983	0.06913	30.5994	0.0157
2	0.44447	0.06383	0.0255	0.0985	0.05177	0.03663	30.4428	0.01473
7	0.35633	0.15747	0.0491	0.1151	0.0846	0.0787	32.0294	0.02633
23	0.09333	0.04424	0.0224	0.0545	0.018	0.02027	21.7961	0.01023
79	0.0743	0.01433	0.0169	0.0611	0.0079	0.02567	23.5894	0.91787

Table 3.2.2

pH Values for Slurry with Addition of CCA

Soil	pH before	pH after	pH change
Brooks Surface	7.6	6.9	0.7
Brooks Medium	8.0	7.2	0.8
Brooks Deep	8.1	8.3	-0.2
Canmore Surface	7.5	7.6	-0.1
Canmore Medium	7.9	7.5	0.3
Canmore Deep	8.1	7.5	0.6
Water	7.5	2.8	4.7
Average value	7.8	6.8	1.0

TABLE 3.2.3 RESULTS FROM CCA EXPERIMENT 3										
ARSENIC - Final Sorbtion values										
Water wash - aqueous phase										
SOIL TYPE \ DAY	0	2	4	7	21	28	50	77	91	114
BS aqueous	1.567	1.126	1.122	1.054	0.995	1.012	0.941	0.949	0.986	1.052
BM aqueous	1.037	0.347	0.646	0.574	0.588	0.584	0.521	0.526	0.497	0.639
BD aqueous	1.292	0.661	0.582	0.592	0.586	0.517	0.254	0.289	0.301	0.286
CS aqueous	1.334	0.391	0.342	0.327	0.325	0.131	0.135	0.072	0.071	0.067
CM aqueous	1.682	1.098	1.047	0.913	0.647	0.605	0.570	0.673	0.550	0.666
CD aqueous	1.900	1.079	1.022	1.008	1.008	0.906	0.871	1.021	0.959	1.054
Water wash control	9.538	9.527	9.865	9.515	7.491	9.646	9.673	12.773	13.195	10.507
Nitric acid wash - labile bound phase										
BS labile bound	0.175	0.316	0.368	0.402	0.374	0.364	0.387	0.387	0.363	0.416
BM labile bound	0.113	0.114	0.182	0.246	0.289	0.263	0.244	0.290	0.255	0.322
BD labile bound	0.308	0.538	0.528	0.504	0.522	0.226	0.112	0.120	0.101	0.113
CS labile bound	0.424	0.925	0.976	0.976	0.991	0.739	0.729	0.394	0.353	0.338
CM labile bound	0.176	0.409	0.463	0.508	0.405	0.402	0.387	0.446	0.388	0.381
CD labile bound	0.168	0.443	0.542	0.550	0.585	0.700	0.627	0.832	0.752	0.770
Nitric acid wash control	0.035	0.033	0.032	0.034	0.505	0.036	0.052	0.145	0.040	0.059
Non-labile (or ion unaccounted for to achieve mass balance)										
SOIL TYPE \ DAY	0	2	4	7	21	28	50	77	91	114
Brooks-surface	0.000	0.220	0.172	0.206	0.293	0.286	0.334	0.327	0.313	0.194
Brooks-medium	0.484	1.174	0.807	0.814	0.758	0.788	0.870	0.819	0.883	0.673
Brooks-deep	0.000	0.337	0.426	0.439	0.428	0.792	1.169	1.126	1.134	1.136
Canmore-surface	0.000	0.337	0.335	0.349	0.336	0.782	0.788	1.186	1.229	1.248
Canmore-medium	0.000	0.111	0.108	0.198	0.566	0.611	0.661	0.500	0.681	0.572
Canmore-deep	0.000	0.106	0.065	0.070	0.036	0.022	0.131	0.000	0.000	0.000
Water	0.000	0.000	0.000	0.000	0.384	0.000	0.000	0.000	0.000	0.000
Initial amount added	8.380	8.380	8.380	8.380	8.380	8.380	8.380	8.380	8.380	8.380

TABLE 3.2.4 RESULTS of CCA EXPERIMENT 3										
CHROMIUM - Final Sorption Values										
Water wash - aqueous phase										
SOIL TYPE \ DAY	0	2	4	7	21	28	50	77	91	114
BS aqueous	1.177	1.246	1.419	1.334	1.232	1.169	1.120	1.184	1.232	1.472
BM aqueous	0.788	0.463	0.928	0.825	0.755	0.850	0.767	0.743	0.738	1.033
BD aqueous	0.861	0.875	0.851	0.862	0.742	0.764	0.353	0.365	0.493	0.403
CS aqueous	0.752	0.260	0.175	0.134	0.028	0.003	0.003	0.000	0.001	0.001
CM aqueous	1.334	1.171	1.141	1.028	0.647	0.637	0.540	0.580	0.517	0.694
CD aqueous	1.528	1.092	1.076	1.053	0.972	0.946	0.837	0.891	0.929	1.053
Water wash control	11.547	11.516	12.102	11.768	7.447	11.510	11.523	13.315	15.816	12.821
Nitric acid wash - labile bound phase										
BS labile bound	0.739	0.561	0.573	0.606	0.480	0.503	0.495	0.496	0.467	0.502
BM labile bound	0.502	0.196	0.334	0.371	0.359	0.334	0.302	0.325	0.302	0.369
BD labile bound	0.957	0.732	0.692	0.670	0.599	0.309	0.160	0.148	0.140	0.158
CS labile bound	1.054	0.815	0.883	0.840	0.777	0.631	0.594	0.276	0.280	0.266
CM labile bound	0.656	0.543	0.570	0.566	0.379	0.400	0.382	0.363	0.366	0.374
CD labile bound	0.747	0.566	0.637	0.604	0.572	0.673	0.574	0.693	0.698	0.726
Nitric acid wash control	0.145	0.238	0.198	0.198	0.940	0.206	0.183	0.000	0.289	0.224
Non-labile (or ion unaccounted for to achieve mass balance)										
SOIL TYPE \ DAY	0	2	4	7	21	28	50	77	91	114
Brooks-surface	0.082	0.191	0.006	0.058	0.286	0.325	0.383	0.318	0.299	0.024
Brooks-medium	0.674	1.306	0.703	0.769	0.850	0.781	0.895	0.897	0.924	0.562
Brooks-deep	0.027	0.238	0.302	0.313	0.504	0.772	1.331	1.332	1.212	1.284
Canmore-surface	0.180	0.911	0.928	1.011	1.180	1.351	1.388	1.710	1.705	1.718
Canmore-medium	0.000	0.231	0.234	0.350	0.919	0.907	1.023	1.002	1.062	0.876
Canmore-deep	0.000	0.299	0.244	0.300	0.414	0.338	0.546	0.374	0.330	0.178
Water	0.000	0.000	0.000	0.000	1.683	0.000	0.000	0.000	0.000	0.000
Initial amount added	10.07	10.07	10.07	10.07	10.07	10.07	10.07	10.07	10.07	10.07

TABLE 3.2.5 RESULTS of CCA EXPERIMENT 3										
COPPER - Final Sorption Values										
Water wash - aqueous phase										
SOIL TYPE \ DAY	0	2	4	7	21	28	50	77	91	114
BS aqueous	0.000	0.023	0.005	0.000	0.000	0.004	0.000	0.004	0.000	0.006
BM aqueous	0.006	0.000	0.004	0.003	0.002	0.001	0.001	0.000	0.002	0.004
BD aqueous	0.004	0.005	0.004	0.004	0.004	0.000	0.000	0.000	0.000	0.000
CS aqueous	0.039	0.005	0.013	0.009	0.008	0.005	0.003	0.000	0.001	0.003
CM aqueous	0.014	0.006	0.005	0.000	0.002	0.001	0.001	0.002	0.000	0.003
CD aqueous	0.025	0.003	0.003	0.003	0.003	0.004	0.007	0.006	0.002	0.004
Water wash control	11.210	11.084	11.531	11.178	8.880	11.087	10.863	10.797	11.575	12.411
Nitric acid wash - labile bound phase										
BS labile bound	1.662	1.503	1.598	1.776	1.376	1.157	1.162	1.106	0.817	1.377
BM labile bound	1.120	0.540	0.867	0.993	0.914	0.909	0.812	0.799	0.673	1.109
BD labile bound	1.405	1.273	1.272	1.171	0.607	0.000	0.000	0.000	0.000	0.000
CS labile bound	1.709	1.477	1.535	1.568	1.391	0.999	0.955	0.347	0.359	0.455
CM labile bound	1.568	1.473	1.483	1.579	0.972	0.975	0.936	0.710	0.728	0.992
CD labile bound	1.794	1.490	1.617	1.548	1.307	1.537	1.352	1.254	1.278	1.807
Nitric acid wash control	0.090	0.174	0.011	0.045	0.227	0.060	0.187	0.000	0.109	0.125
Non-labile (or ion unaccounted for to achieve mass balance)										
SOIL TYPE \ DAY	0	2	4	7	21	28	50	77	91	114
Brooks-surface	0.336	0.459	0.384	0.211	0.613	0.824	0.828	0.876	1.169	0.603
Brooks-medium	0.826	1.413	1.081	0.957	1.036	1.043	1.140	1.153	1.277	0.840
Brooks-deep	0.425	0.556	0.558	0.659	1.222	2.028	2.333	2.201	2.083	2.418
Canmore-surface	0.226	0.491	0.426	0.397	0.576	0.970	1.016	1.629	1.613	1.516
Canmore-medium	0.351	0.454	0.446	0.356	0.959	0.957	0.997	1.222	1.206	0.938
Canmore-deep	0.126	0.452	0.326	0.394	0.636	0.405	0.587	0.685	0.666	0.135
Water	0.000	0.000	0.000	0.000	0.903	0.000	0.000	0.000	0.000	0.000
Initial amount added	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01	10.01

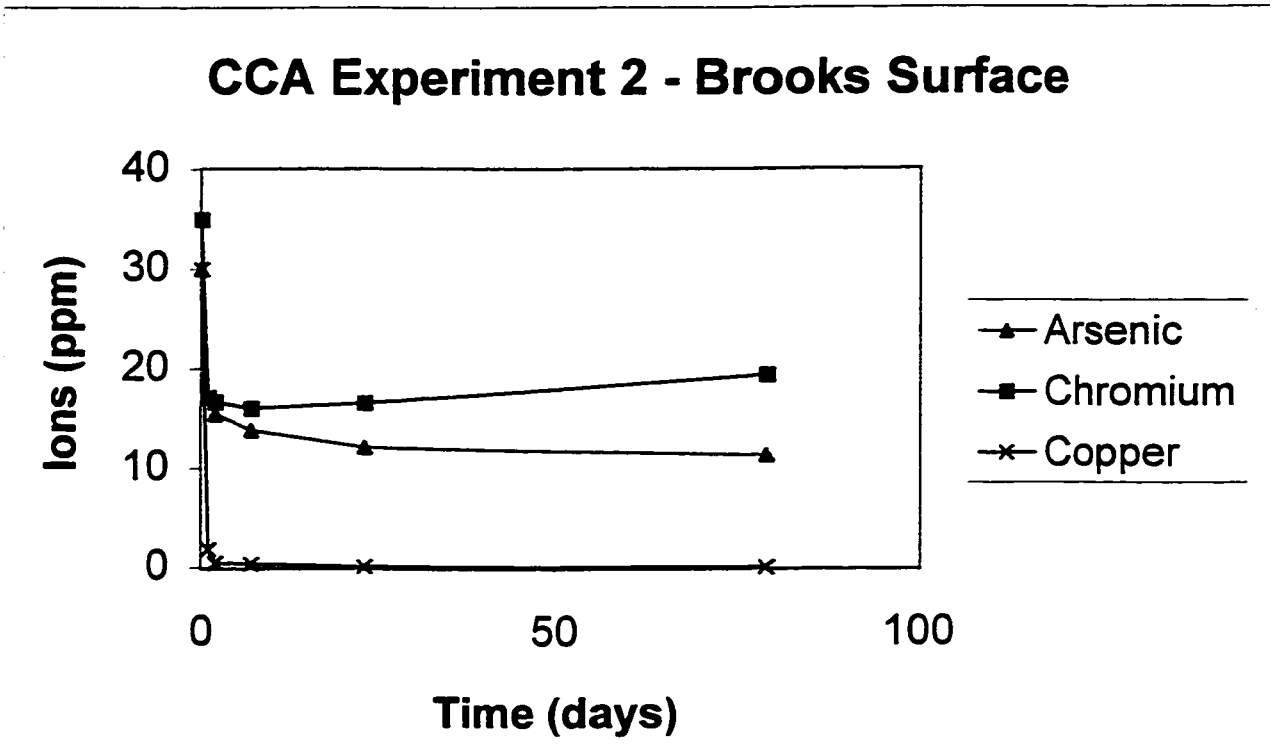
and 3. It was found that for each of the six soils, the order of preference for sorption of the metal ion, as shown by its decreasing concentration in the aqueous phase, was the same in both experiments. (See Figure 3.2.1 for two examples of these graphs or Appendix C (Figure C.1-C.12) for the complete set of aqueous phase graphs.) This result, despite quite different initial concentrations, was considered an indication that the results were real and repeatable.

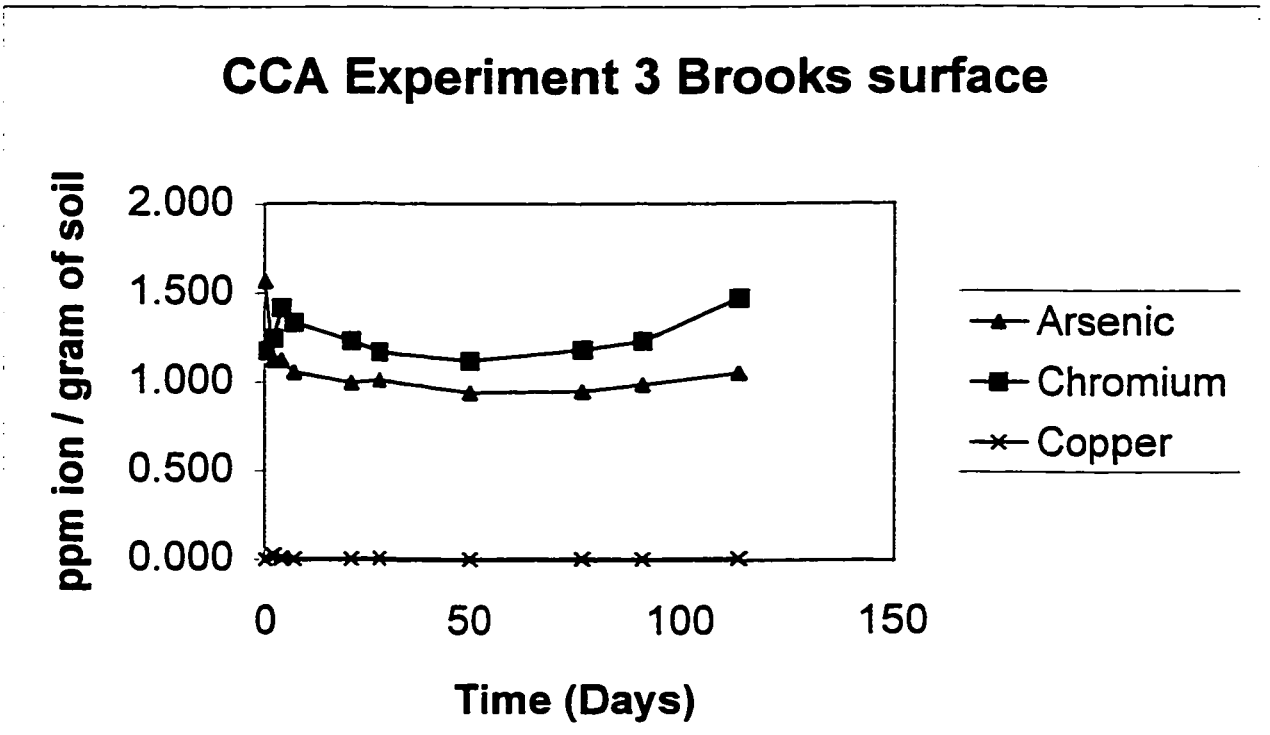
3.3 COPPER NAPHTHENATE

3.3.1 Introduction

The investigation of soil and water concentrations of copper naphthenate over time provided some unique challenges in that both a metal cation and an organic anion were involved. The method used for the CUNAP analyses was again adapted from the PCP method, which was in turn adapted from the method of Langford and Gamble (110,111). The microfiltration was done the same way as with PCP but using a different extracting solution. As with PCP and CCA the filtrate from the soil-water slurry plus a water rinse of equal volume gave rise to the aqueous phase data and two equivalent aliquots of an appropriate extracting solution gave rise to the labile uptake values. Nonlabile uptake was again determined by subtracting these two values from the original slurry concentration of each species. Concentrations of naphthenate were determined using SPME

Figure 3.2.1 Comparison of Metal Ion Levels in Aqueous Phase





in tandem with GC and concentrations of copper ion were subsequently determined using ICP.

The stock solution of copper naphthenate used in the kinetics experiment was actually a synthetic solution. Analysis (see section 3.3.2 and 3.3.3) showed commercial CUNAP to be a complex mixture of hydrocarbons containing only one naphthenic acid component. This component was synthesised in the lab to ensure the purity of the solution used in these preliminary kinetic studies. As with PCP and CCA it was felt that the complications arising from trace materials in the commercial products would diminish the capacity of the researchers to study the interaction of the active compounds with soil. Since naphthenic acids as a group are defined (section 1.3.3) as "the carboxylic acids derived from petroleum during refining" the term CUNAP was maintained for the copper 2-ethylhexanoate that was used as a model compound.

3.3.2 Experiment

Before beginning the kinetics experiment, samples of copper naphthenate wood preservative were obtained as a 2% copper solution in kerosene (Van Waters and Rogers) and a 2.35% copper solution in kerosene (Timber Specialties Ltd) and analysed by Dr. E.A.Dixon. Gas Chromatographic analysis of the intact wood preservative was performed using a Hewlett Packard 5890 GC with a DB5 (5% phenylmethylpolysiloxane) column (30 m x 0.552 mm, 1.5 μm Film). This was done isothermally (110°C) and the FID detector temperature was 280°C. Helium flow rate was 5mL/min. Next, the acid fraction was extracted

using sodium bicarbonate and ether. This provided sufficient material for analysis by GC-MS (column OV101, 12 m x 0.2 mm i.d.; injection temperature 250°C; detector temperature 280°C). A pure sample of 2-ethylhexanoic acid (Aldrich) was later run under identical conditions.

Copper 2-ethylhexanoate was prepared by reacting 2-ethylhexanoic acid with sodium hydroxide and copper (II) sulphate pentahydrate. Following filtration of the solid and purification, a 98% yield of the copper salt was obtained. The copper salt was heated in an oven of 80°C for one week, then analysed by ICP. The ICP parameters were torch gas flow – high; auxiliary gas flow – 1.0L/min; flush pump rate – 200rpm; analysis pump rate –100 rpm; nebulizer pressure – 30 psi. Three wavelengths were scanned with the central line being 324.7 nm (as in CCA). Calibration was done as with the CCA (section 3.2.2). Finally, a 250 ppm stock solution was prepared, by dissolving 62.5 milligrams of this salt in water to a volume of 250 mL, and labelled CUNAP.

One gram soil samples were weighed into 25x150 mm Pyrex culture screw cap tubes (Corning) using a Mettler analytical balance. Forty-five millilitres of distilled water was added to each test tube, which was then placed in a test tube rack on a Khan shaker (Eberbach). The test tubes were shaken for 48 hours to allow the soil to wet thoroughly. Room temperature was maintained at 22–23°C. After 48 hours CUNAP was added as 10 mL of a 250 ppm stock solution using a 10 mL Yankee Volumetric pipette. Immediately after mixing, the first one mL aliquot was removed using a disposable Tuberculin BD 1-cc syringe. The slurry was filtered through a 13 mm diameter, 0.45 μm pore size, nylon syringe filter

(Chromatographic Specialties). The soil trapped on the filter was then rinsed with two 0.5-mL aliquots of distilled water. The three filtrates added together became Sample A and were stored in a 4 mL clear screwtop vial with hole cap and PTFE/Silicon septum (Supelco), as were all other samples. The soil on the syringe filter was then rinsed with two 1 mL aliquots of 4M nitric acid to give sample B. Every third sample was rinsed instead with two 1 mL aliquots of 10% sodium bicarbonate solution, generating sample C.

When ready to be analysed the pH of the sample was adjusted to 1.6 and it was exposed to an 85 μm Polyacrylate coated SPME fibre (Supelco) for 15 min. with stirring. GC analyses to determine the concentration of naphthenate were performed using a Hewlett Packard 5890 GC with a DB5 – 5% phenylmethylpoly-siloxane column (30 m x 0.552 mm, 1.5 μm Film). GC analysis was done isothermally (110°C). FID detector temperature was 280°C. Helium flow rate was 5mL/min. After finishing with the GC the samples were run on the ICP (torch gas flow – high; auxiliary gas flow – 1.0L/min; flush pump rate – 200rpm; analysis pump rate – 100 rpm; nebulizer pressure – 30 psi; wavelength 324.7 nm) to determine the copper concentration. The soils used have been discussed previously.

3.3.3 Results

Gas Chromatographic analysis of the intact commercial grade copper naphthenate revealed a complex mixture of hydrocarbons containing no carboxylic acids. Extraction of the acid fraction using sodium bicarbonate proved to be effective and sufficient material for analysis was obtained. GC-MS analysis

of the product indicated the presence of only one component. This was later identified as 2-ethylhexanoic acid by comparison with a pure sample of 2-ethylhexanoic acid. When the copper salt of 2-ethylhexanoic acid was prepared and heated it was shown that the salt crystallised with two molecules of water of crystallisation.

To facilitate analysis of the results, data obtained from this experiment were tabulated (see Table 3.3.1 & 3.3.2) and then converted into a variety of graphs. The graphs show comparisons of all six soils with respect to change of concentration of copper (Figure 3.3.1) and naphthenate (Figure 3.3.2) in the aqueous phase over time and change in Cu/naphthenate labile (Figure 3.3.3 & 3.3.4) and nonlabile (Figure 3.3.5 & 3.3.6) uptake over time. The aqueous, labile and nonlabile concentrations of copper and naphthenate were then shown for each soil. All of these graphs are found in Appendix D (see Figures D.1-D.12).

Since SPME was such a new technique when first employed in this experiment it was thought important to assess its usefulness. In assessing the aqueous phase naphthenate results it was noticed that out of 88 filtrate samples, 46 of them gave a reading of 0 ppm using the SPME-GC method[13]. Since a standard sample was run after every zero reading to establish that the SPME

[13] The blanks were not included in this count because they should be zero. That is, the blanks were not expected to have a peak for naphthenate and thus a reading of zero could not be counted as correct or incorrect.

TABLE 3.3.1 Values of copper from Copper Naphthenate					
aqueous	0	3	7	21	35
Brooks Surface	7.7692	6.0400	2.0949	0.7611	0.4220
Brooks Medium	6.2143	4.1160	1.3064	0.7319	0.3707
Brooks Deep	0.9665	0.1290	0.0000	0.0233	0.0178
Canmore Surface	1.0333	0.2573	0.0638	0.0232	0.0359
Canmore Medium	1.2607	0.1940	0.0347	0.0161	0.0348
Canmore Deep	2.1614	0.2863	0.0419	0.0218	0.0405
Control	5.1130	4.4150	5.2020	5.3840	6.4540
labile					
Brooks Surface	0.3775	0.8757	0.6557	2.8410	
Brooks Medium	0.5776	1.4229	2.7710	2.5470	
Brooks Deep	1.7248	2.2032	0.1338	1.9523	
Canmore Surface	1.7475	1.6416	1.8975	1.2743	
Canmore Medium	1.7489	2.1247	1.5042	1.4714	
Canmore Deep	1.4611	2.0464	1.7533	1.4134	
Control	0.0650	0.1490	0.2882		
nonlabile					
Brooks Surface	0.0000	1.1243	5.2894	4.4379	
Brooks Medium	1.2481	2.5011	3.9626	4.7611	
Brooks Deep	5.3487	5.7078	7.9062	6.0644	
Canmore Surface	5.2592	6.1411	6.0787	6.7425	
Canmore Medium	5.0304	5.7213	6.5011	6.5525	
Canmore Deep	4.4175	5.7073	6.2448	6.6048	
Control	2.8620	3.4760	2.5498	2.6560	

TABLE 3.3.2 Values of Naphthenate from Copper Naphthenate					
aqueous	0	3	7	21	35
Brooks Surface	21.993	22.927	25.777	0.000	0.000
Brooks Medium	23.567	27.040	24.883	0.540	1.440
Brooks Deep	16.420	9.696	0.000	0.360	0.000
Canmore Surface	6.858	13.663	10.592	0.000	0.000
Canmore Medium	15.120	10.682	0.000	0.640	2.280
Canmore Deep	17.250	18.753	9.356	0.000	0.000
Control	15.160	13.510	12.455	14.660	17.040
labile					
Brooks Surface	0.000	7.070	0.000	1.660	0.490
Brooks Medium	7.570	7.390	2.390	1.550	1.300
Brooks Deep	0.000	1.490	0.000	1.690	1.500
Canmore Surface	0.000	1.760	0.000	1.120	6.980
Canmore Medium	0.000	1.220	0.000	1.010	0.000
Canmore Deep	3.180	2.580	1.690	0.620	11.690
Control	6.870	3.050	1.700	1.550	11.530
nonlabile					
Brooks Surface	15.4167	7.4133	11.6328	35.7500	36.9200
Brooks Medium	6.2733	2.9800	10.1374	35.3200	34.6700
Brooks Deep	20.9900	26.2243	37.4100	35.3600	35.9100
Canmore Surface	30.5517	21.9867	26.8184	36.2900	30.4300
Canmore Medium	22.2900	25.5083	37.4100	35.7600	35.1300
Canmore Deep	16.9800	16.0767	26.3639	36.7900	25.7200
Control	15.3800	20.8500	23.2547	21.2000	8.8400

Figure 3.3.1 CUNAP EXPERIMENT 1- Aqueous levels of Copper

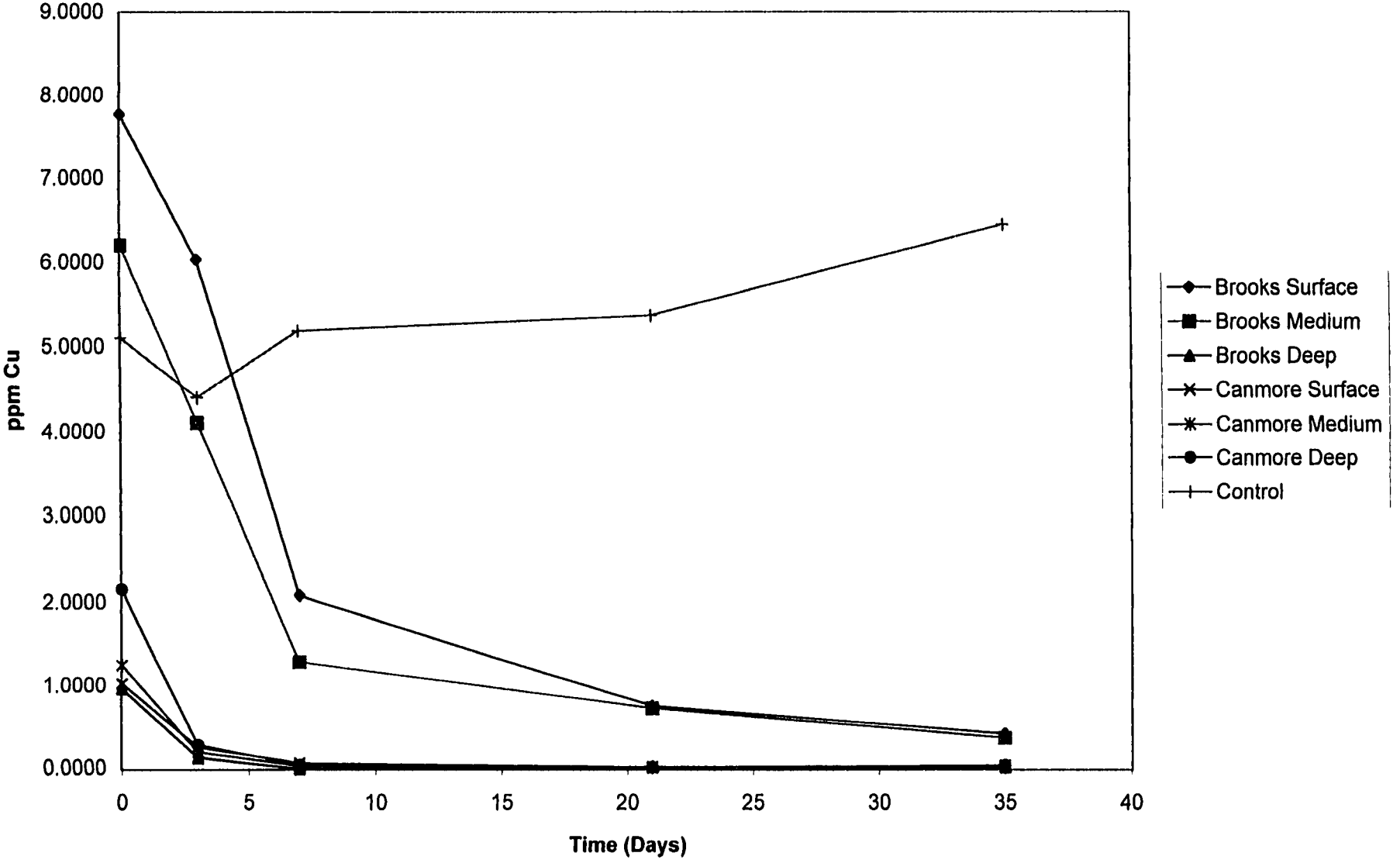


Figure 3.3.2 CUNAP EXPERIMENT 1 Aqueous levels of Naphthenate

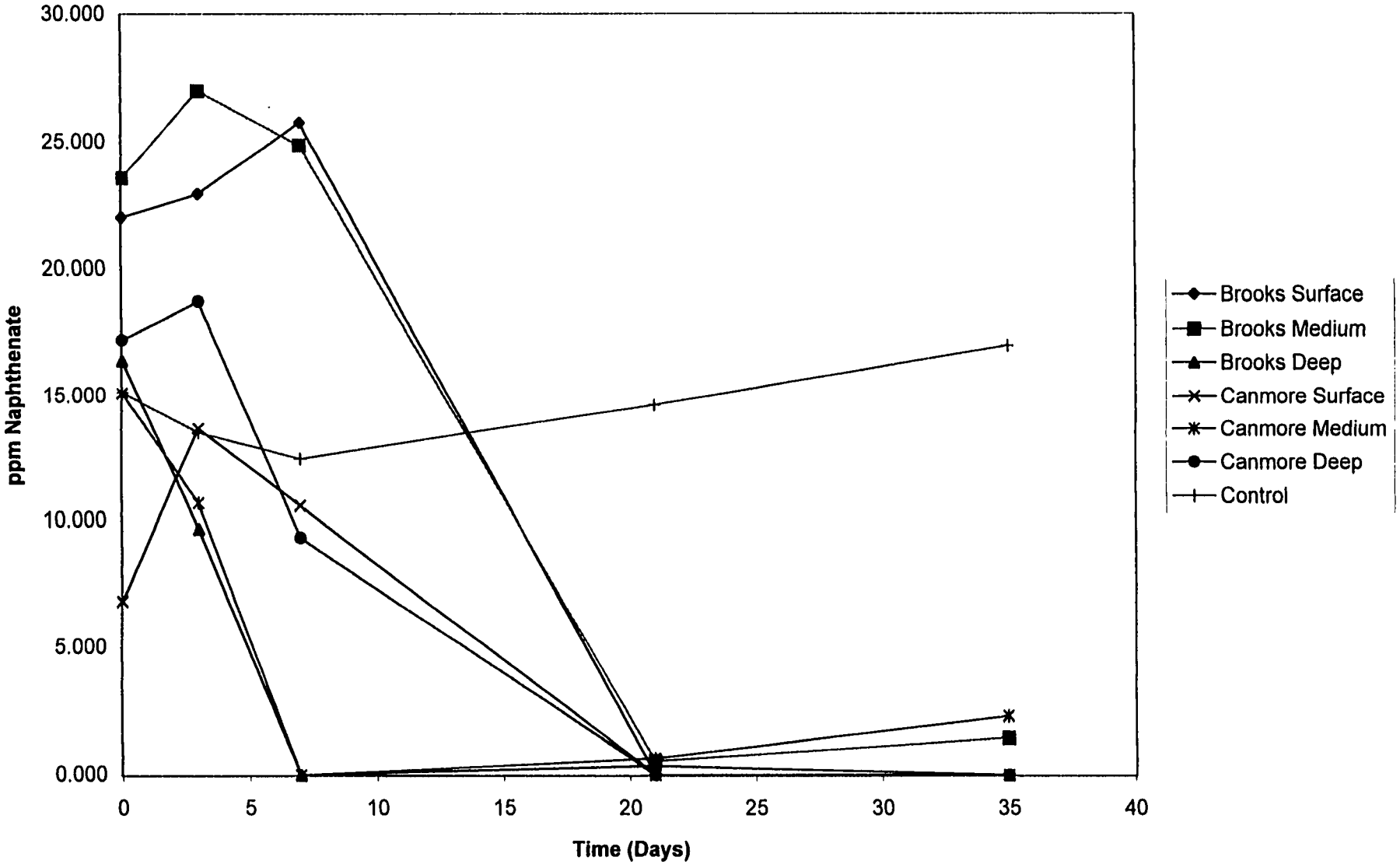


Figure 3.3.3 CUNAP EXPERIMENT 1 - Copper Labile in 4M Nitric Acid

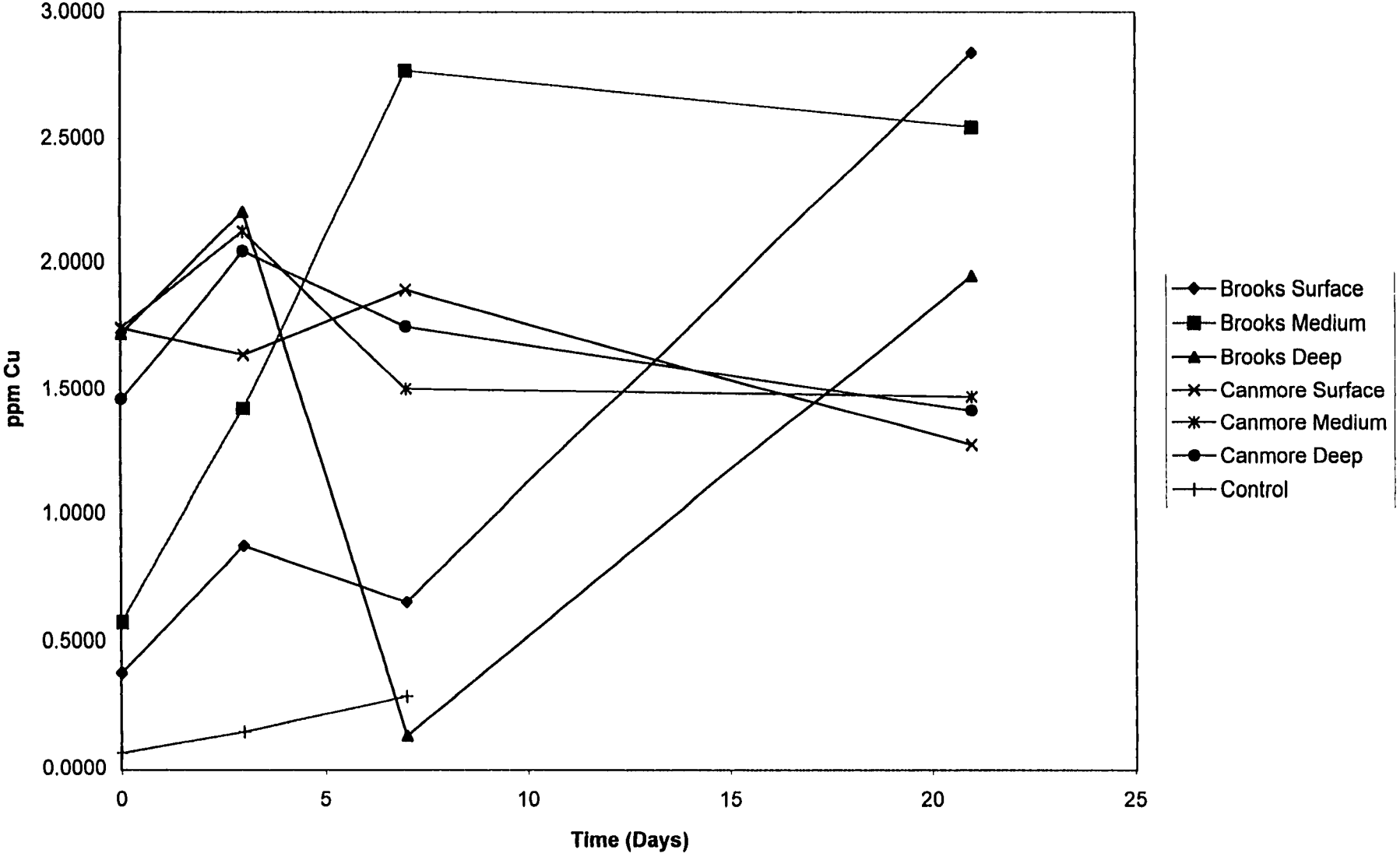


Figure 3.3.4 CUNAP EXPERIMENT 1 Naphthenate Labile in 4 M Nitric Acid

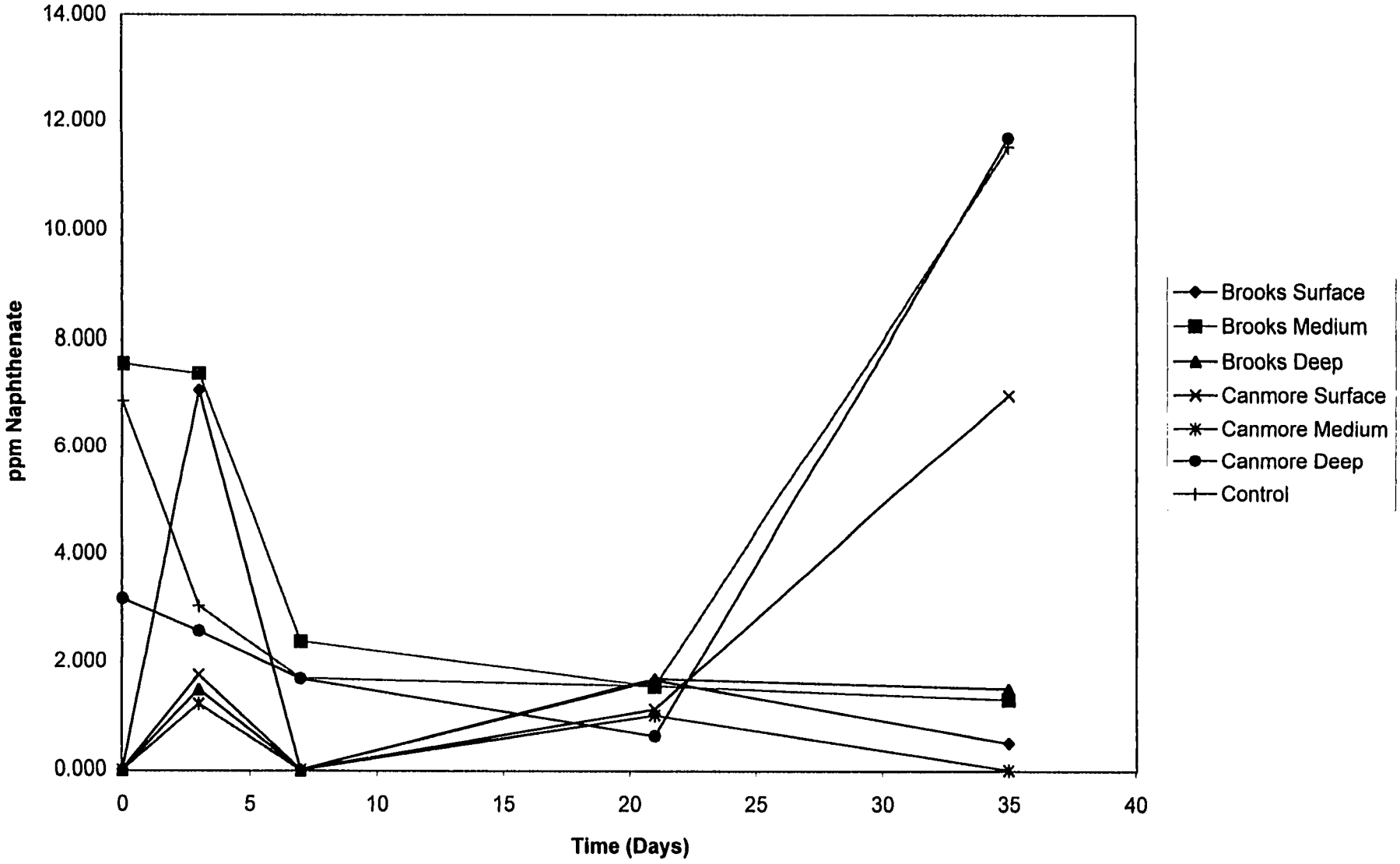


Figure 3.3.5 CUNAP EXPERIMENT 1 - Copper Nonlabile in water or 4 M nitric acid

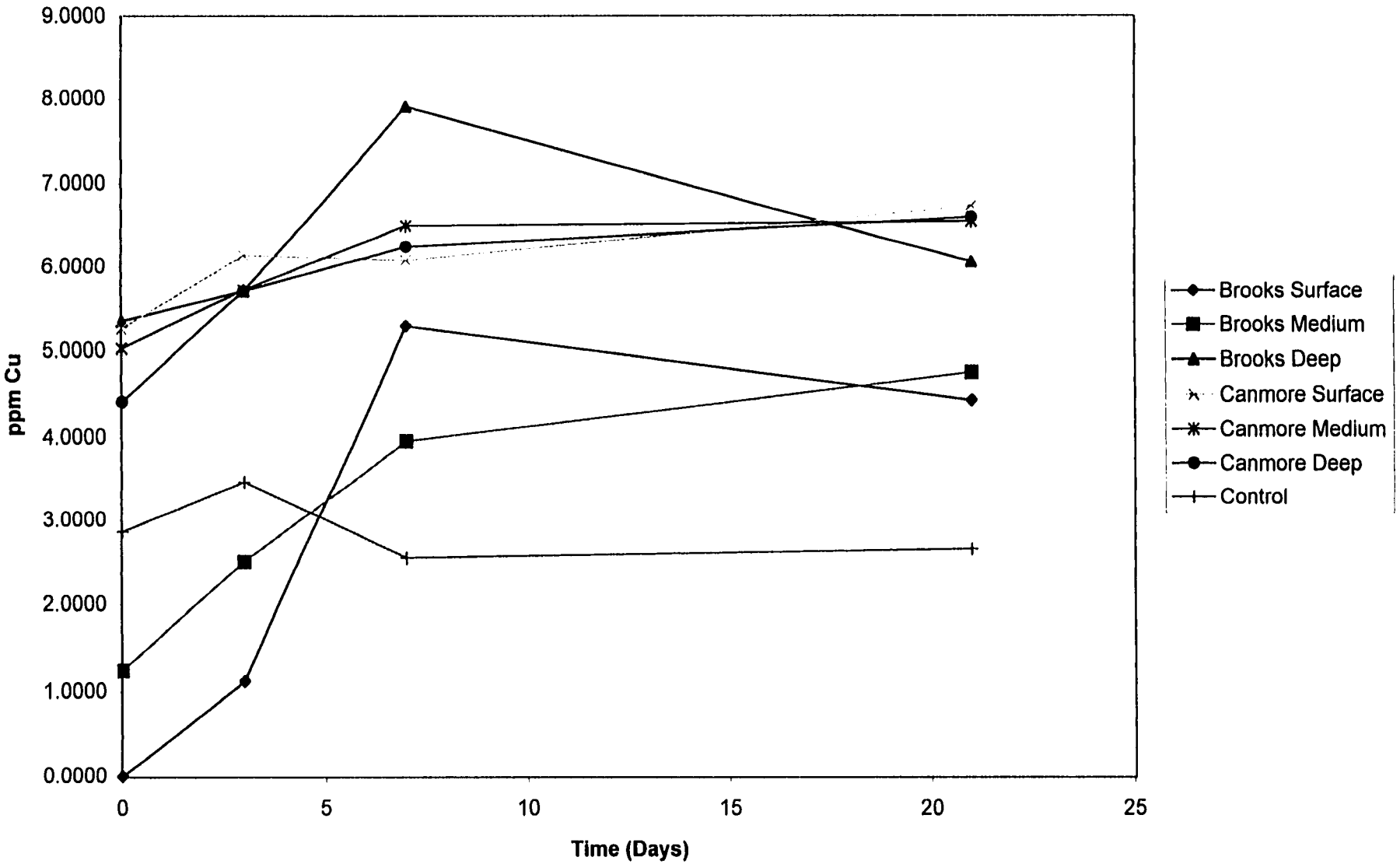
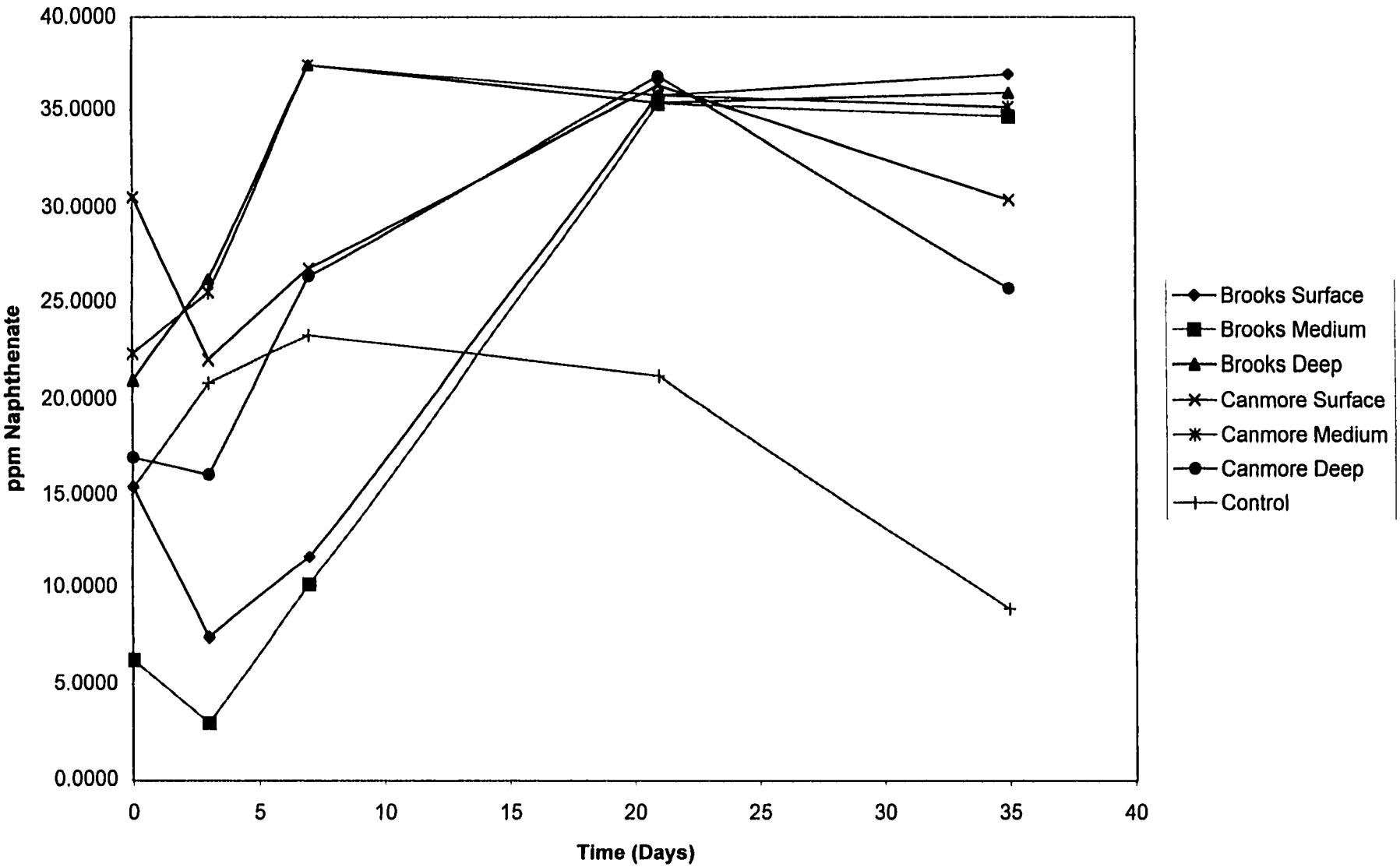


Figure 3.3.6 CUNAP EXPERIMENT 1 Naphthenate Nonlabile in Water or 4 M Nitric Acid



fibre was still functional, it appears that the problem was not the SPME. In many samples an extremely small peak appeared on the GC, at a longer retention time than expected for CUNAP. Since it also appeared on the chromatograms of the soil blanks (no CUNAP added), it was thought to be a function of some compound in the soil rather than a degradation product of the naphthenate. The labile extraction process went well with respect to copper but the naphthenate component was not as easy to extract. 4M Nitric acid, while a good way to extract copper, is less successful for naphthenate. Most of the GC chromatograms showed a significant peak at 3.4 min (the peak for the copper naphthenate standards and for the samples in the aqueous extraction came at 2.1 min.). It seems possible this may indicate the formation of an anhydride but further studies would be needed to test this hypothesis.

4 DISCUSSION

One aim of this study was to examine the interaction of the three major wood preservatives in use in Canada today, with soil. Creosote was not studied because its use is being phased out. A comparison of the other three preservatives, Pentachlorophenol, Chromated Copper Arsenate and Copper Naphthenate and their interactions with soil showed several interesting trends.

It is clear that all three compounds show the expected two stage uptake from the aqueous phase into soil – that is, an initial rapid uptake occurring within the first 7-21 days, followed by a slower more continuous uptake over the remaining time period. (See Figures 3.1.1,3.3.1,3.3.2,4.1.1-4.1.6) This is consistent with a model of rapid sorption of compounds to the surface layers of particles followed by a slower sorption process with diffusion to the interior soil spaces being the rate-limiting process. The surface sorbed state would correspond to the labile fraction (Figure 3.1.2, 3.3.3, 3.3.4, 4.1.7-4.1.9), which gradually approaches equilibrium, while the intraparticle or interior sorbed state would correspond to the nonlabile fraction (Figure 3.1.3, 3.3.5, 3.3.6, 4.1.10-4.1.12), which was continually increasing with time.

The initial fast sorption process was within the time parameters noted for some compounds (19) but unlike reports in the literature (10,48,49) of equilibrium attained in less than 30 days, the majority of the systems did not reach equilibrium within the time period of the study. If equilibrium, at least at the solution/solid interface, is measured by the concentration of compound present in solution reaching a steady state then only the Canmore Surface with PCP, As

Figure 4.1.1 CCA Experiment 2 - Summary of Aqueous Phase Arsenic Levels

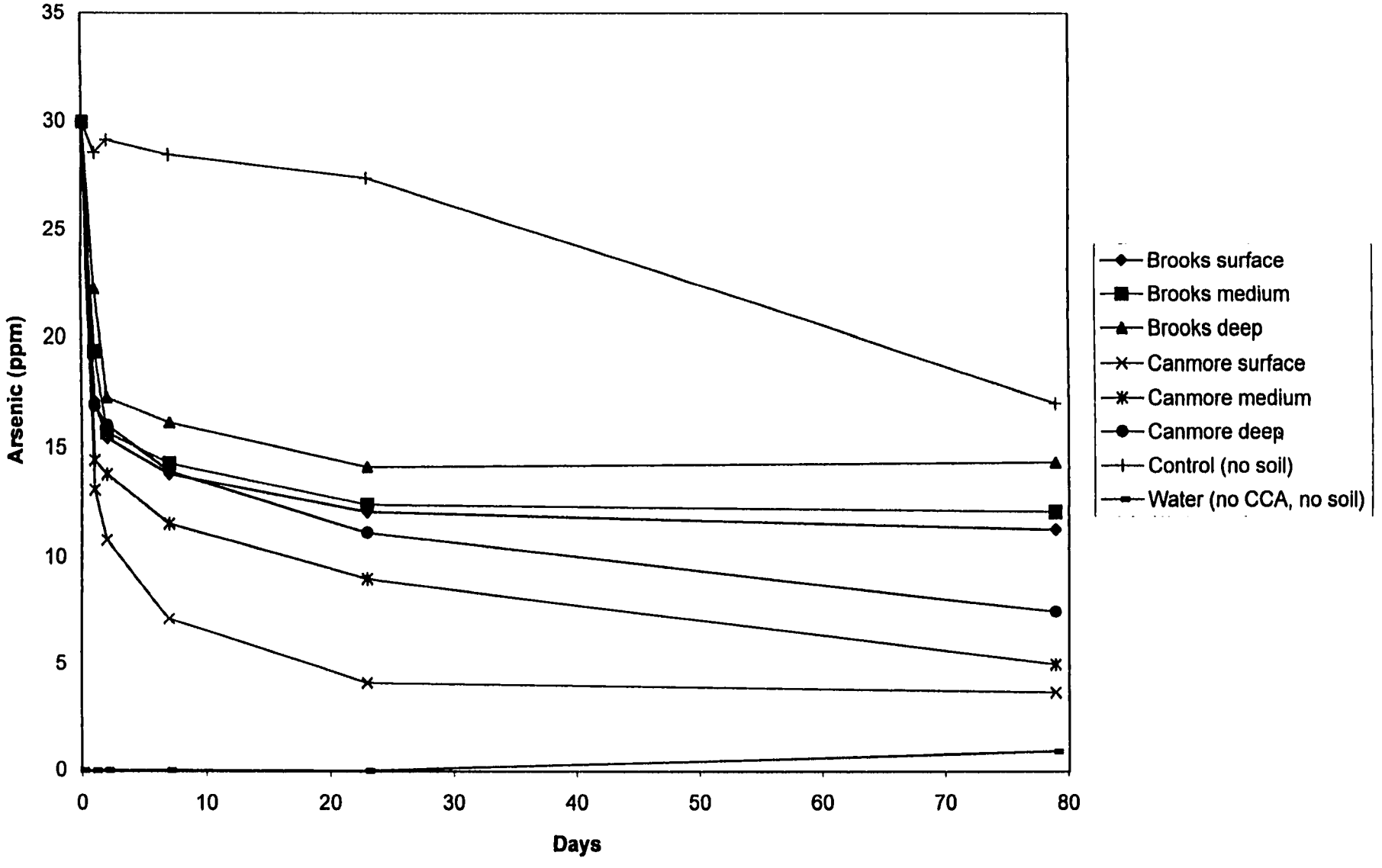


Figure 4.1.2 CCA Experiment 2 - Summary of Aqueous Phase Chromium Levels

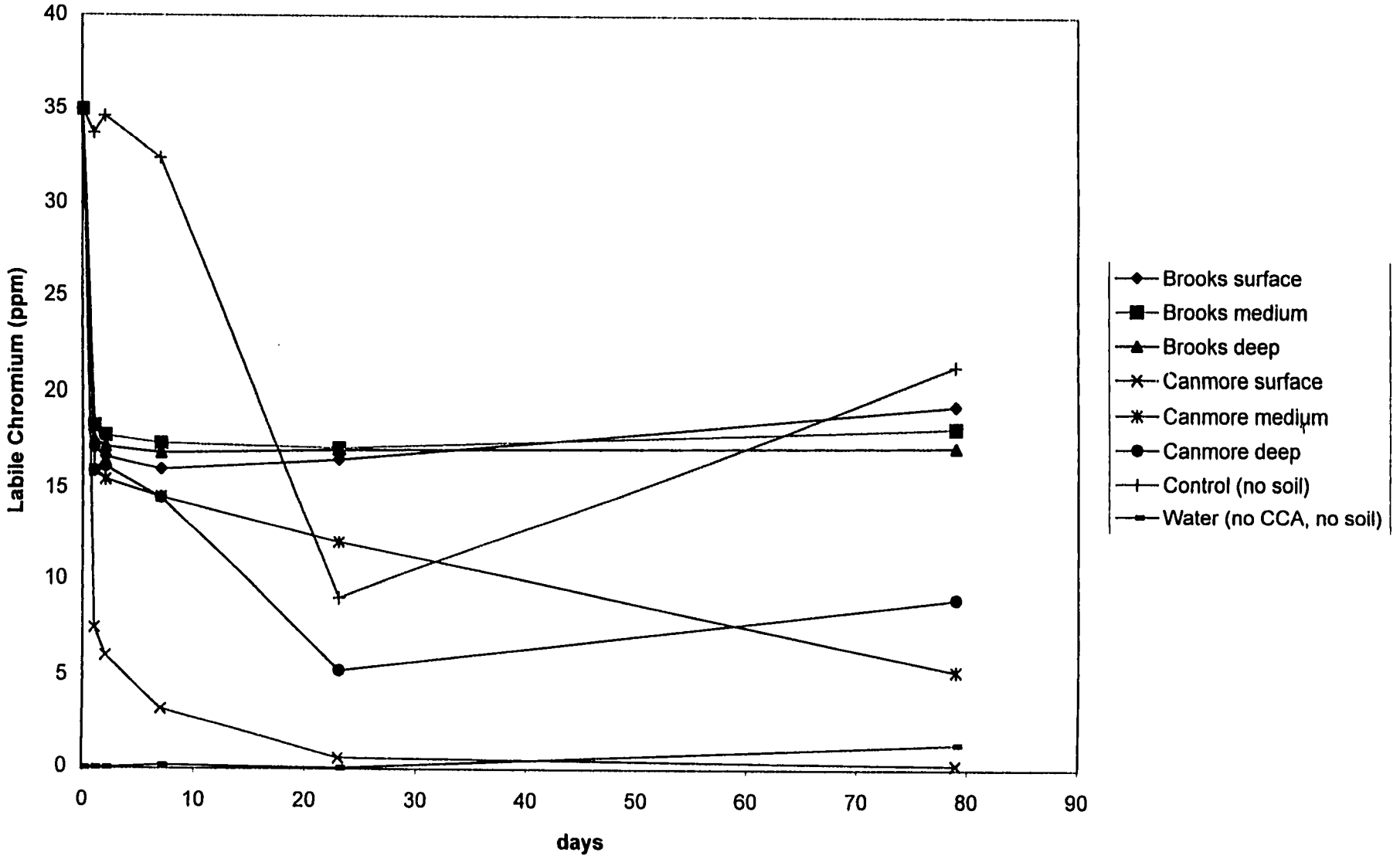


Figure 4.1.3 CCA Experiment 2 - Summary of Aqueous Phase Copper Levels

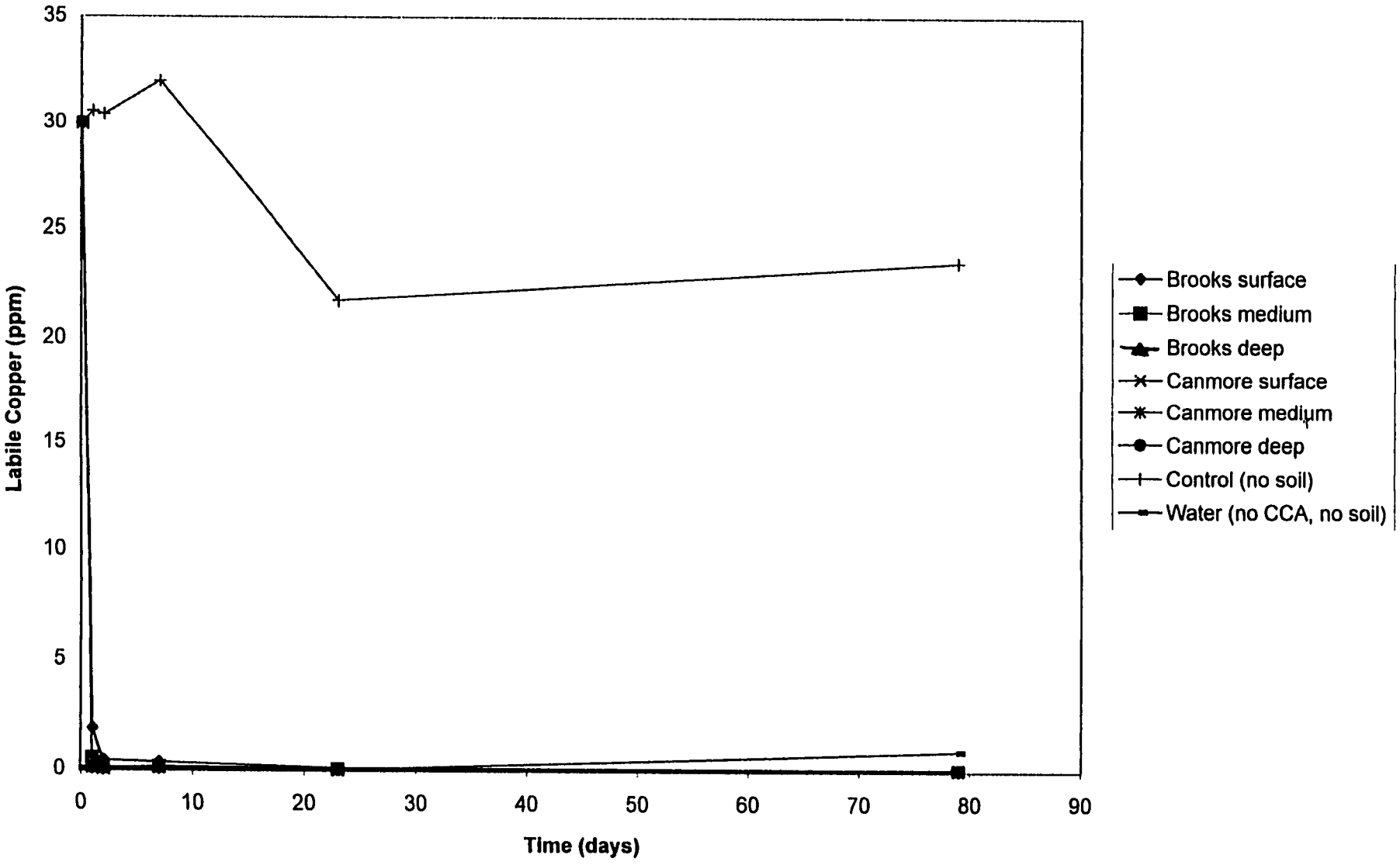


Figure 4.1.4 CCA EXPERIMENT 3 - Summary of Aqueous Phase Arsenic Levels

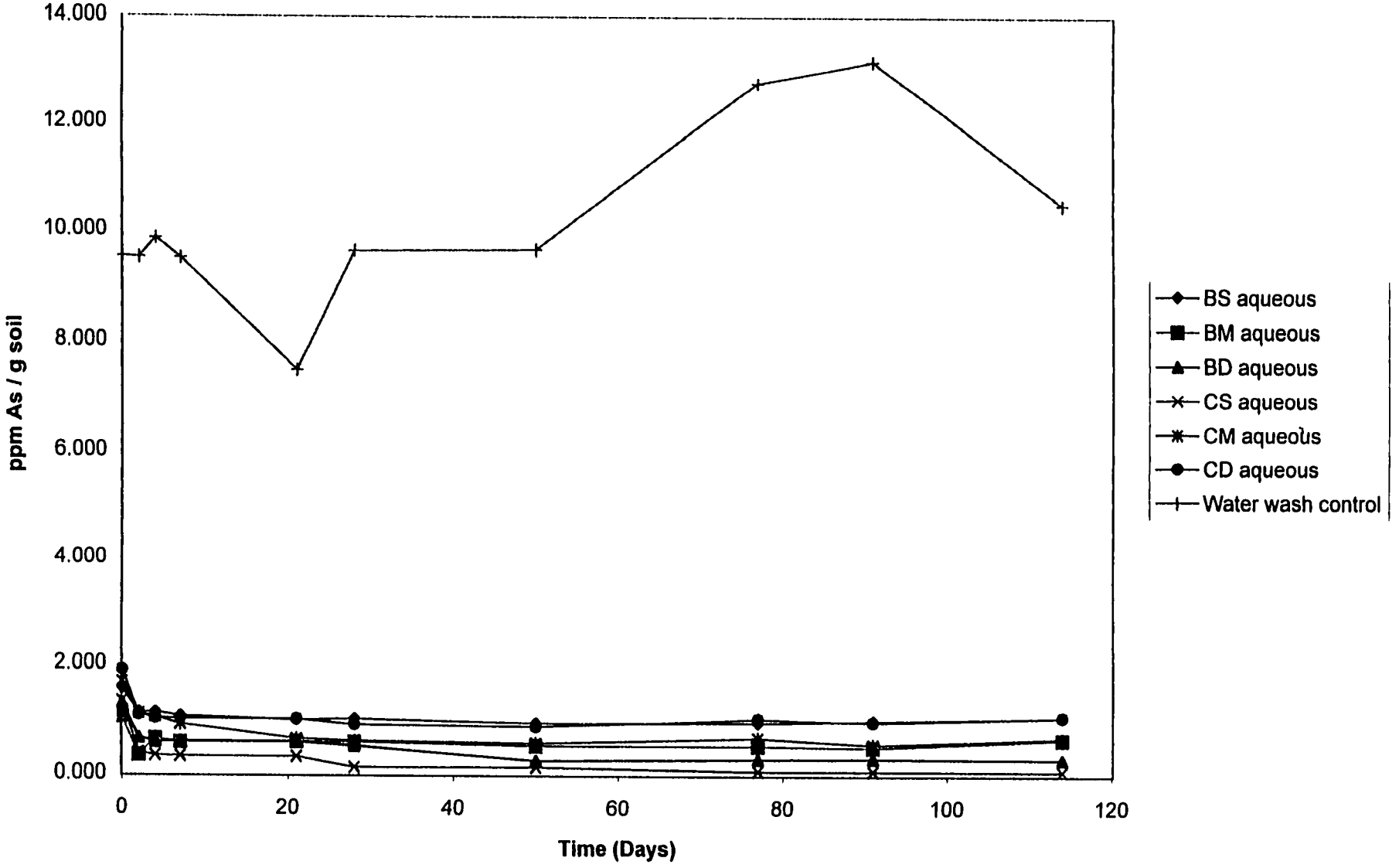


Figure 4.1.5 CCA EXPERIMENT 3 - Summary of Aqueous Phase Chromium Levels

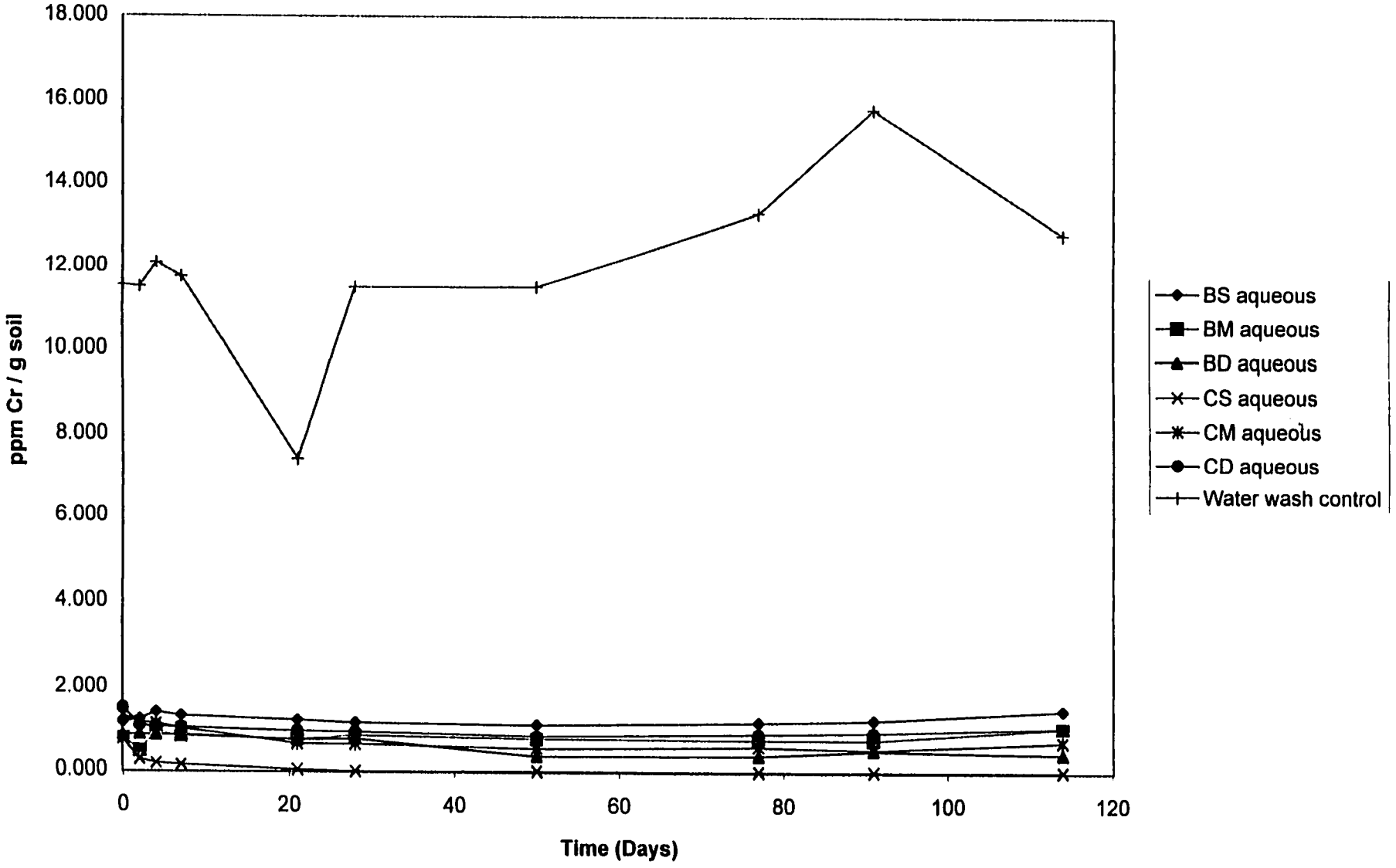


Figure 4.1.6 CCA EXPERIMENT 3 - Summary of Aqueous Phase Copper Levels

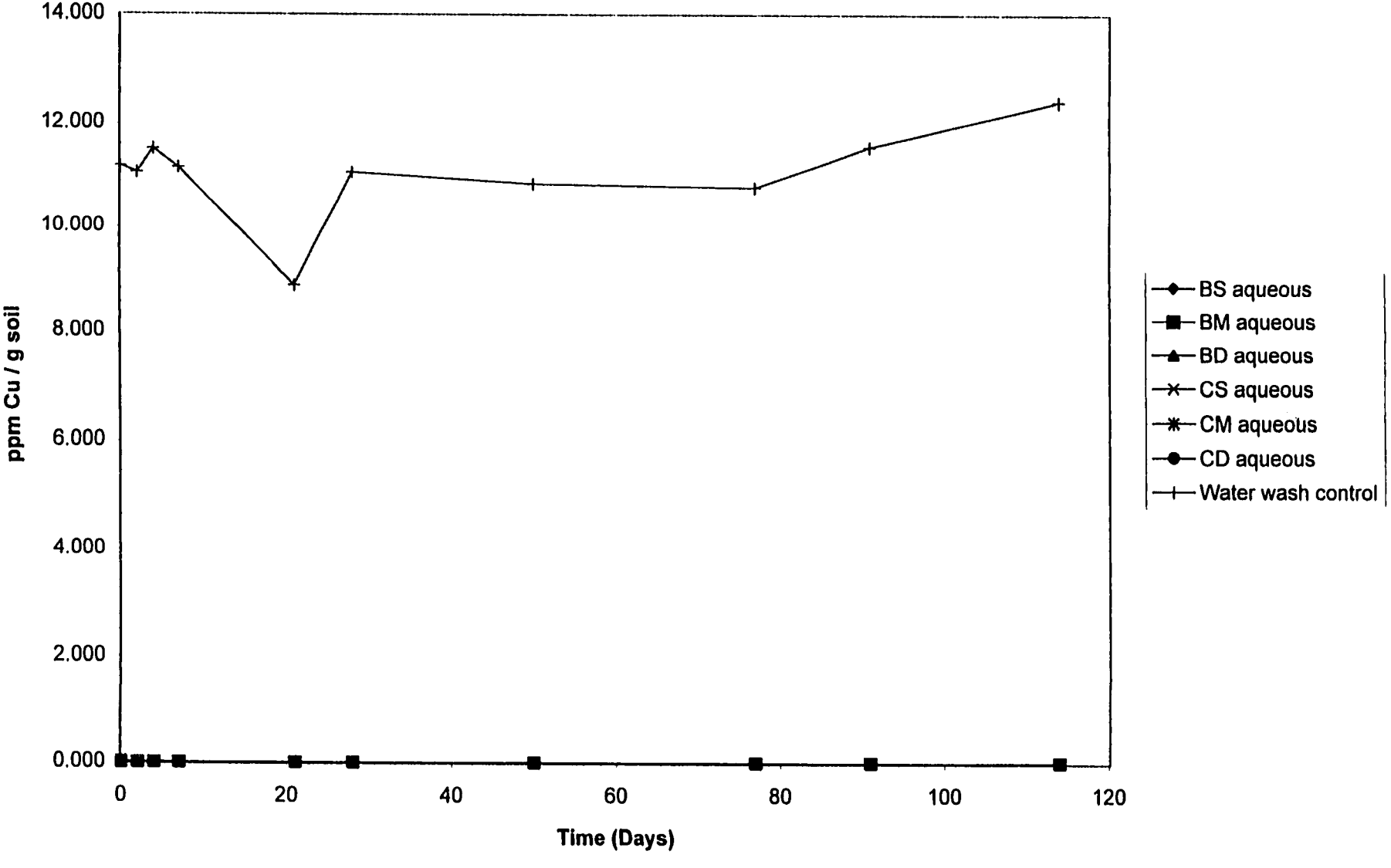


Figure 4.1.7 CCA EXPERIMENT 3 - Summary of "Labile in 4M Nitric Acid" Arsenic Levels

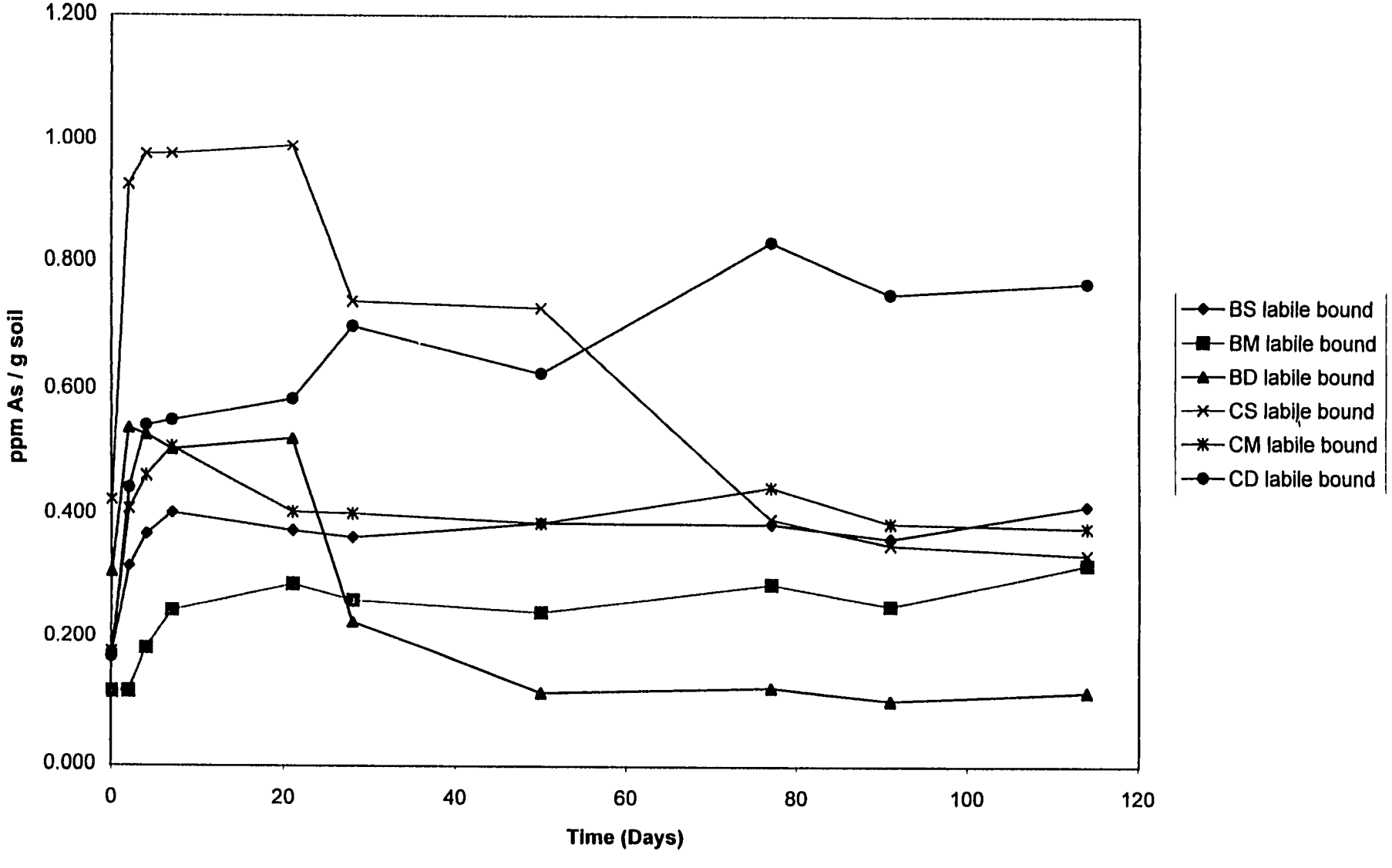


Figure 4.1.8 CCA EXPERIMENT 3 - Summary of "Labile in 4M Nitric Acid" Chromium Levels

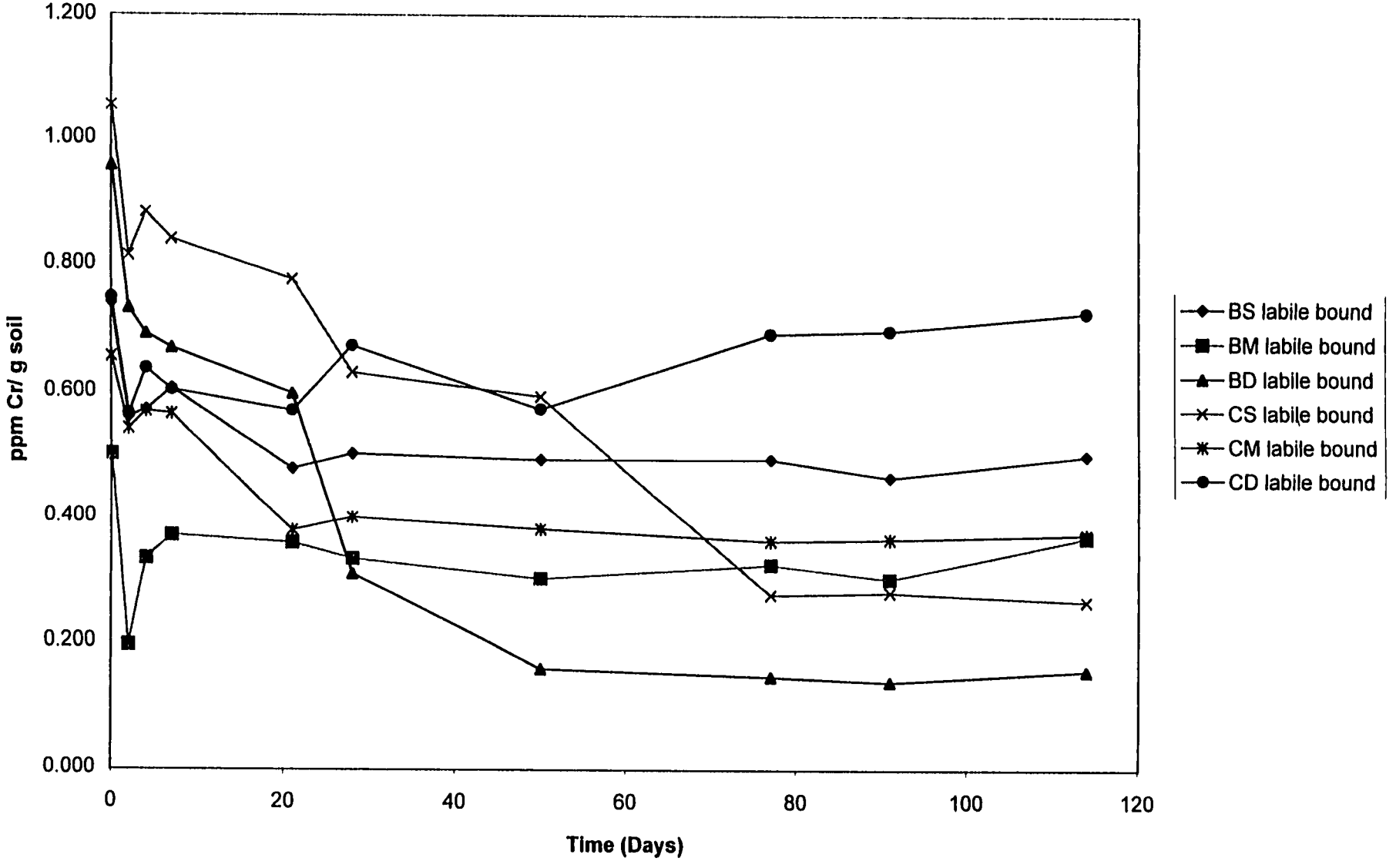


Figure 4.1.9 CCA EXPERIMENT 3 - Summary of "Labile in 4M Nitric Acid" Copper Levels

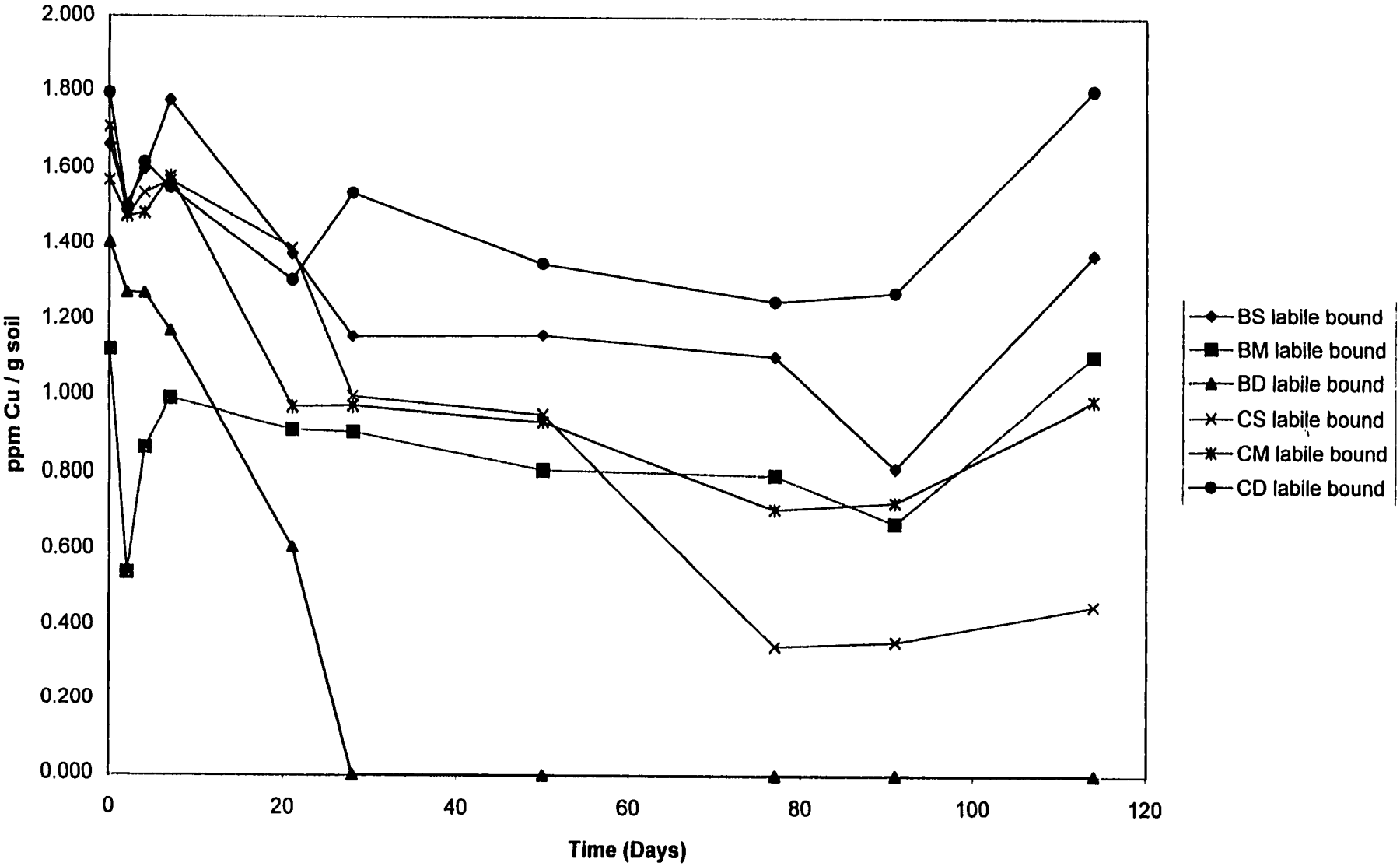


Figure 4.1.10 CCA EXPERIMENT 3 - Summary of "Nonlabile in Water or 4M Nitric Acid" Arsenic Levels

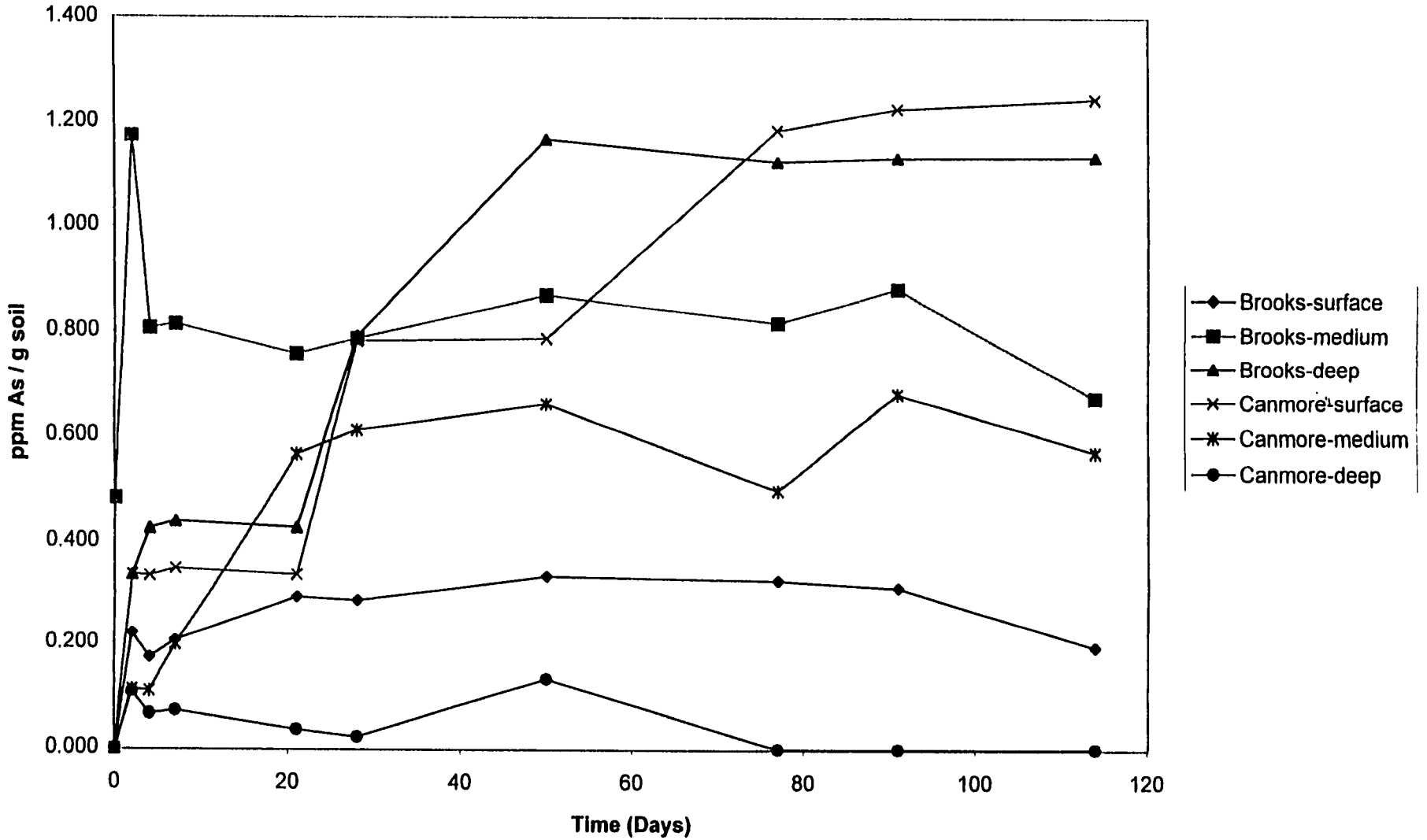


Figure 4.1.11 CCA EXPERIMENT 3 - Summary of "Nonlabile in Water or 4M Nitric Acid" Chromium Levels

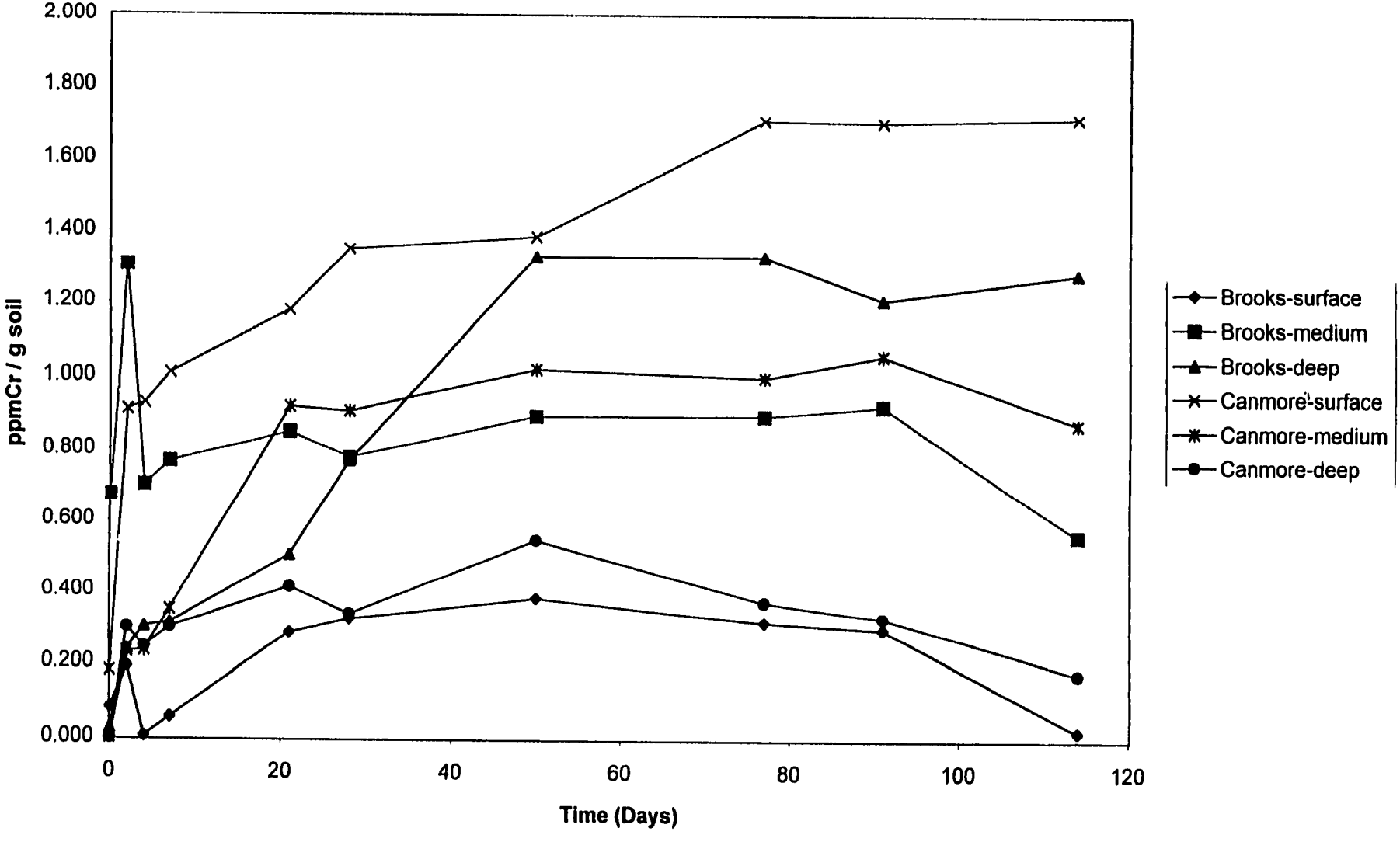
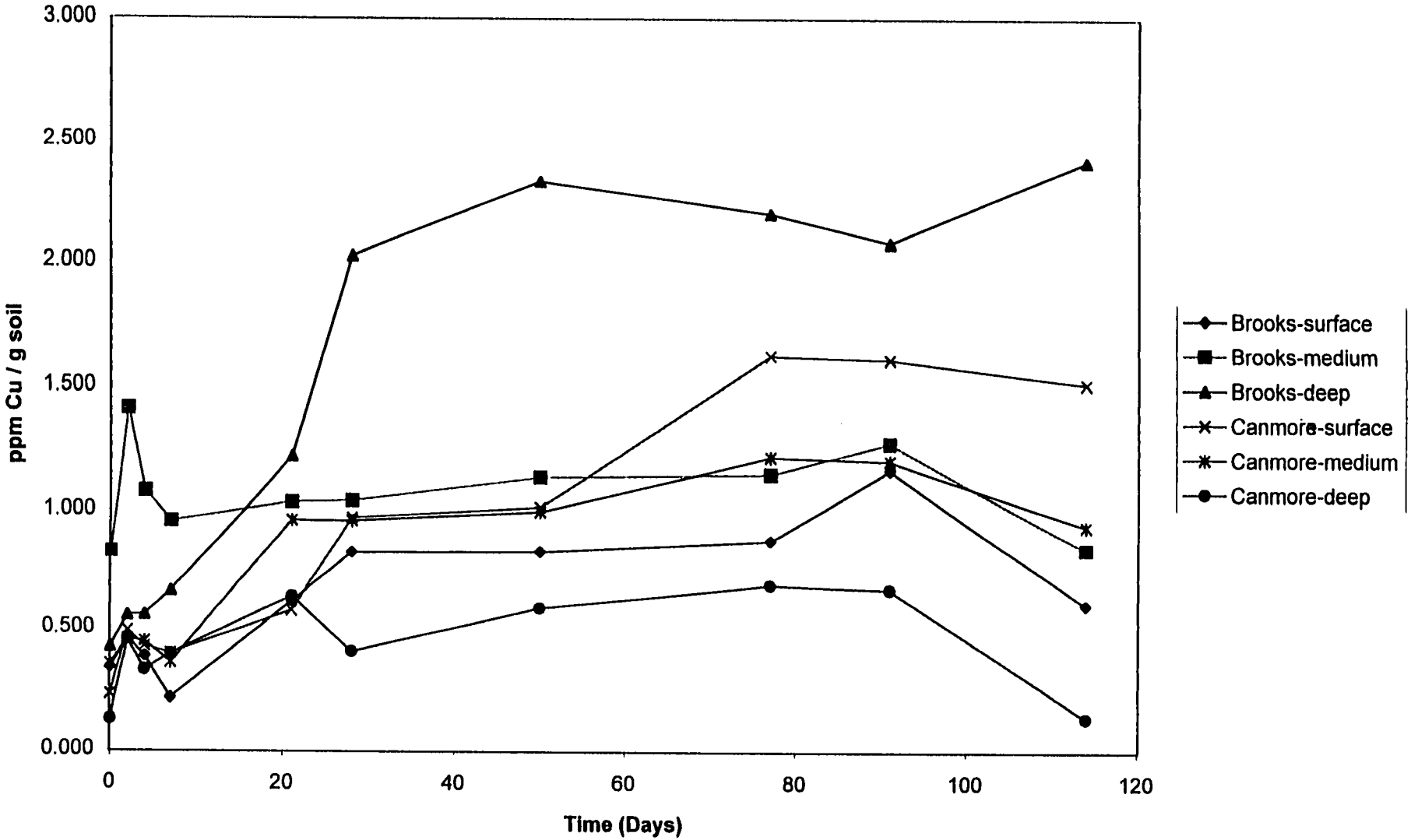


Figure 4.1.12 CCA EXPERIMENT 3 - Summary of "Nonlabile in Water or 4M Nitric Acid" Copper Levels



and Cr (from CCA) and the Cu in CCA (for all soils) truly reached equilibrium. Pignatello (19) suggests that perhaps the literature reports of hours to days to reach equilibrium refer to the slowing of the fast component of sorption rather than overall sorption equilibrium. Indeed true equilibrium of the sorption process may require many months which could only be shown by further investigations utilising time periods of one to two years.

The PCP experiment showed, in the control and several of the soils (Canmore Surface, Brooks Deep and Brooks Medium), an initial rapid loss of PCP from the aqueous phase, followed by its apparent return, within the first seven days (see Figure 3.1.1). The binding of PCP to the glassware, composed principally of silicon dioxide, is of interest since the bound PCP is nonlabile in methanol and the binding involves almost half the PCP. This behaviour is decreased in the presence of soil suggesting that soil competes successfully with the glass for at least some of the PCP. The sorption profile for the Canmore Surface soil is almost identical to that of glass, which is surprising because the Canmore Surface soil contains the highest percentage of organic matter over the six soils studied. In theory, the binding of PCP to the organic matter fraction should be a major factor in the uptake of PCP by soil but this does not appear to be the case. Further studies into the nature of the interaction of PCP with soil and glassware are required before conclusions may be drawn regarding the true mechanism of PCP uptake. This phenomenon was not observed with either CCA or CUNAP.

PCP achieved a reasonably steady state in solution by day 35 for all soils tested. The Canmore soils appeared to be achieving a steady state with regard to the labile and nonlabile fractions by Day 35. The same could not be said for the Brooks soils. This may be because the Brooks soils had a large surface area composed primarily of mineral surfaces, which would encourage amphiphilic bonding. The sorption of PCP to Brooks soil was not yet completed by day 35 because of this large surface area. This would tend to support Pignatello's assertion that true equilibrium may require months (19). Even so, by day 35, approximately 38% of the PCP appears to be nonlabile which fits the suggested literature value of 20-50% irreversibly sorbed (77). Of course, there is some variation by soil type, as expected.

In the CCA study, copper was sorbed quickly, as expected. Indeed, all the soils showed a rapid decrease in the amount of copper available in the aqueous phase within minutes of the addition of the CCA to the slurry. Since copper is capable of both ion exchange (with a timescale of about 10^{-12} s) and chemisorption (a timescale of a few minutes to hours) with the mineral and organic portions of the soil, this is not surprising. Much of this was labile in nitric acid, especially after 90 days. The increase in labile copper after 90 days may be a function of the physical breakdown of the soil particles after shaking for so long in water. This breakdown would increase the surface area of the soil and expose previously inaccessible sites to the nitric acid. The net effect would be to increase the amount of copper removed during the nitric acid wash. There is some precedent for this idea in the literature. Henselwood (129) found that after

about 60 days with shaking much of the soil structure was destroyed and the number of particles increased.

Both chromium and arsenic bound best to the soil with the highest concentration of iron, which was the Canmore surface soil. This suggests that the metals were converted to the chromate and arsenate or arsenite anions and formed directional, inner sphere, complexes with the iron oxide. These results seem consistent with the current understanding of anion binding to soil.

The CUNAP study was interesting in that it showed that the copper and naphthenate do not act independently. Rather, the sorption of copper was delayed by about 5 days, which could only be attributed to the presence of the naphthenate anion. It is postulated that hemimicellar formation may have occurred and that copper was not released until the naphthenate began to be sorbed to the soil surfaces. One could also postulate that the naphthenate is chelating the copper and that copper is only released once the naphthenate is sorbed. Further studies are required before anything more conclusive might be stated as to the nature of this interaction.

The ongoing uptake by soil of PCP, CCA and CUNAP, especially into nonlabile sites has implications with regard to soil contamination and the resulting contamination of associated groundwater. It is likely that these compounds will be less mobile and less liable to biodegradation than expected using values from studies occurring over short time periods. This would lead to increased residence times in contaminated sites and possibly decreased

contamination of groundwaters. Certainly this will increase the difficulty of remediation of these environmental contaminants.

5 DIRECTIONS FOR FURTHER STUDY

A kinetics experiment with PCP should be conducted, over a period of six months to a year, now that there is a functional method in place. One question to ask is: will all the soils achieve equilibrium? Another question is: would this occur before the soil particles begin to break down? Third: how long does it take for the soils under consideration to break down significantly? That is, if soils that are shaken constantly gradually break into smaller and smaller particles, which increases the surface area and reduces the number of inaccessible sites?

The studies with CUNAP should be repeated and continued for at least two or three months. Studies should also be done to determine whether the delayed peaks are due to degradation or possible anhydride formation. The SPME technique presents some interesting possibilities but needs to be investigated further.

Studies should also be done with sonication of the soil after some period of time to see if it is possible to achieve 100% recovery of the compounds added to the soil. Other extracting solutions could also be used to see if the compounds are truly nonlabile or simply need to be extracted with a different solvent.

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Figure A.1 Brooks Surface Soil Particle Size Distribution

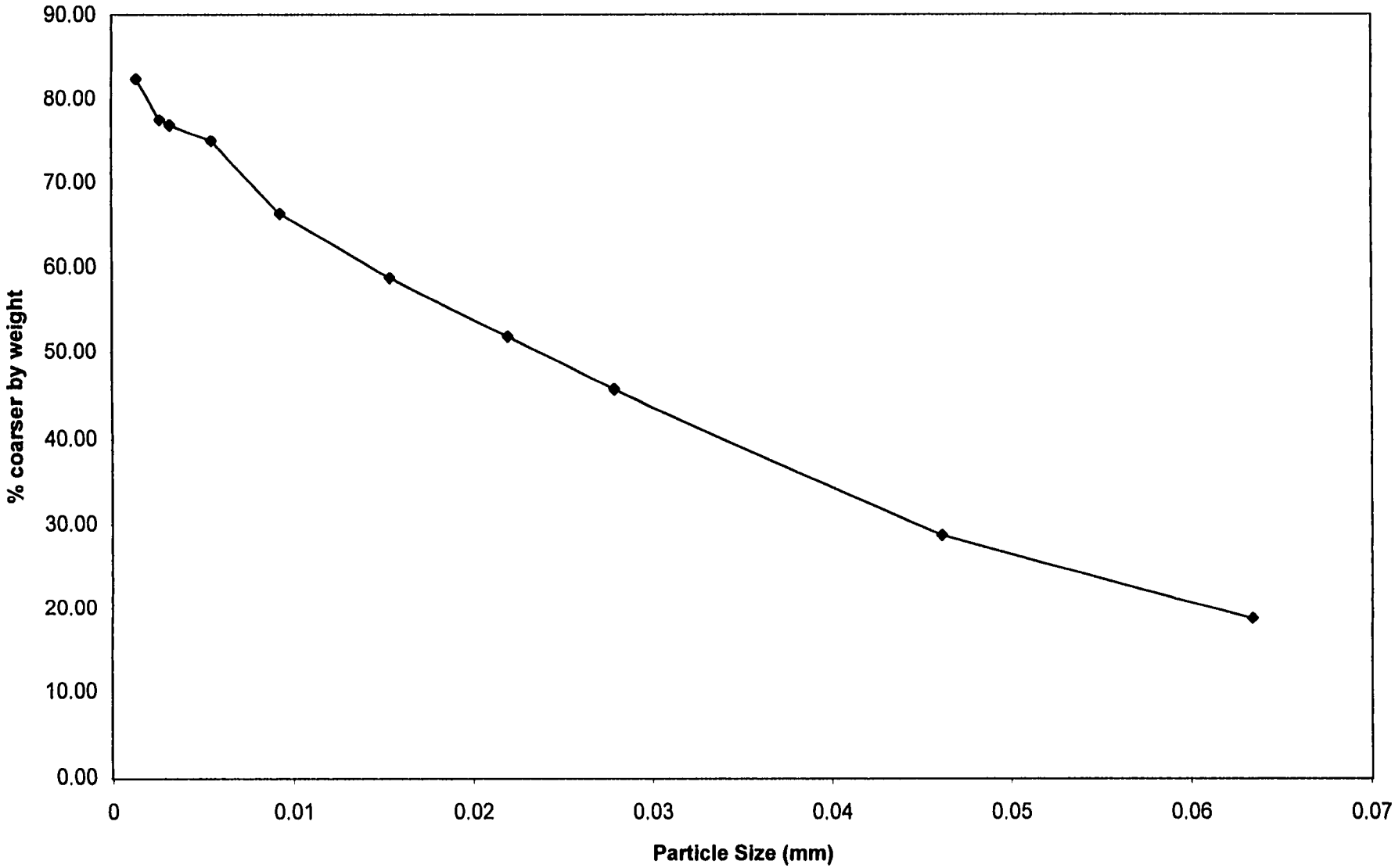
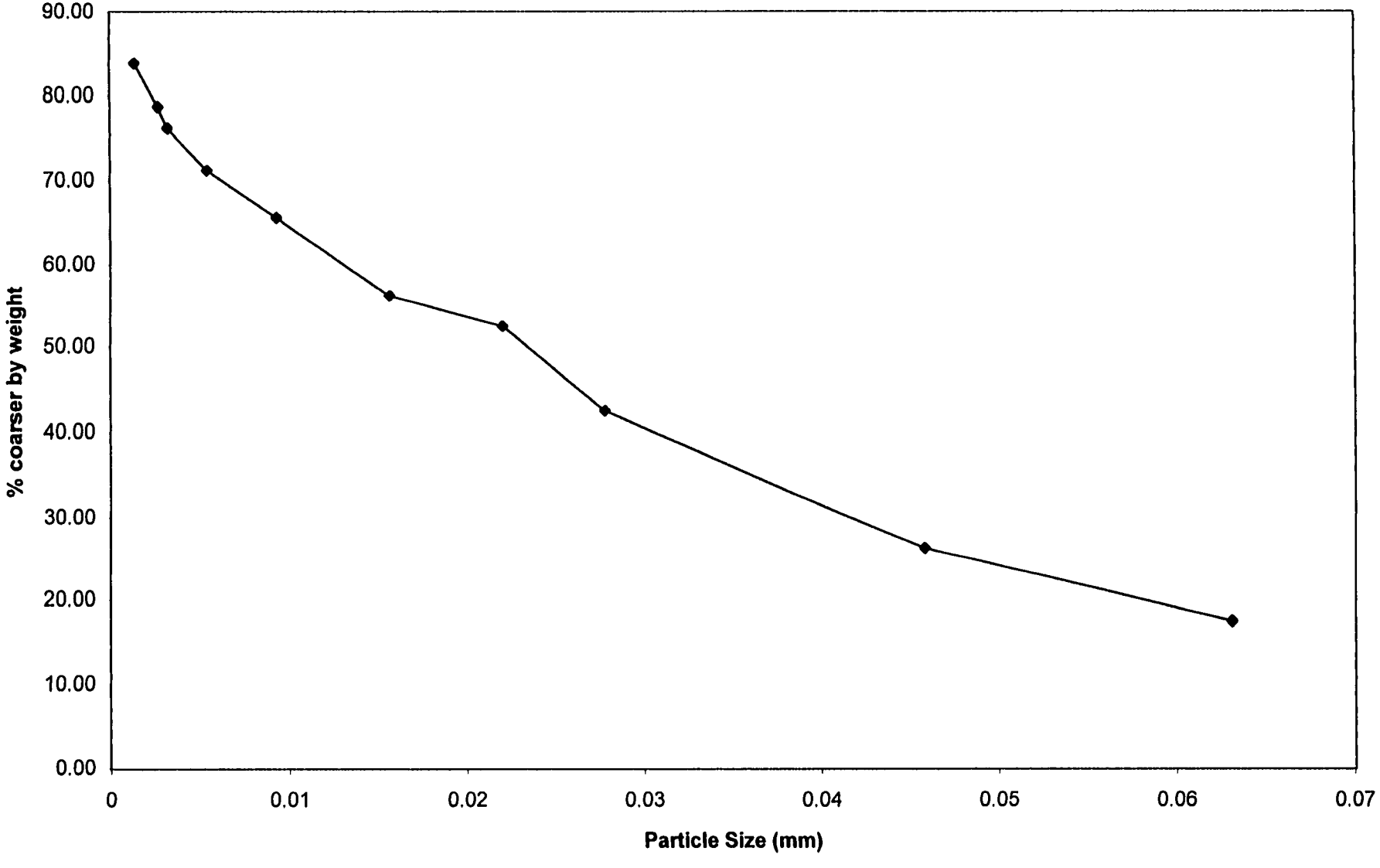


Figure A.2 Brooks Medium Soil Particle Size Distribution



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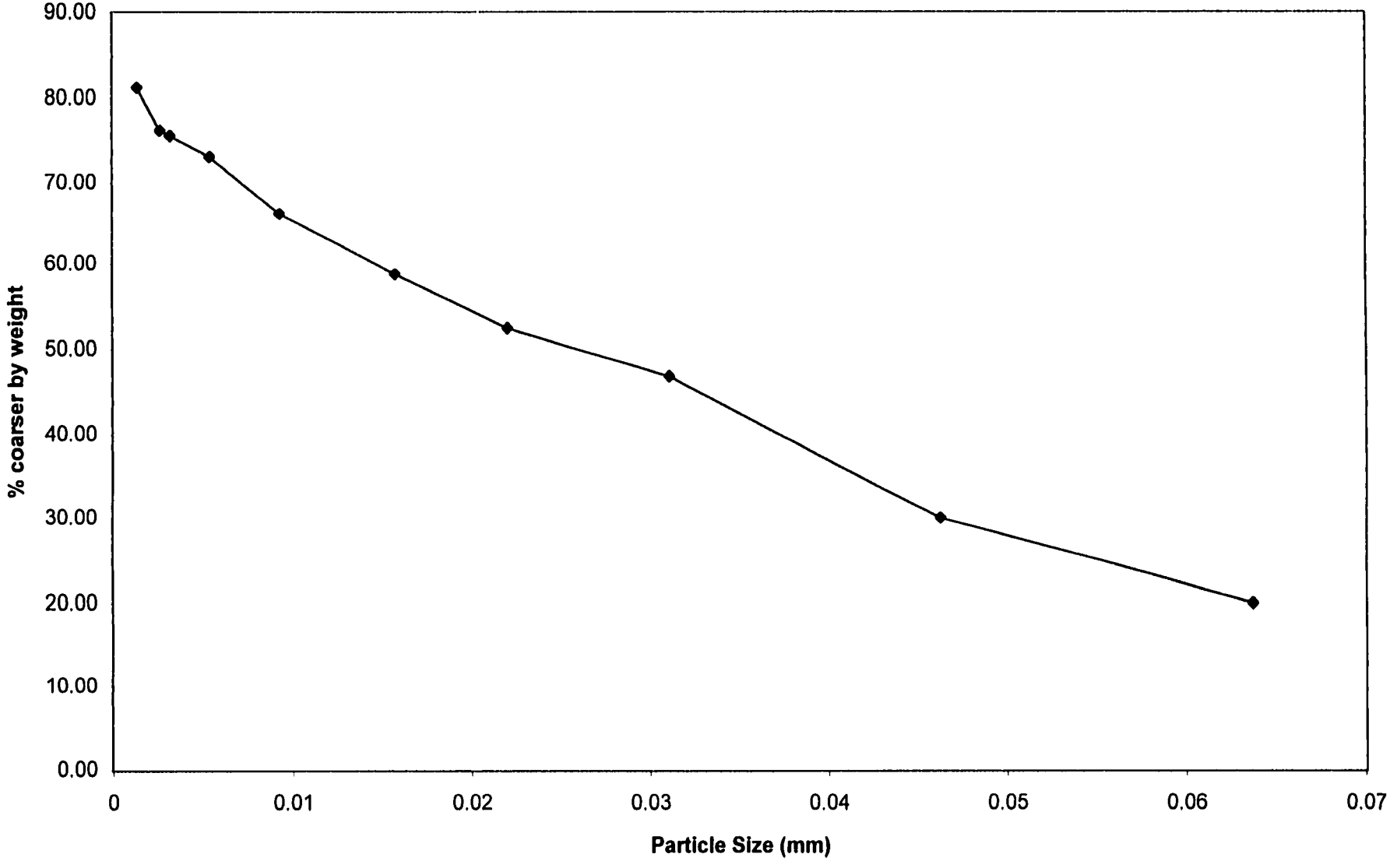
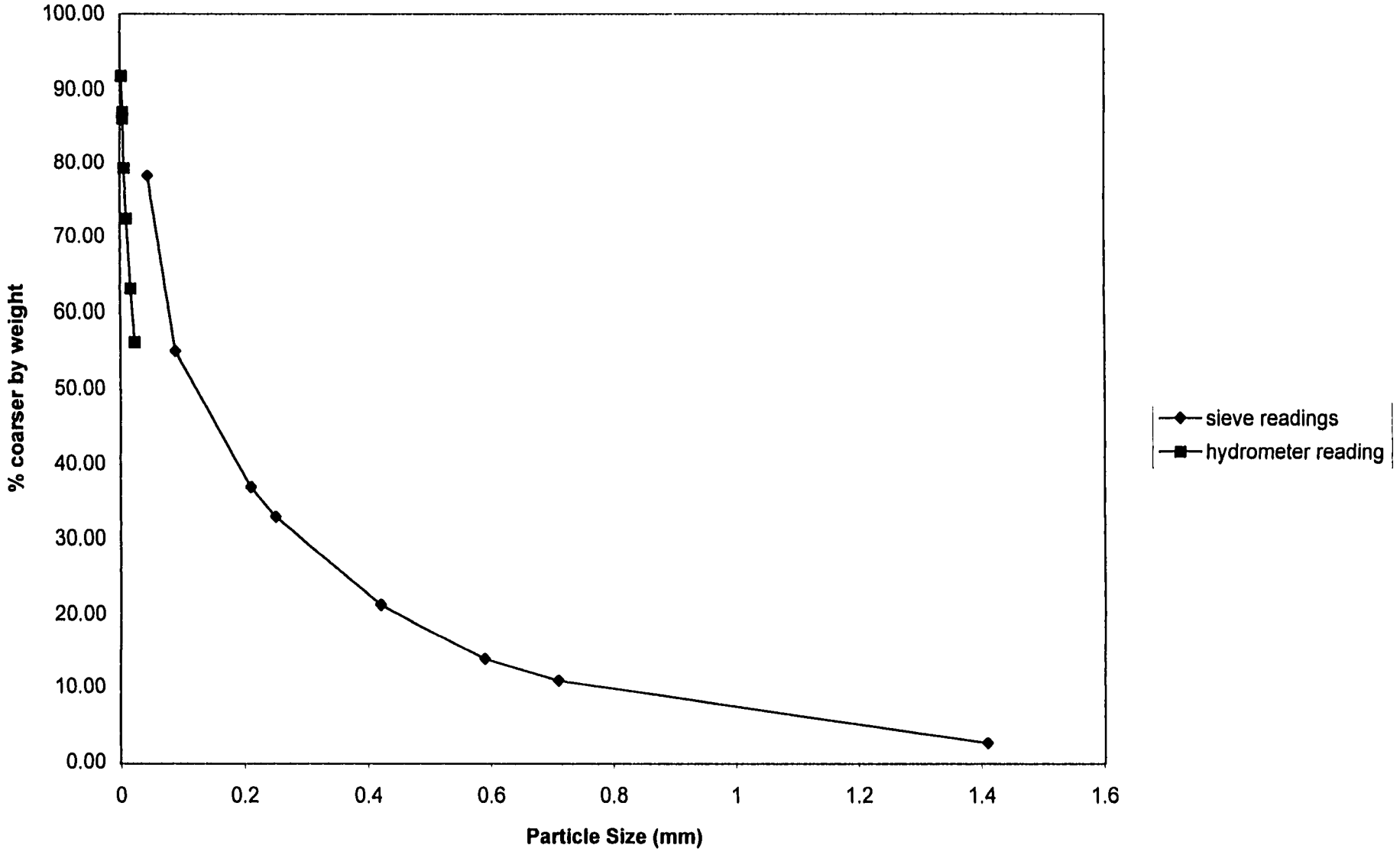


Figure A.4 Canmore Surface Soil Particle Size Distribution



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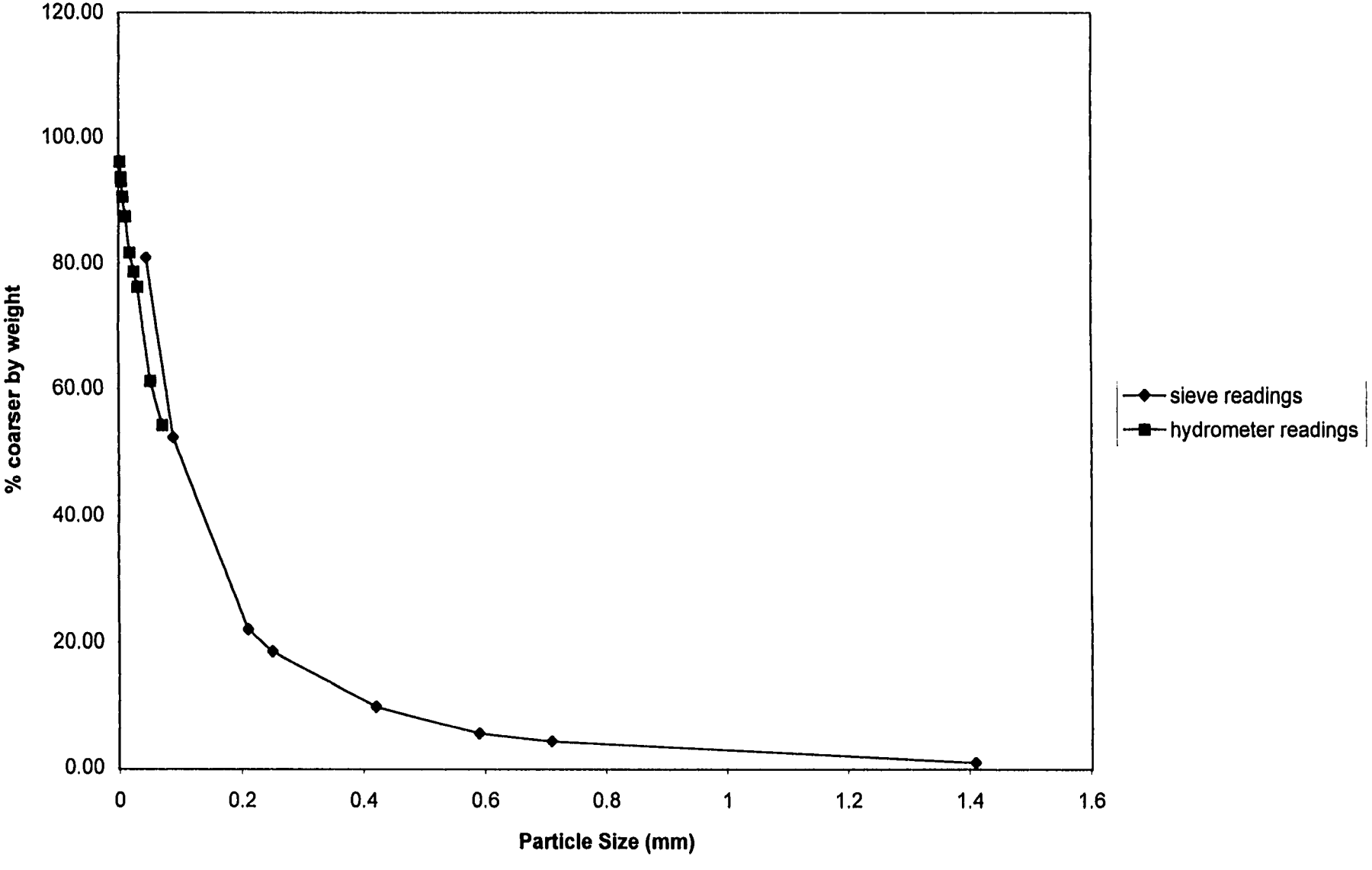

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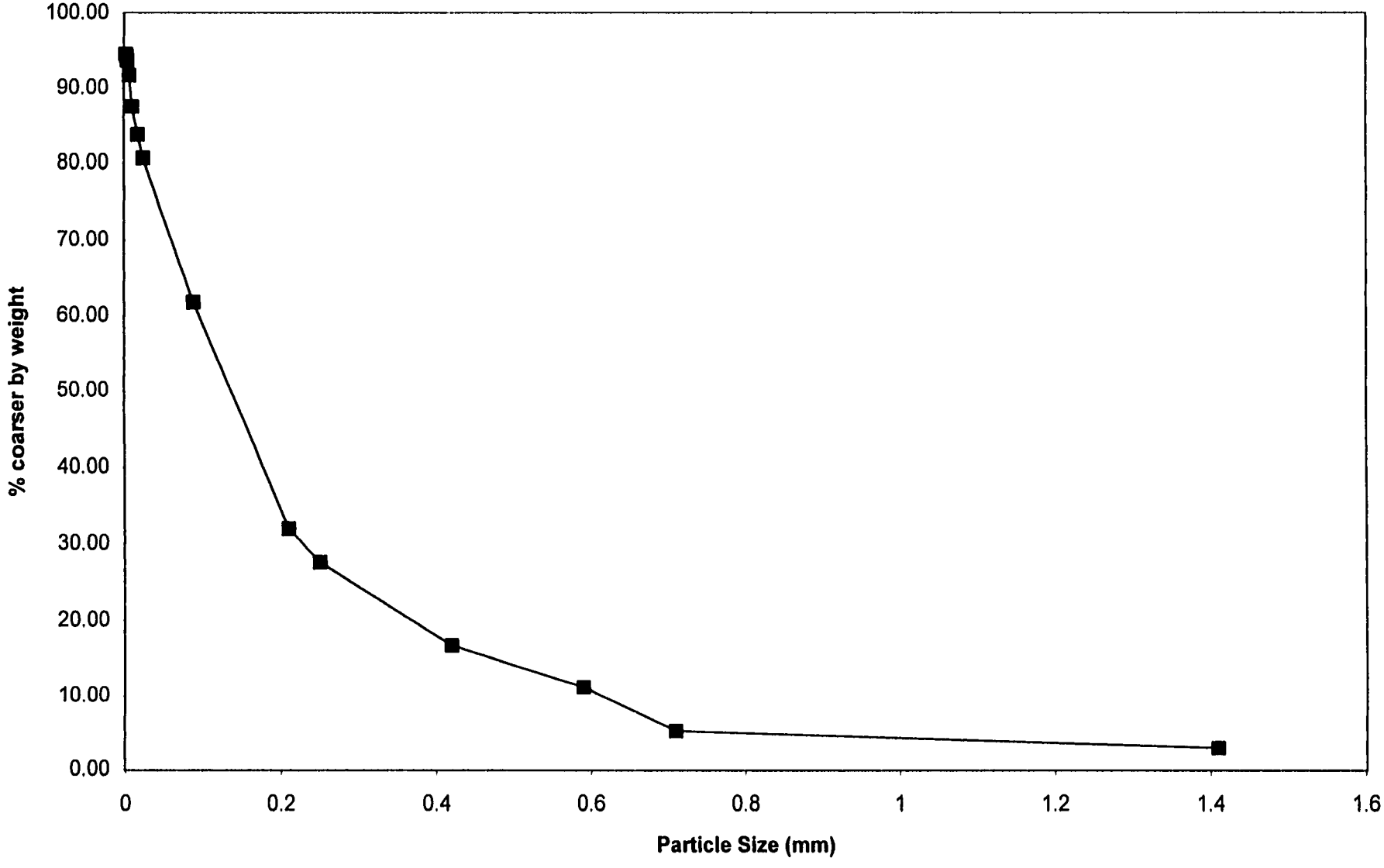
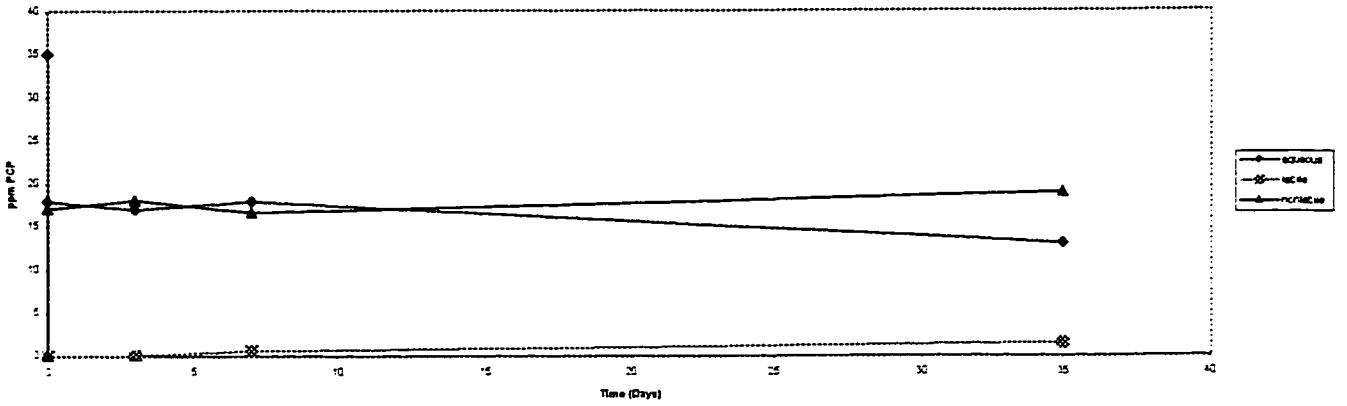


Figure B.1
PCP EXPERIMENT 3 COMPARISON OF FRACTIONS

Brooks Surface



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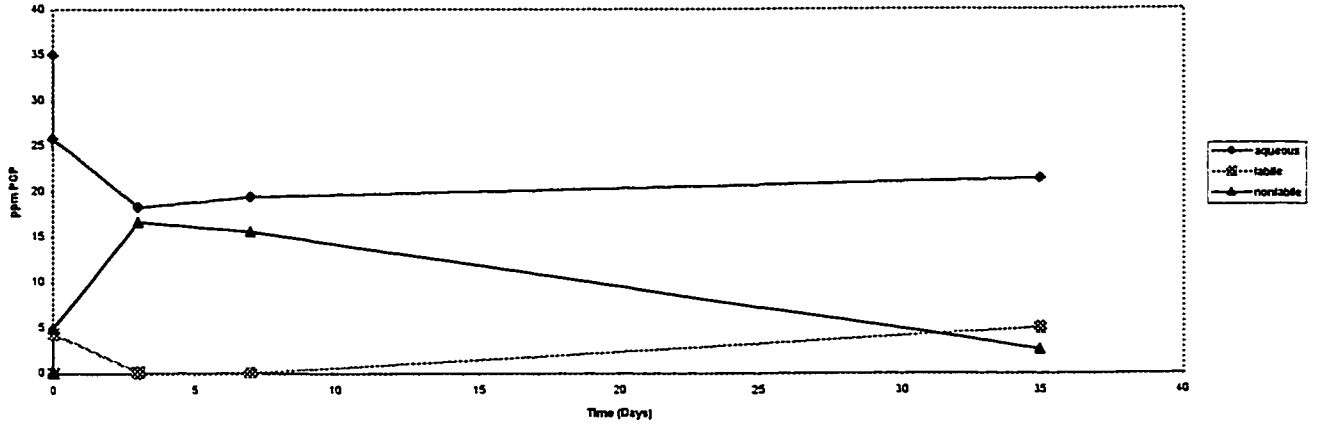

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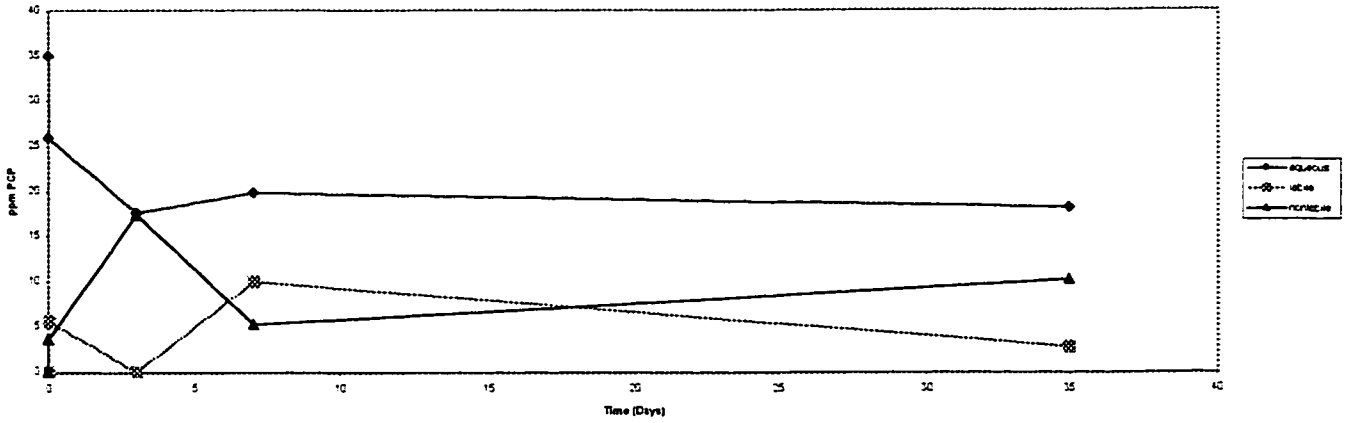


Figure B.2
PCP EXPERIMENT 3 COMPARISON OF FRACTIONS

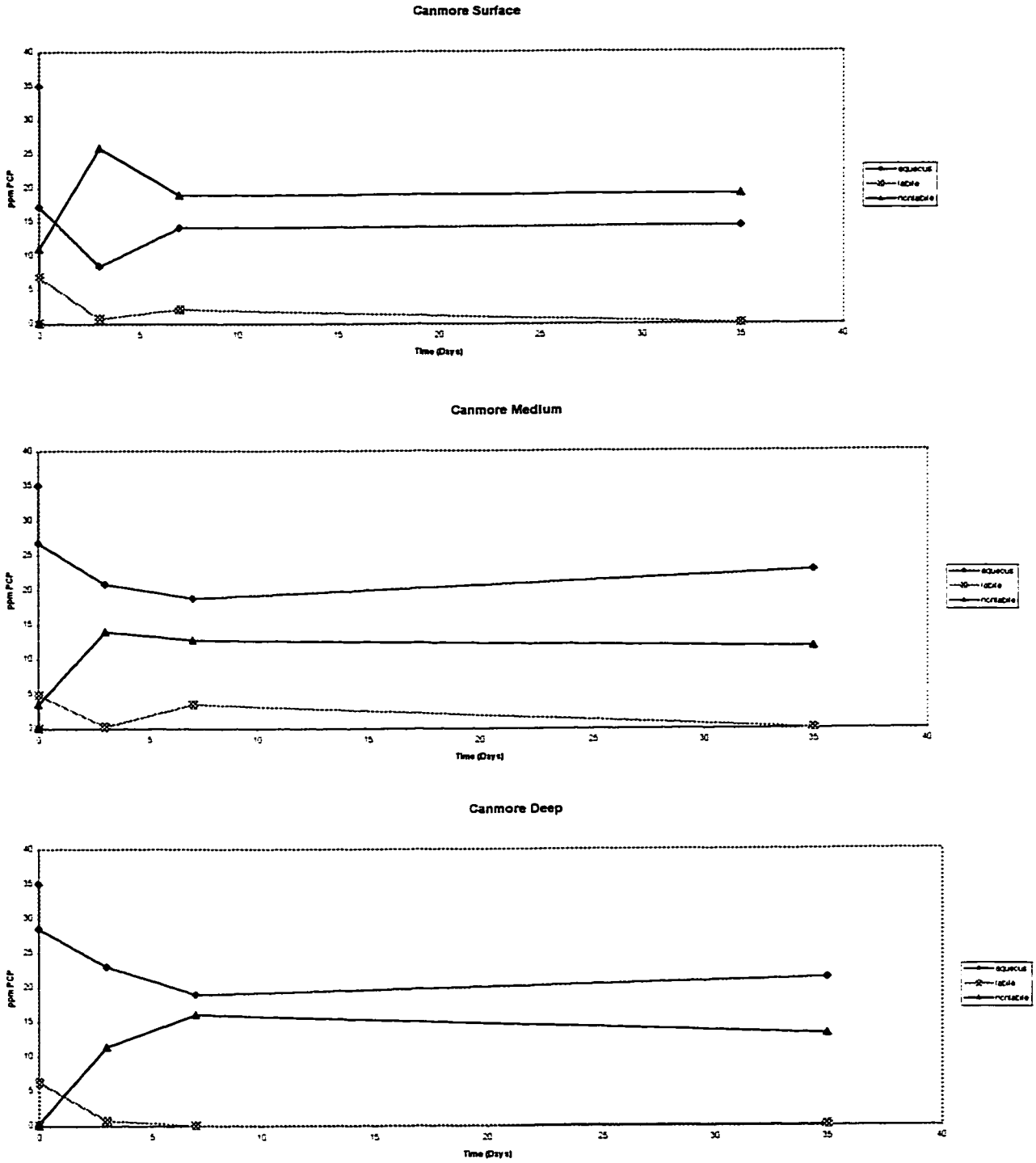


Figure C.1 CCA Experiment 2 - Brooks Surface Comparison of Metal Ions in Aqueous Phase

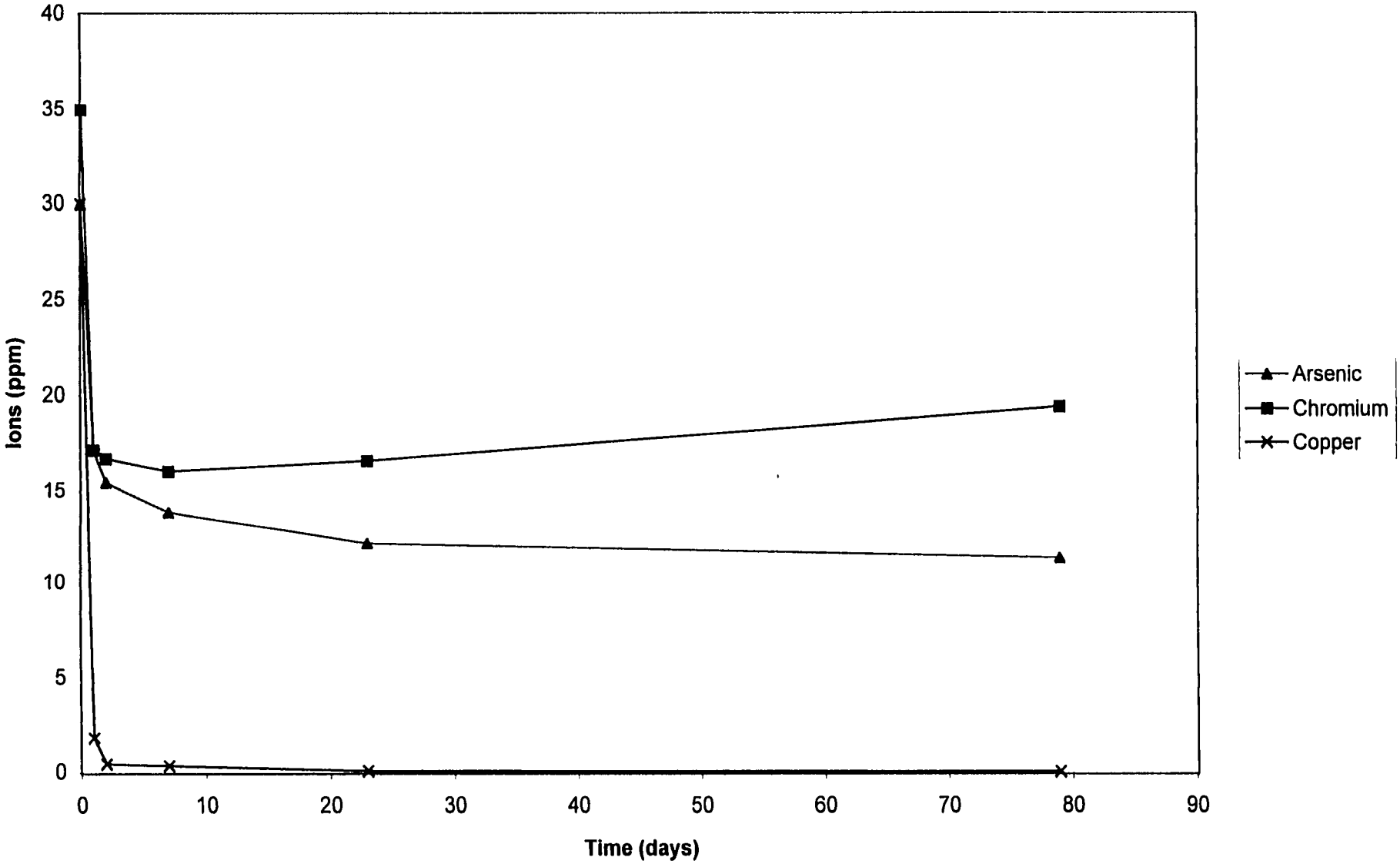


Figure C.2 CCA Experiment 2 - Brooks Medium Comparison of Metal Ions in Aqueous Phase

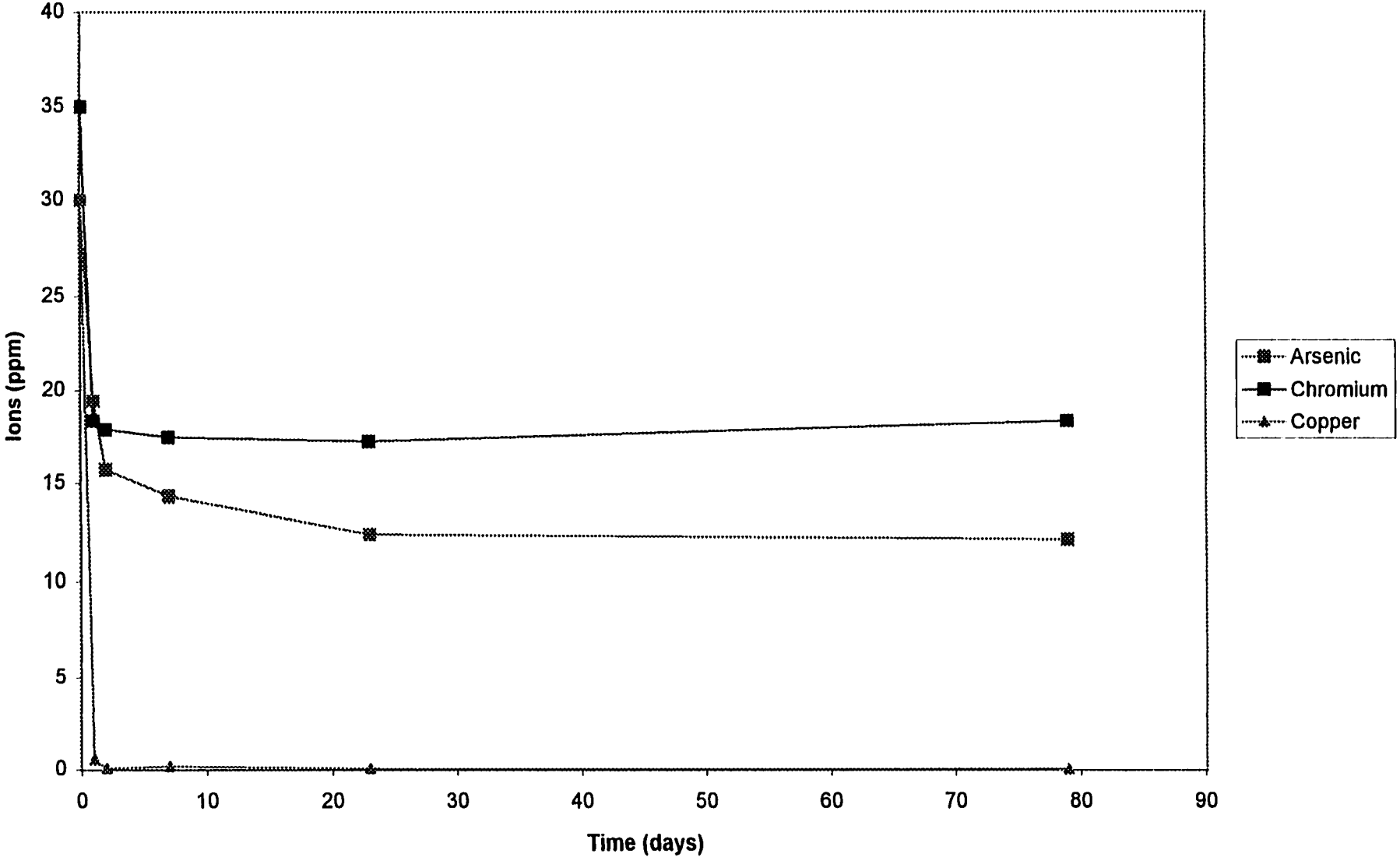


Figure C.3 CCA Experiment 2 - Brooks Deep Comparison of Metal Ions in Aqueous Phase

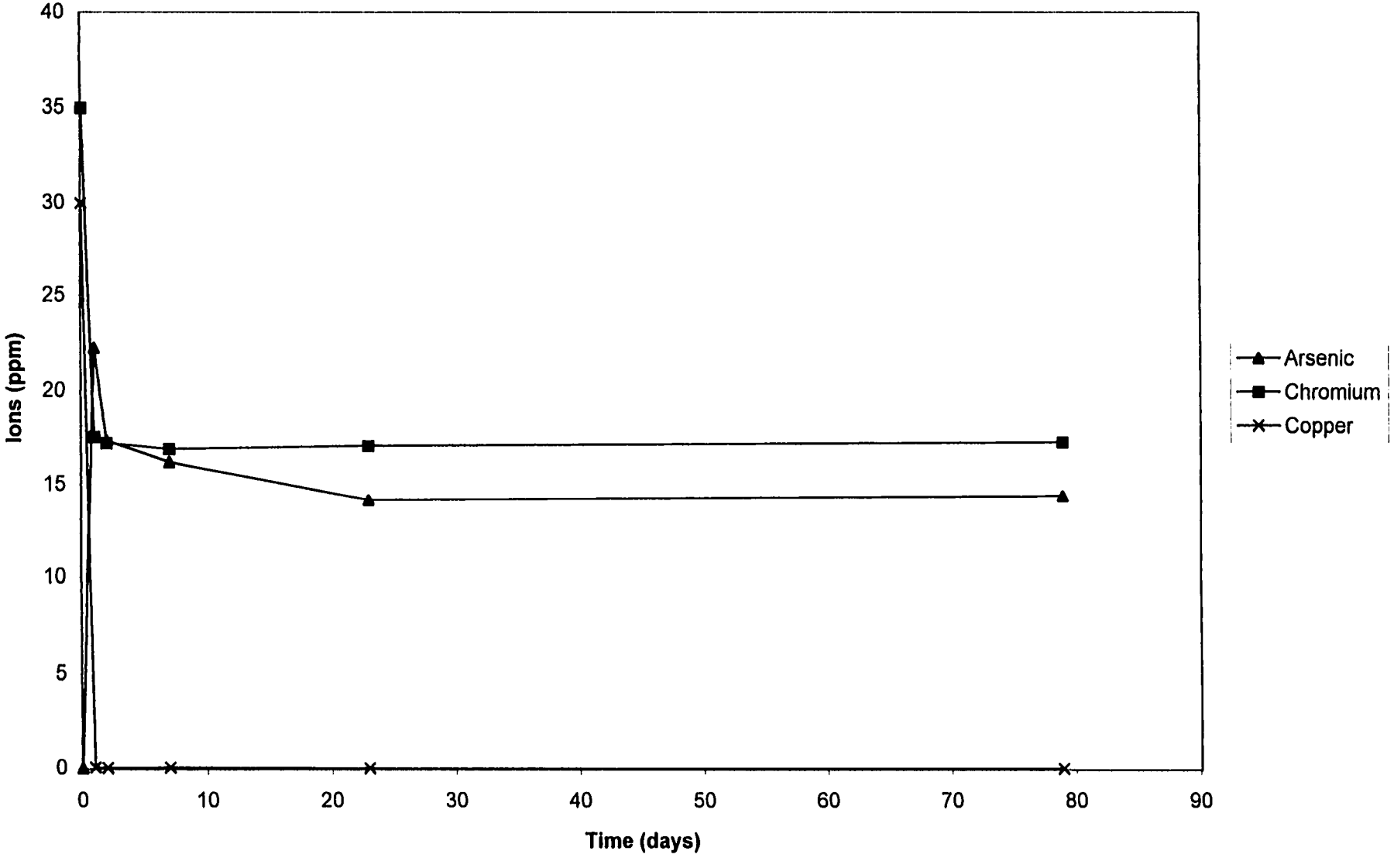


Figure C.4 CCA Experiment 2 - Canmore Surface Comparison of Metal ons in Aqueous Phase

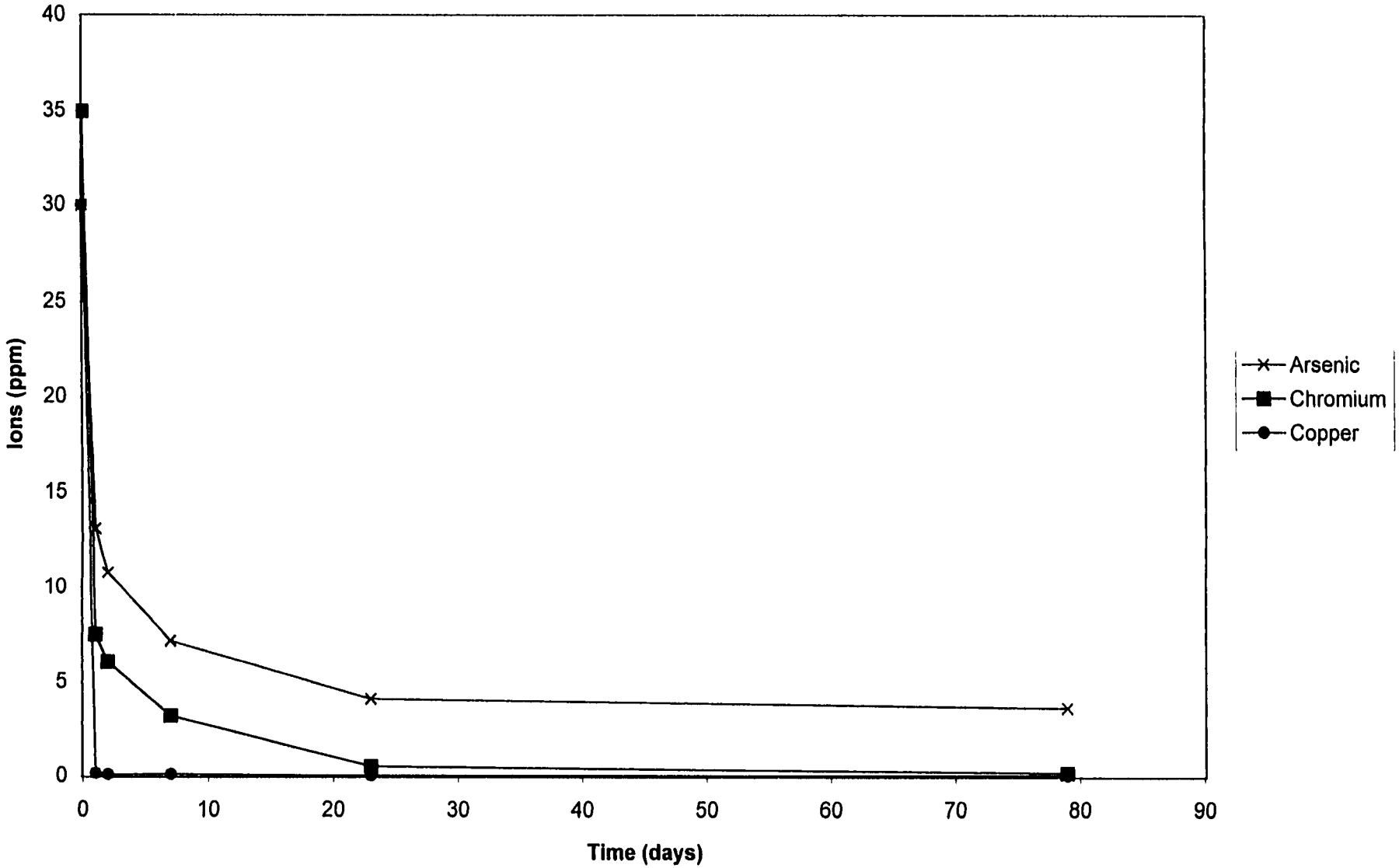


Figure C.5 CCA Experiment 2 - Canmore Medium Comparison of Metal Ions in Aqueous Phase

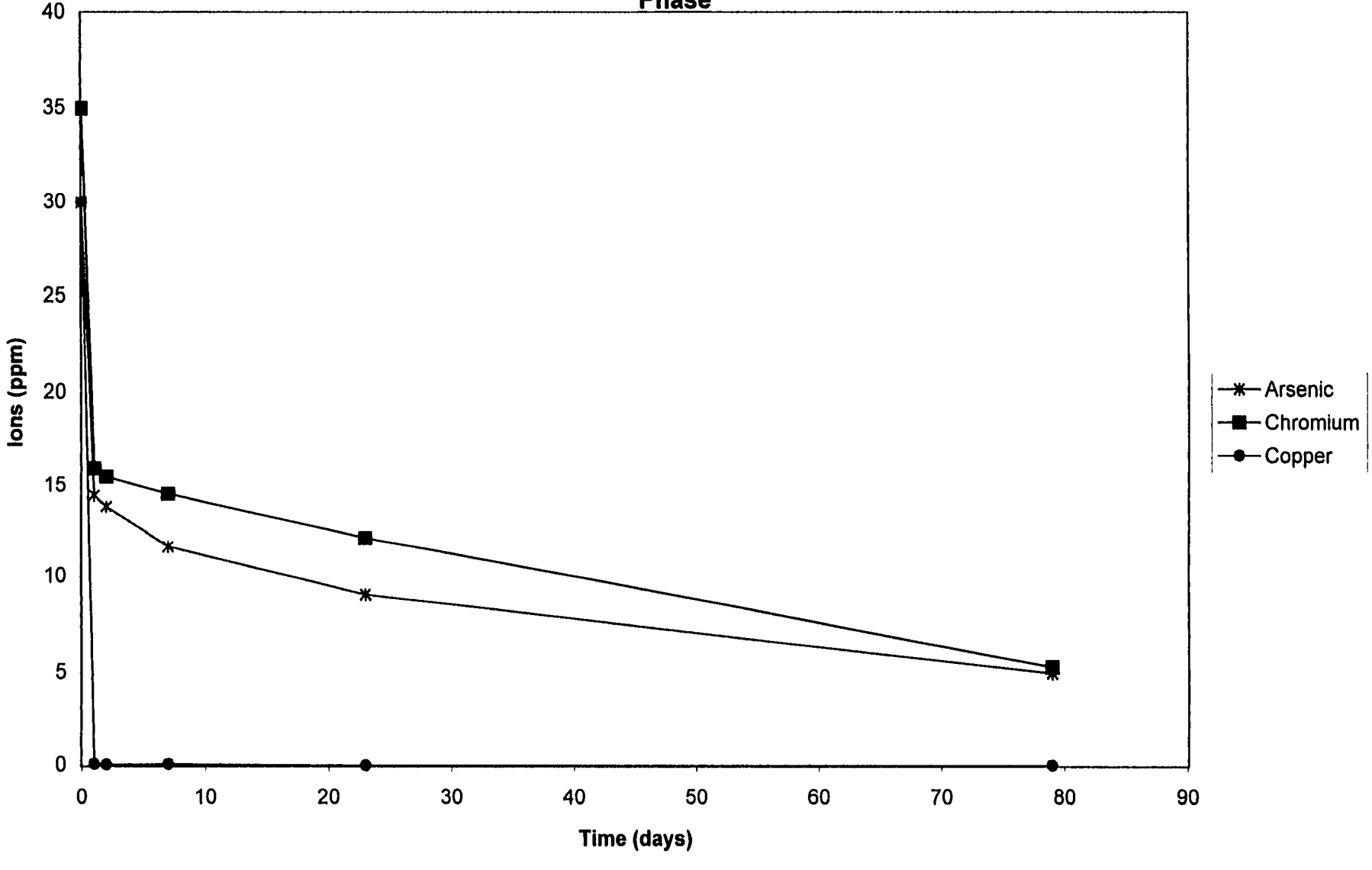


Figure C.6 CCA Experiment 2 - Canmore Deep Comparison of Metal Ions in Aqueous Phase

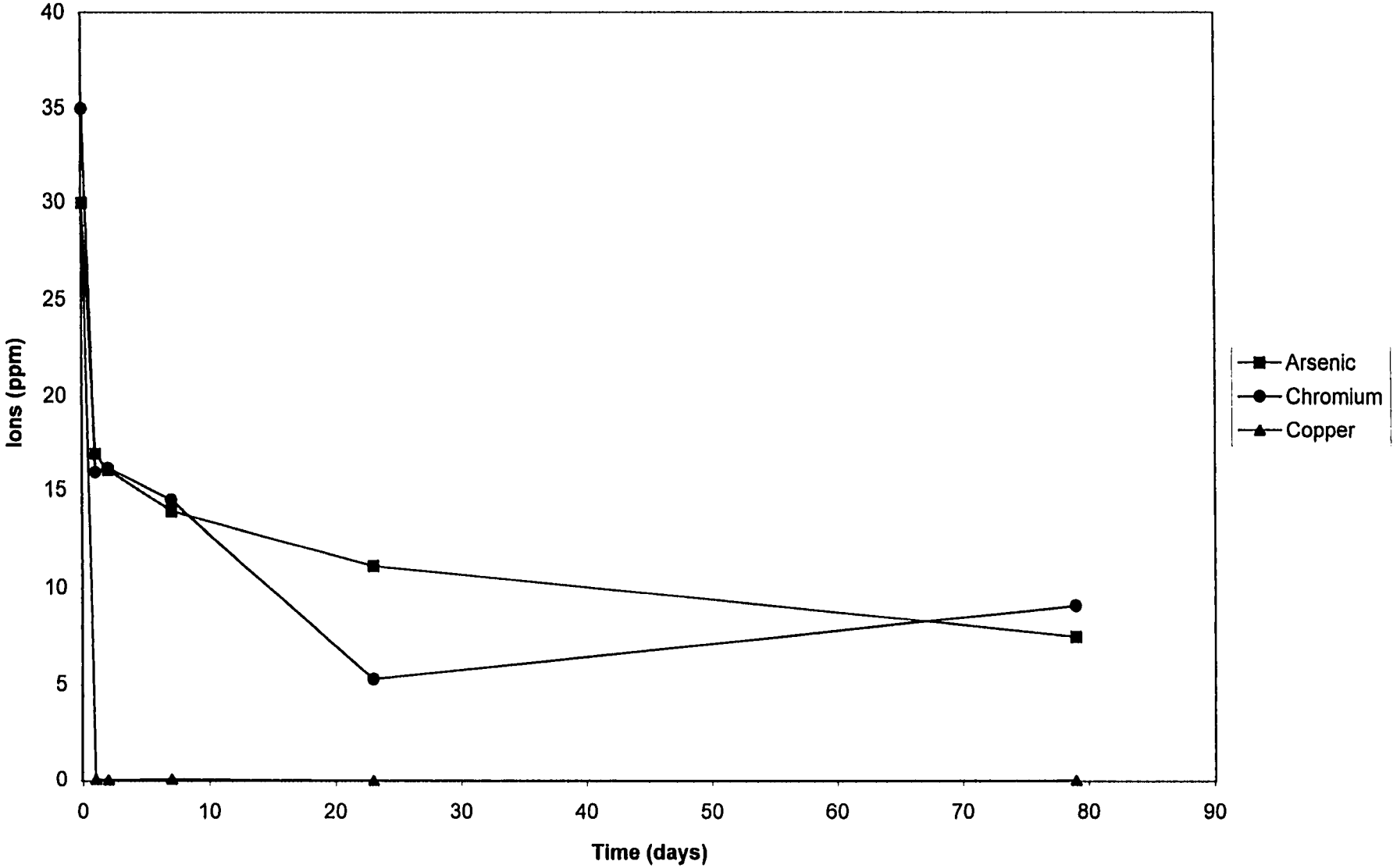


Figure C.7 CCA Experiment 3 Brooks surface Comparison of Metal Ions in aqueous phase

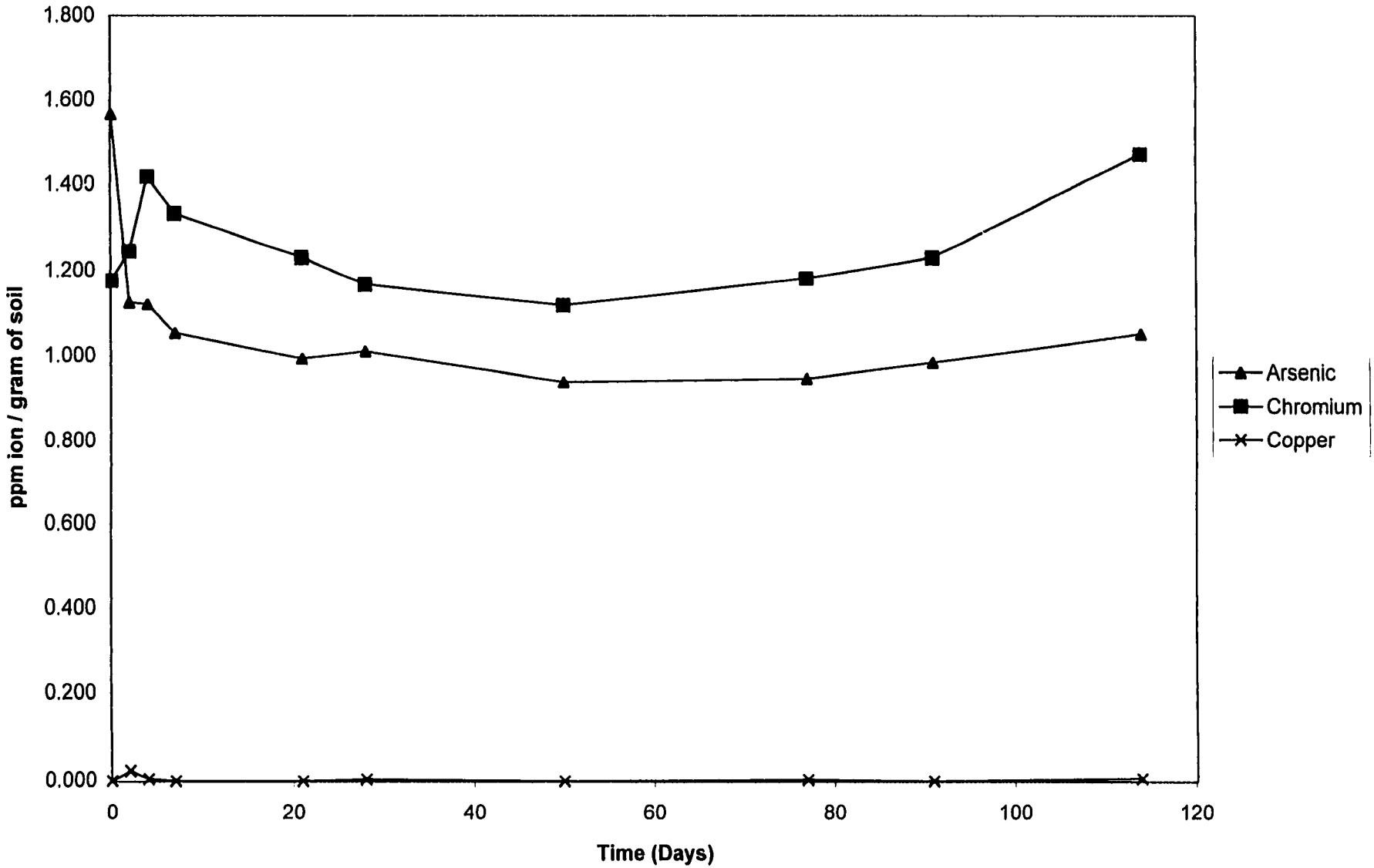
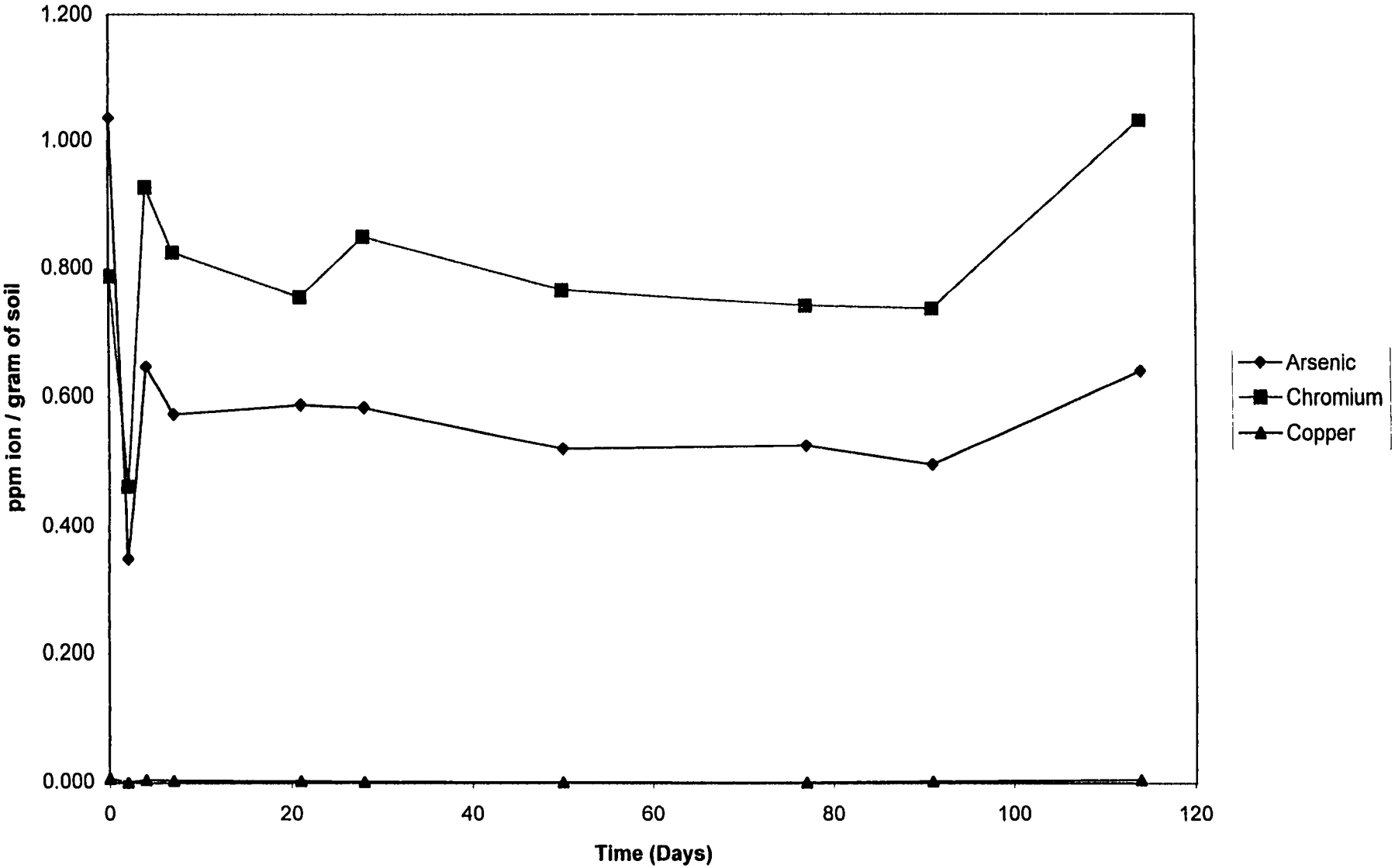
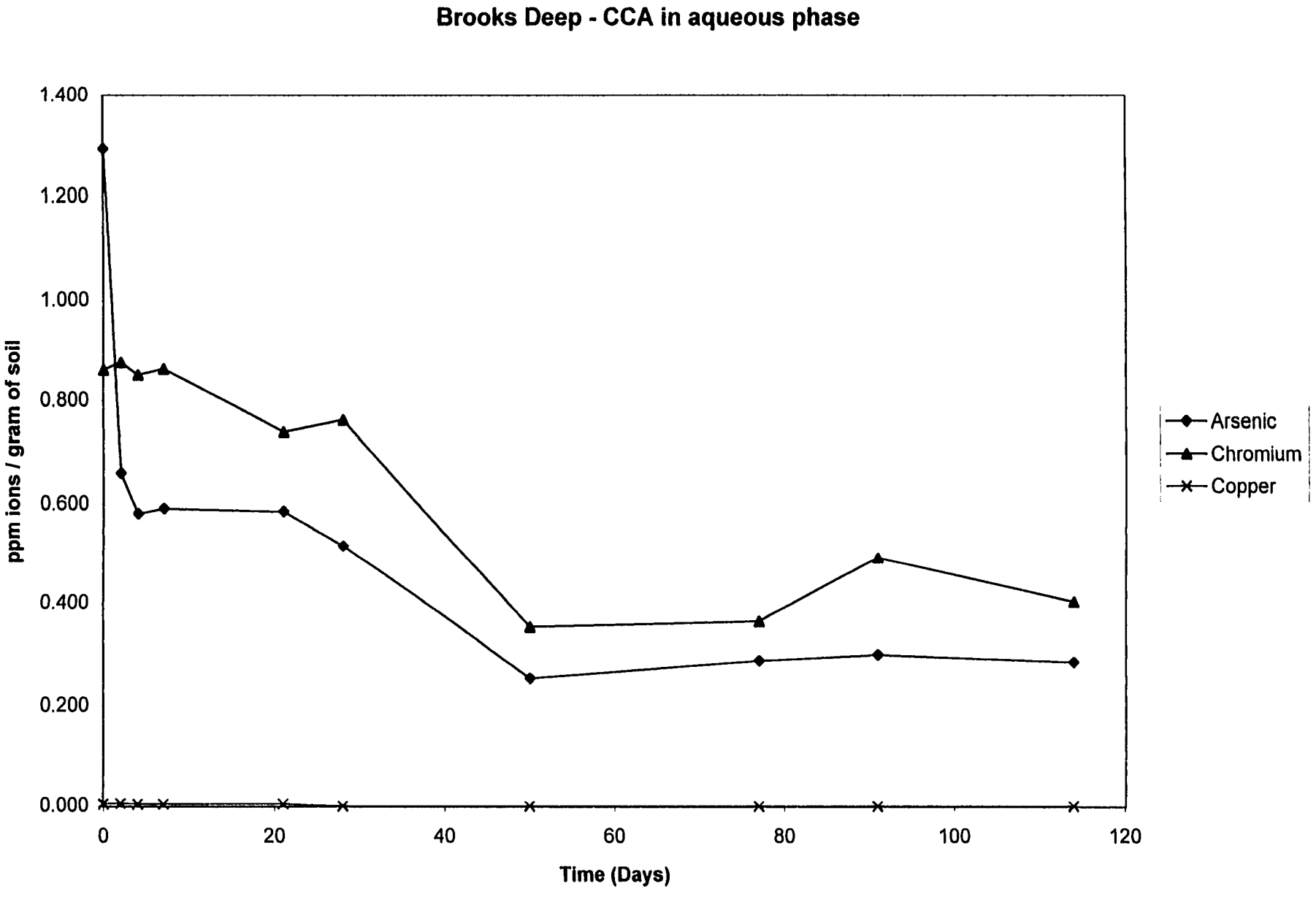
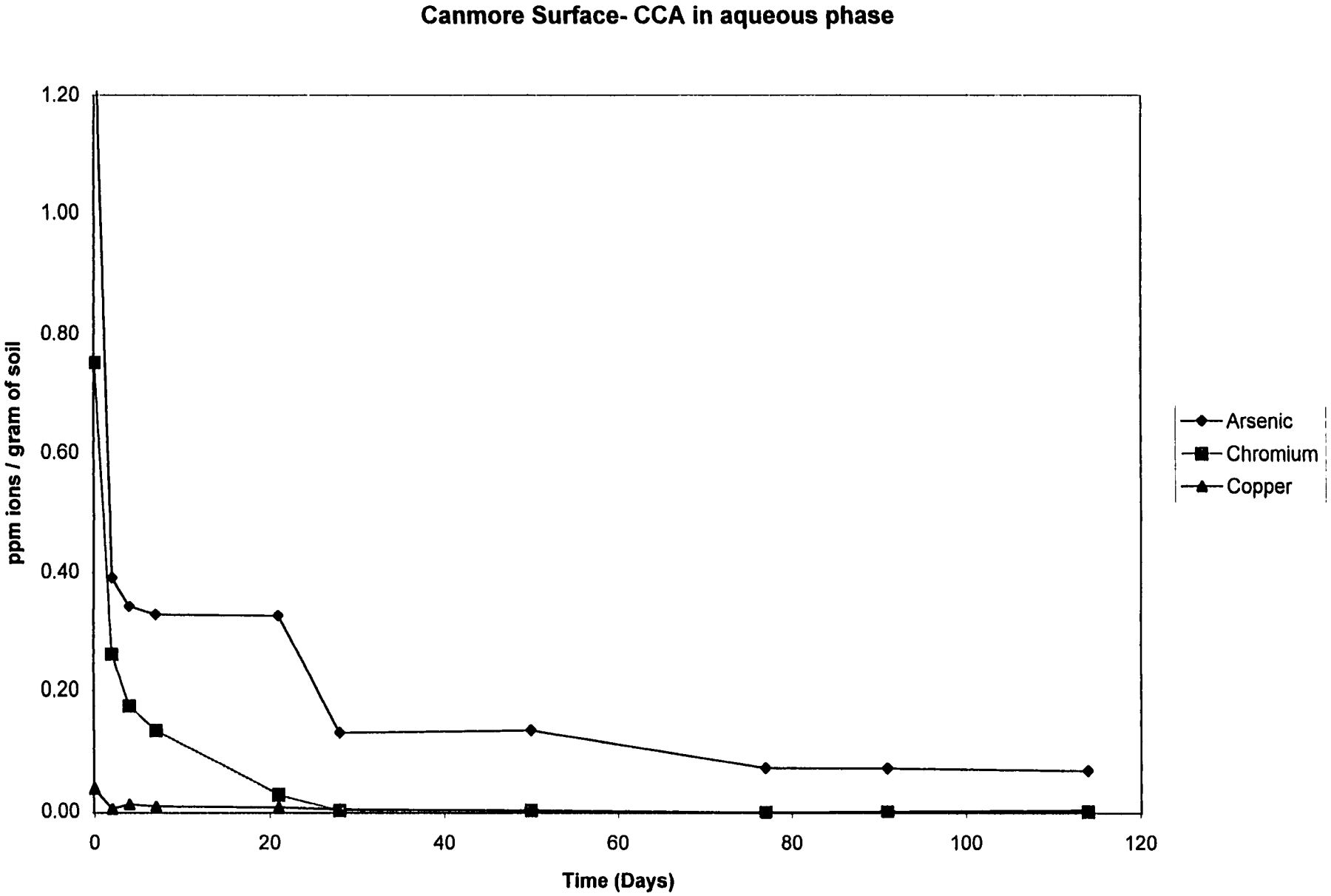
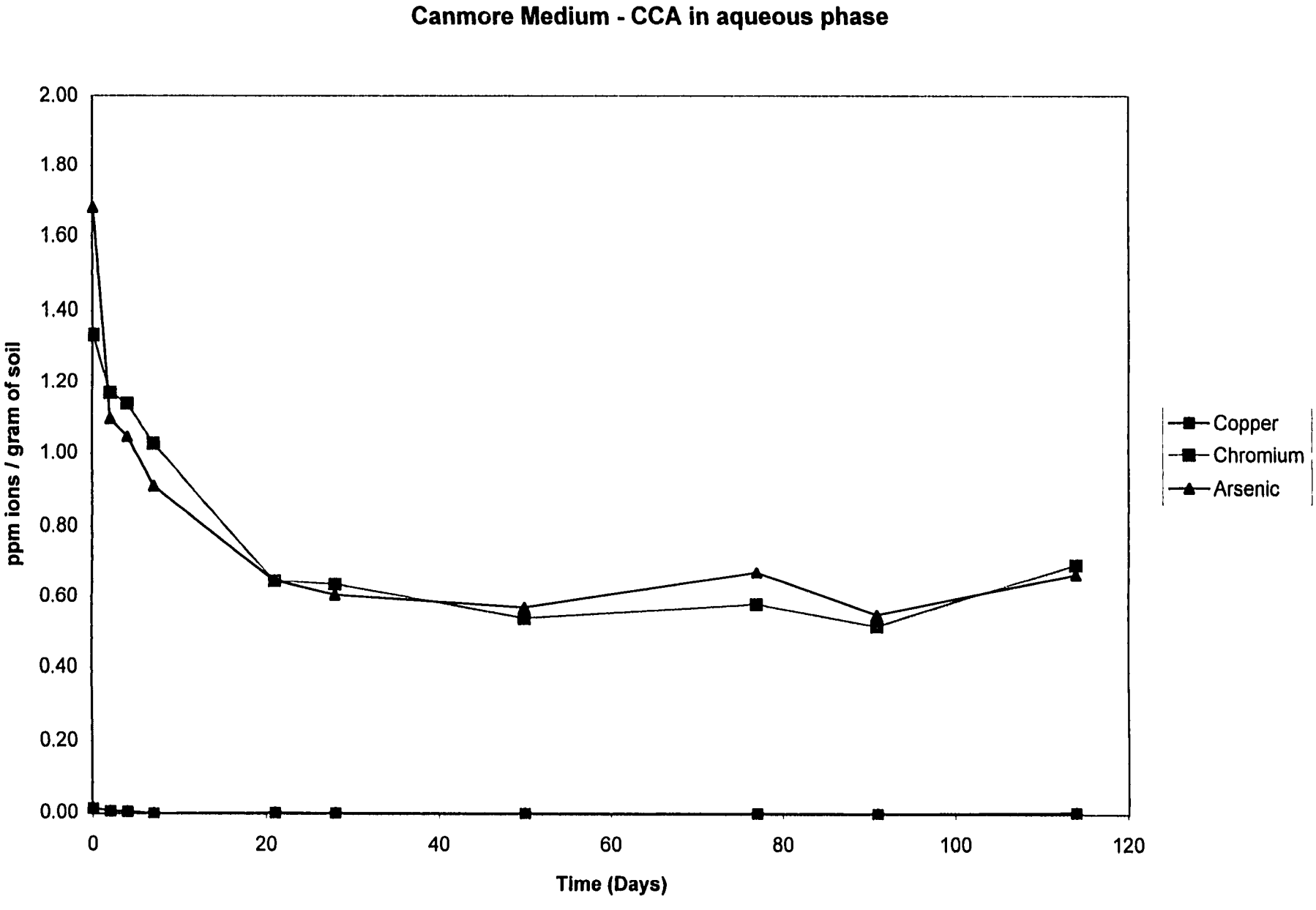


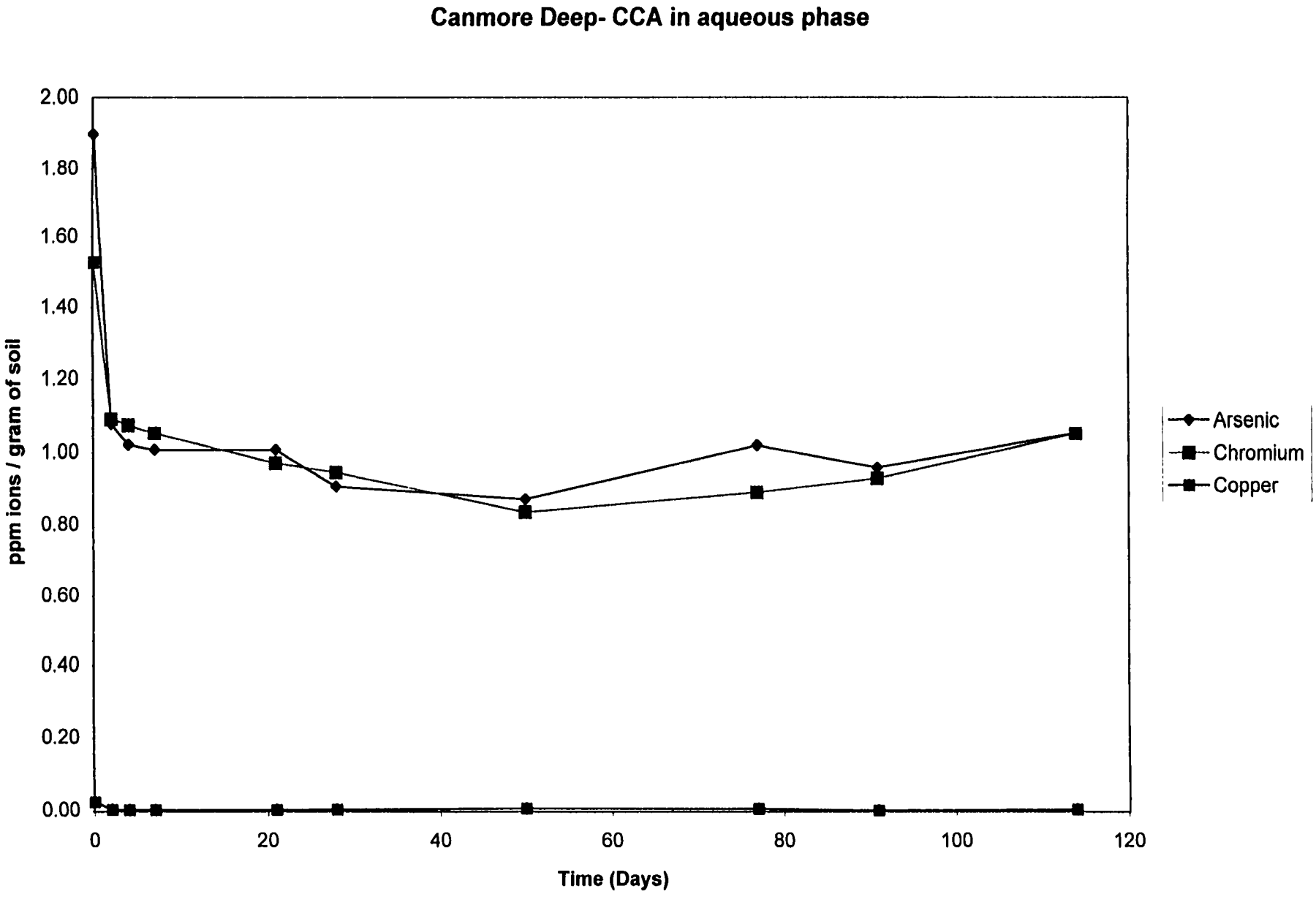
Figure C. 8 Brooks medium - CCA in aqueous phase

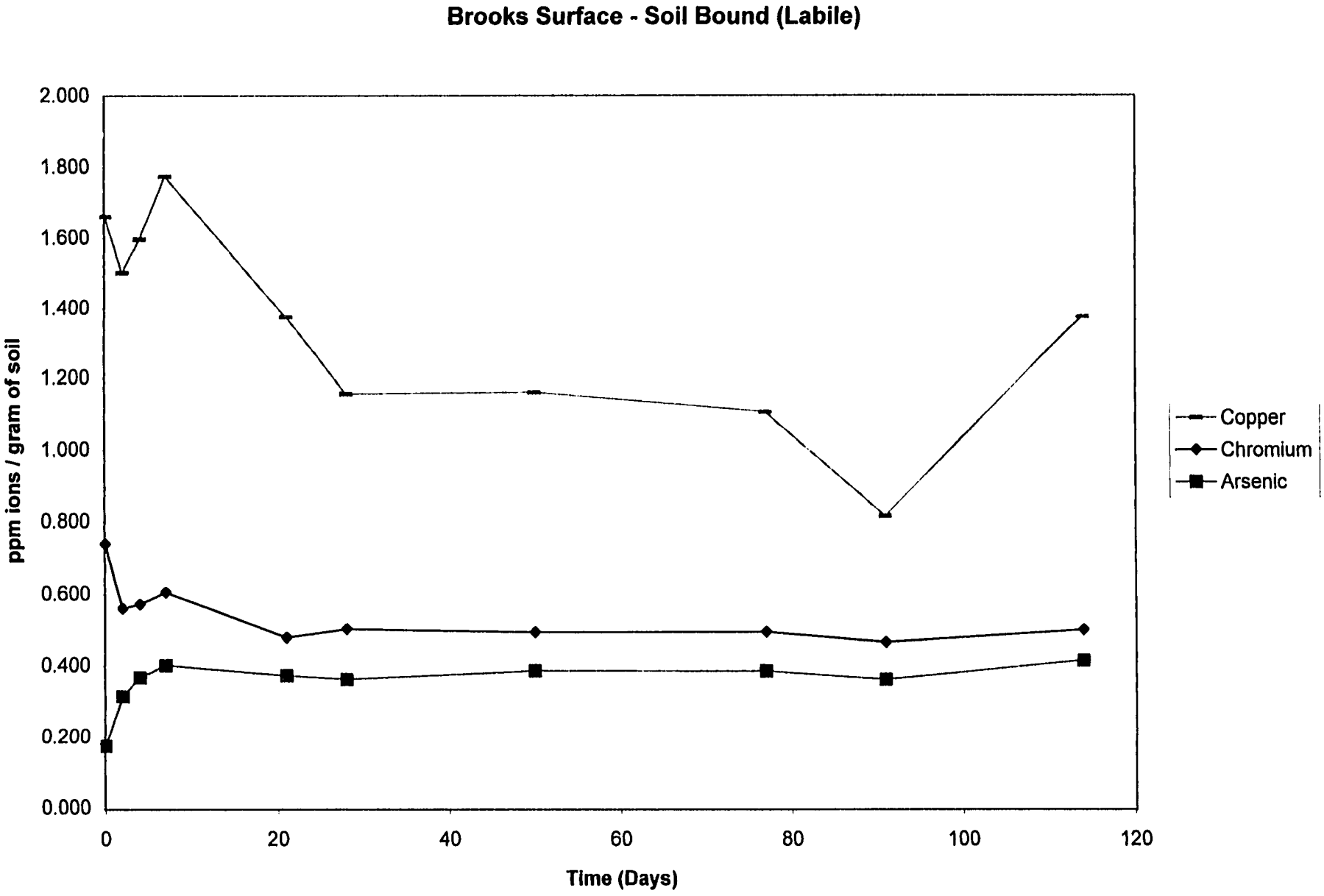


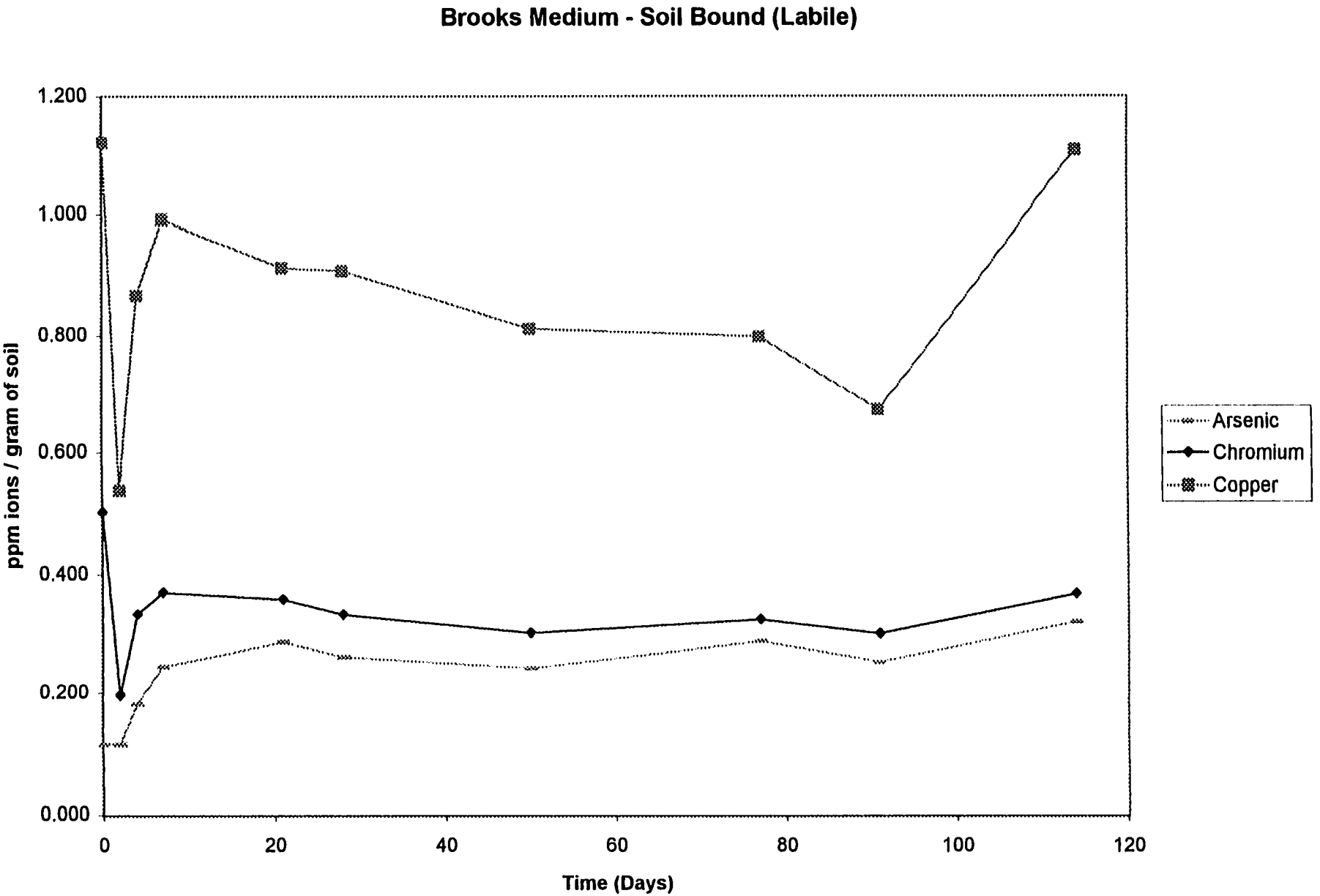

Brooks Deep - CCA in aqueous phase
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
Arsenic
Chromium
Copper

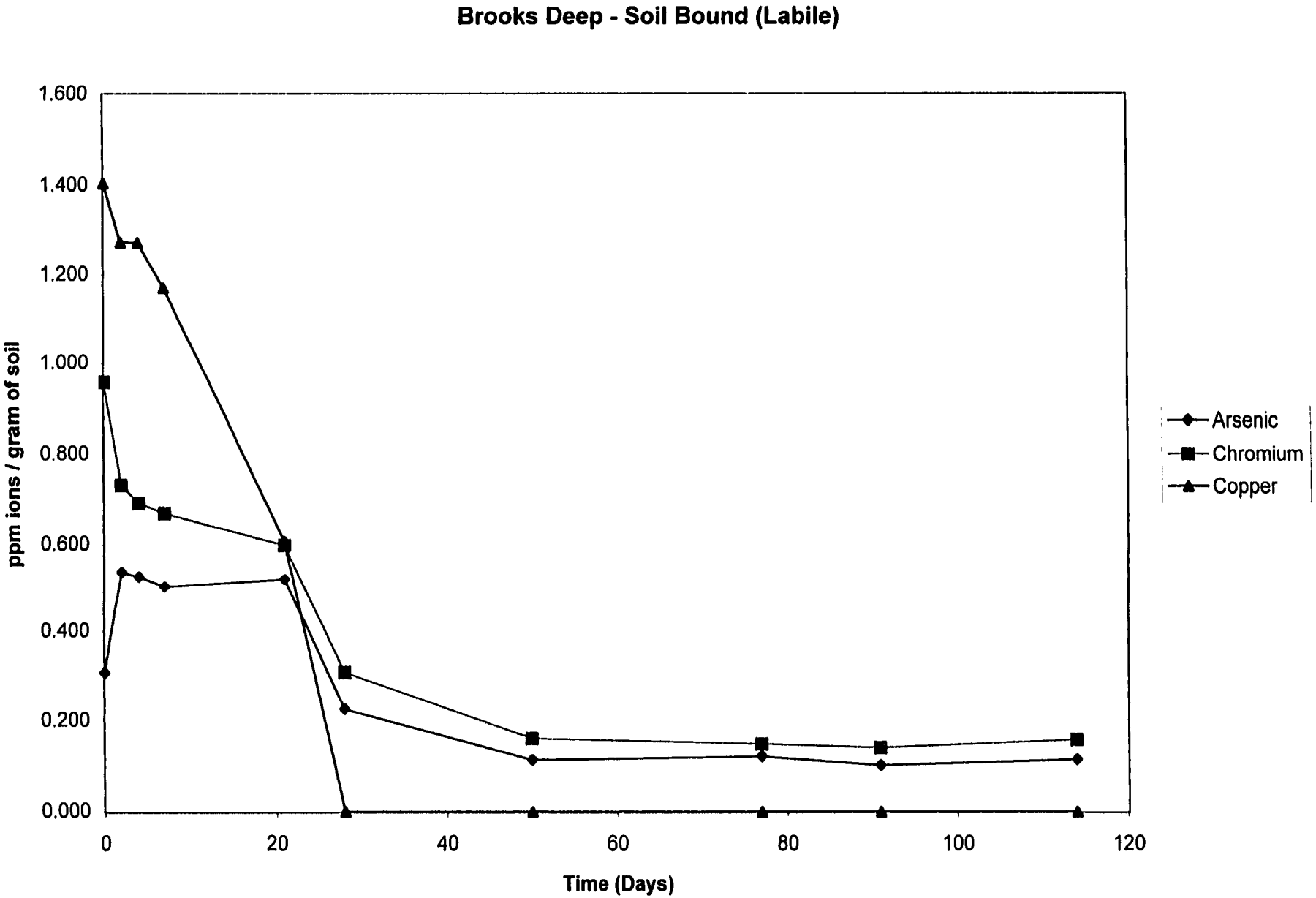

Canmore Surface- CCA in aqueous phase
ppm ions / gram of soil
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0
20
40
60
80
100
120
Time (Days)
Arsenic
Chromium
Copper

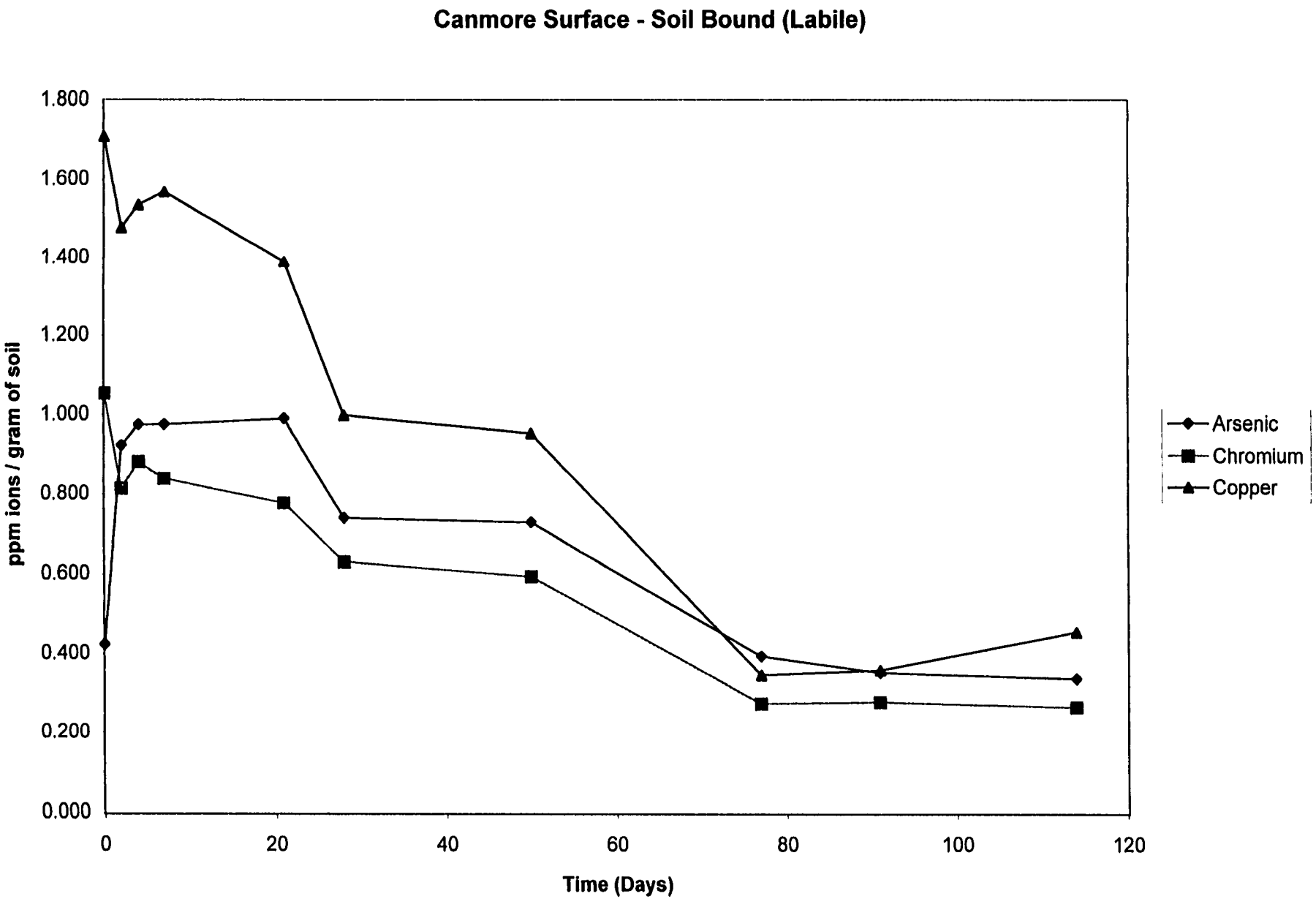

Canmore Medium - CCA in aqueous phase
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
Copper
Chromium
Arsenic

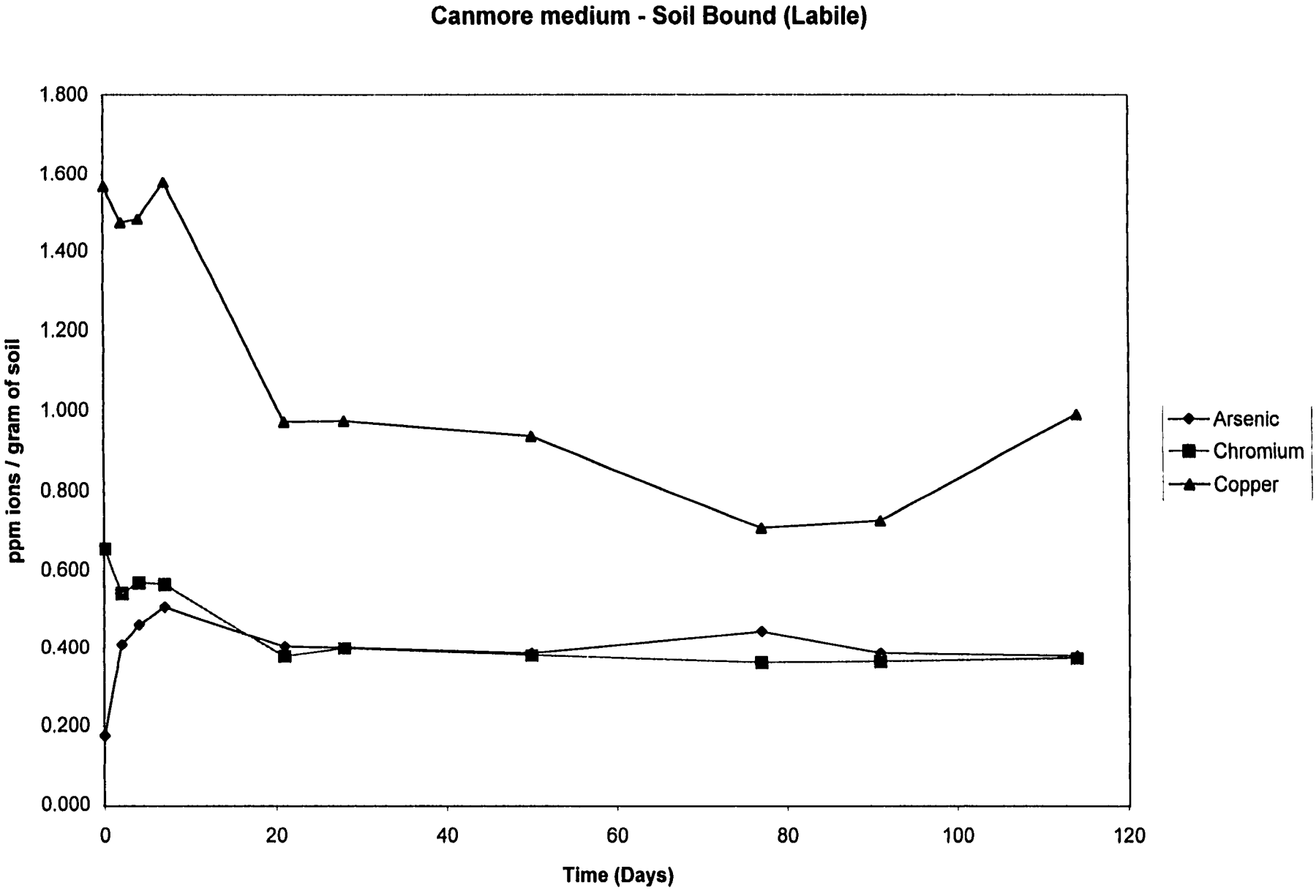

Canmore Deep- CCA in aqueous phase
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
Arsenic
Chromium
Copper

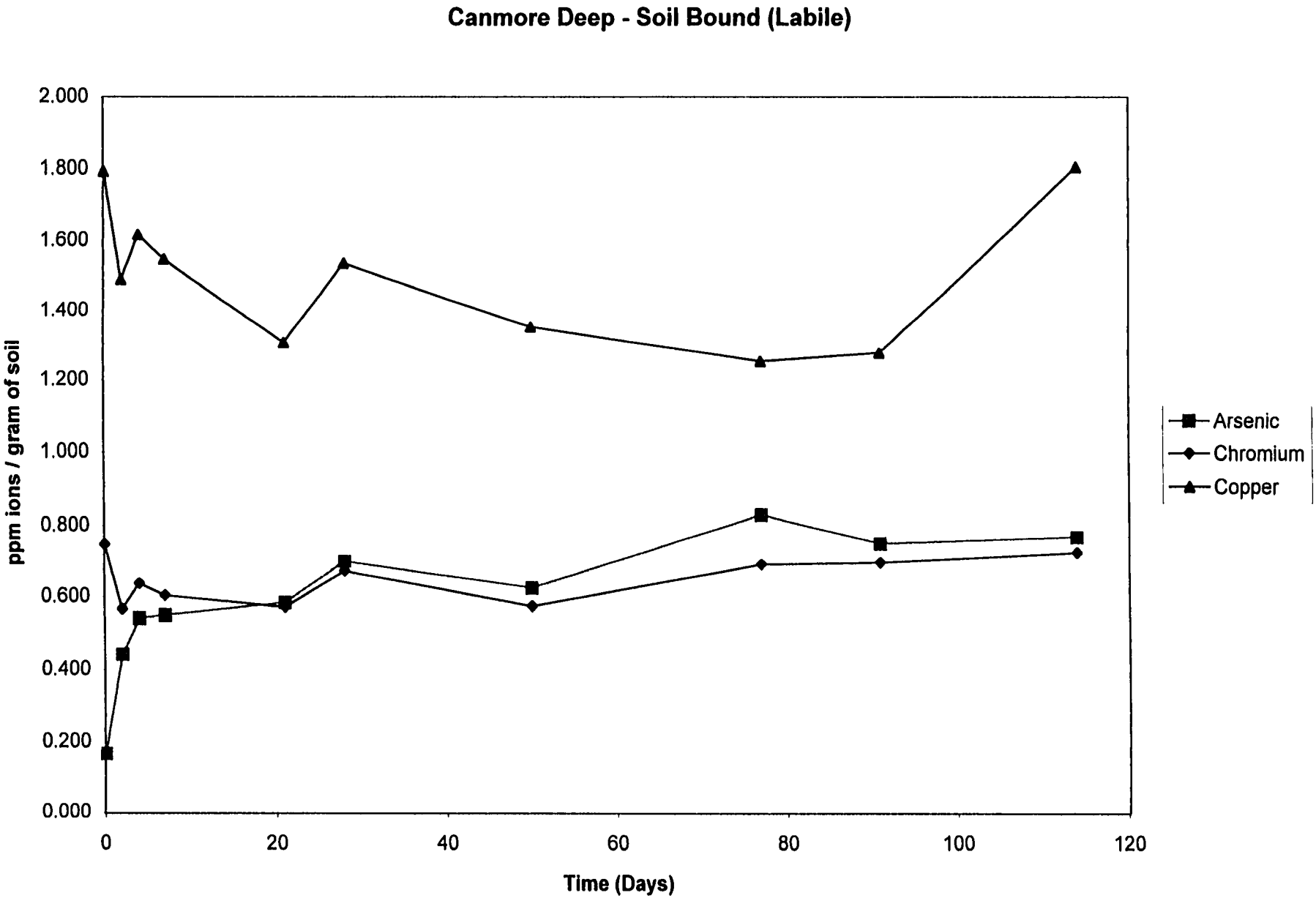

Brooks Surface - Soil Bound (Labile)
2.000
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
Copper
Chromium
Arsenic

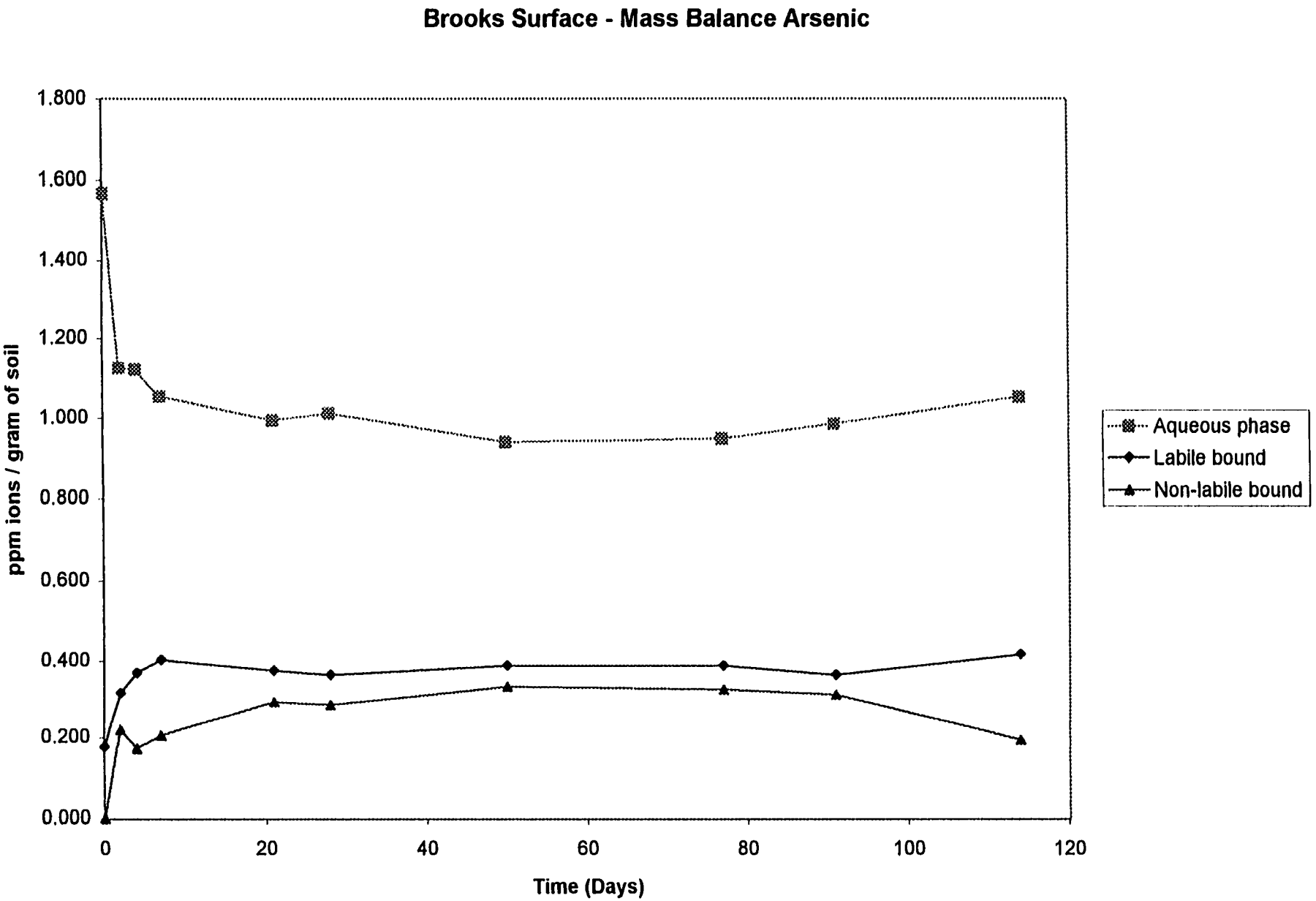

Brooks Medium - Soil Bound (Labile)
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
Arsenic
Chromium
Copper

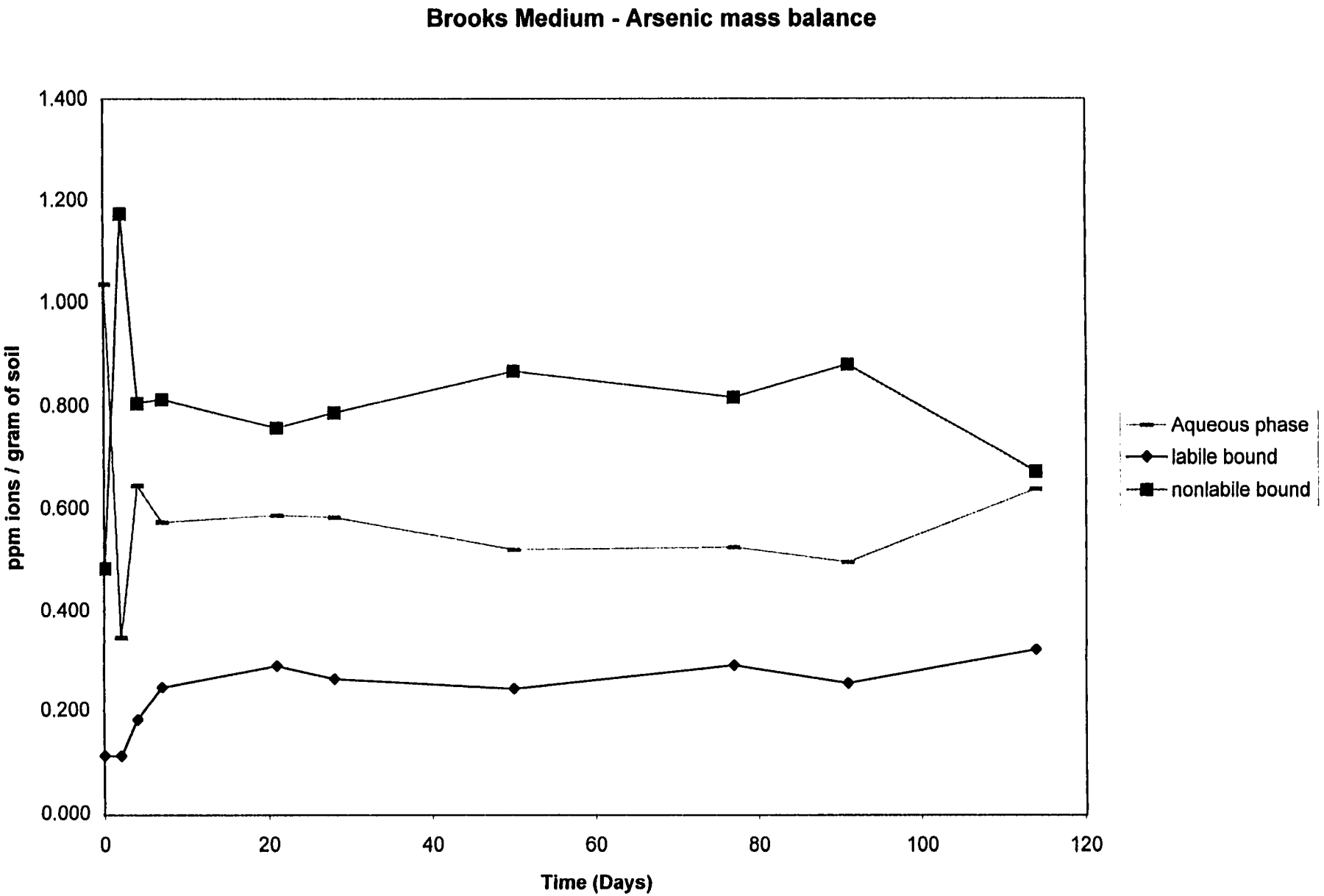

Brooks Deep - Soil Bound (Labile)
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
Arsenic
Chromium
Copper

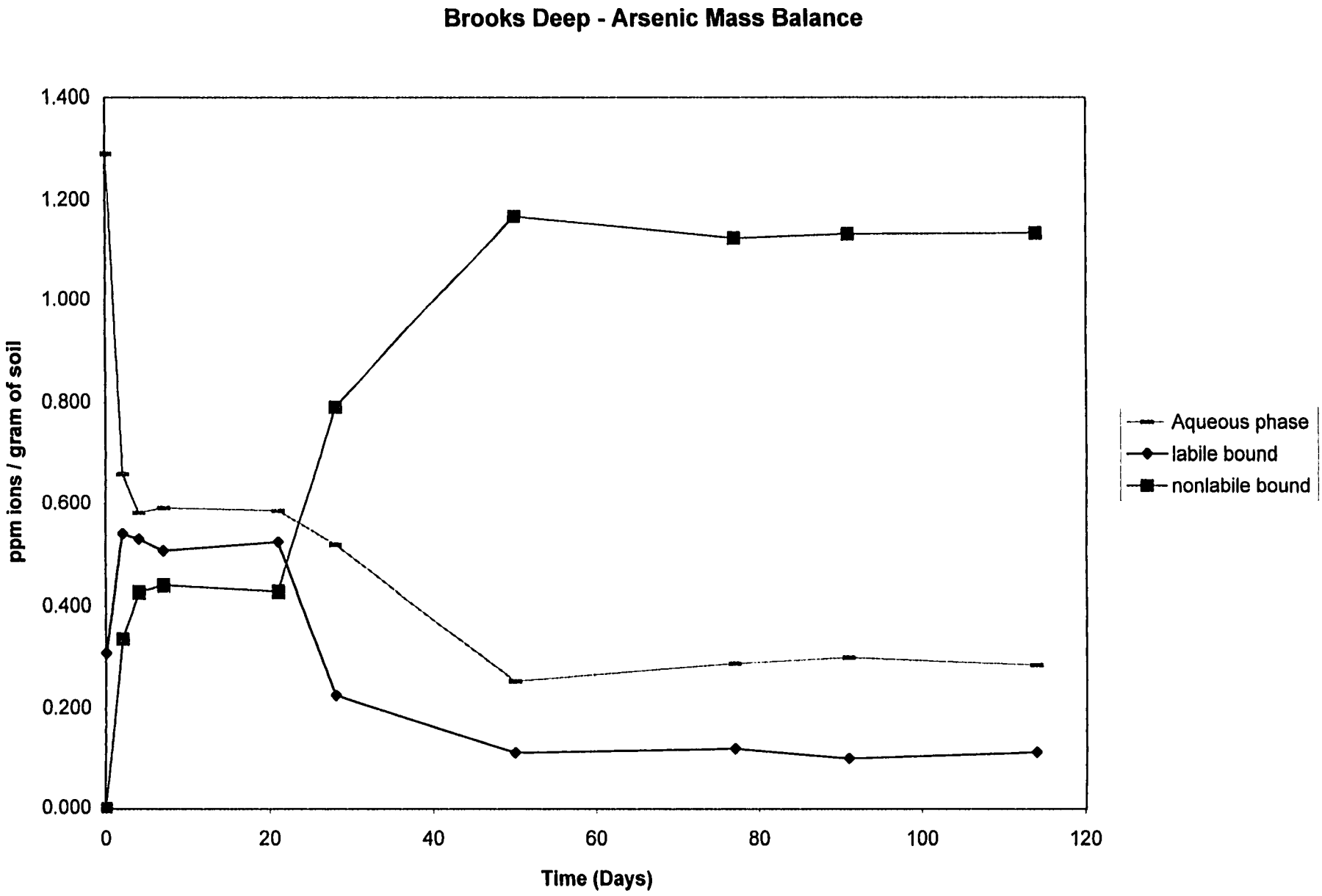

Canmore Surface - Soil Bound (Labile)
ppm ions / gram of soil
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
0
20
40
60
80
100
120
Time (Days)
Arsenic
Chromium
Copper

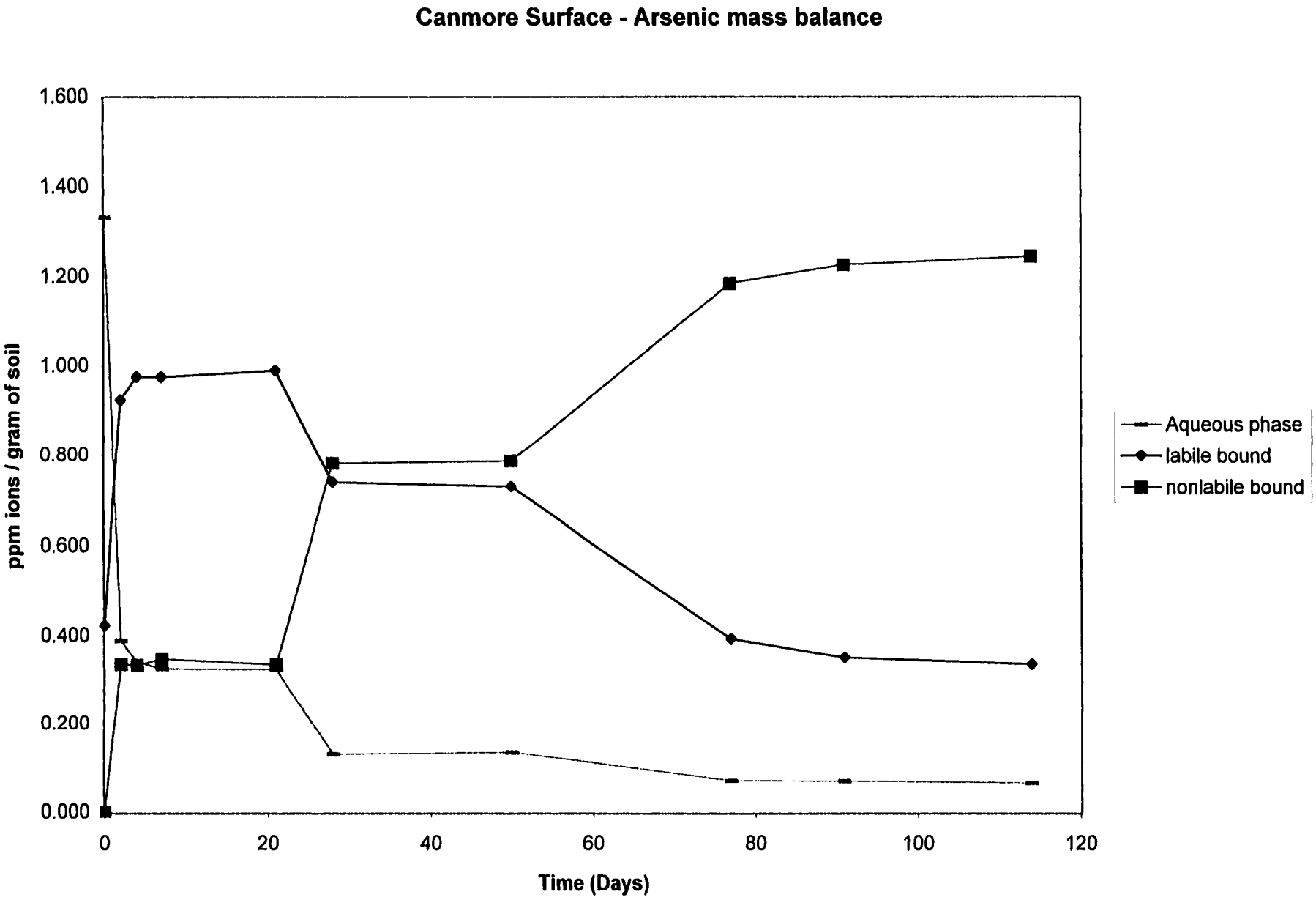

Canmore medium - Soil Bound (Labile)
ppm ions / gram of soil
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
0
20
40
60
80
100
120
Time (Days)
Arsenic
Chromium
Copper

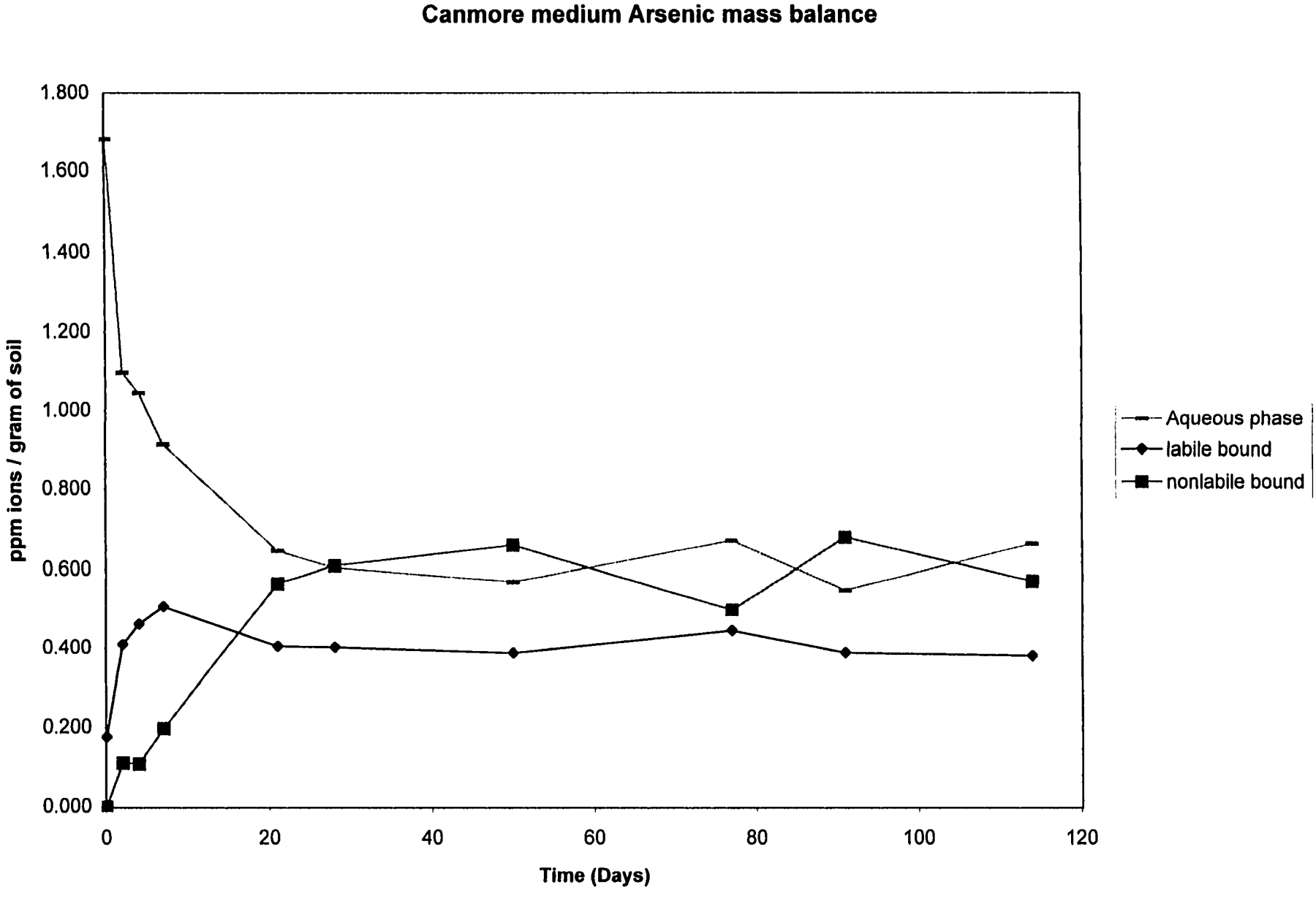

Canmore Deep - Soil Bound (Labile)
2.000
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
Arsenic
Chromium
Copper

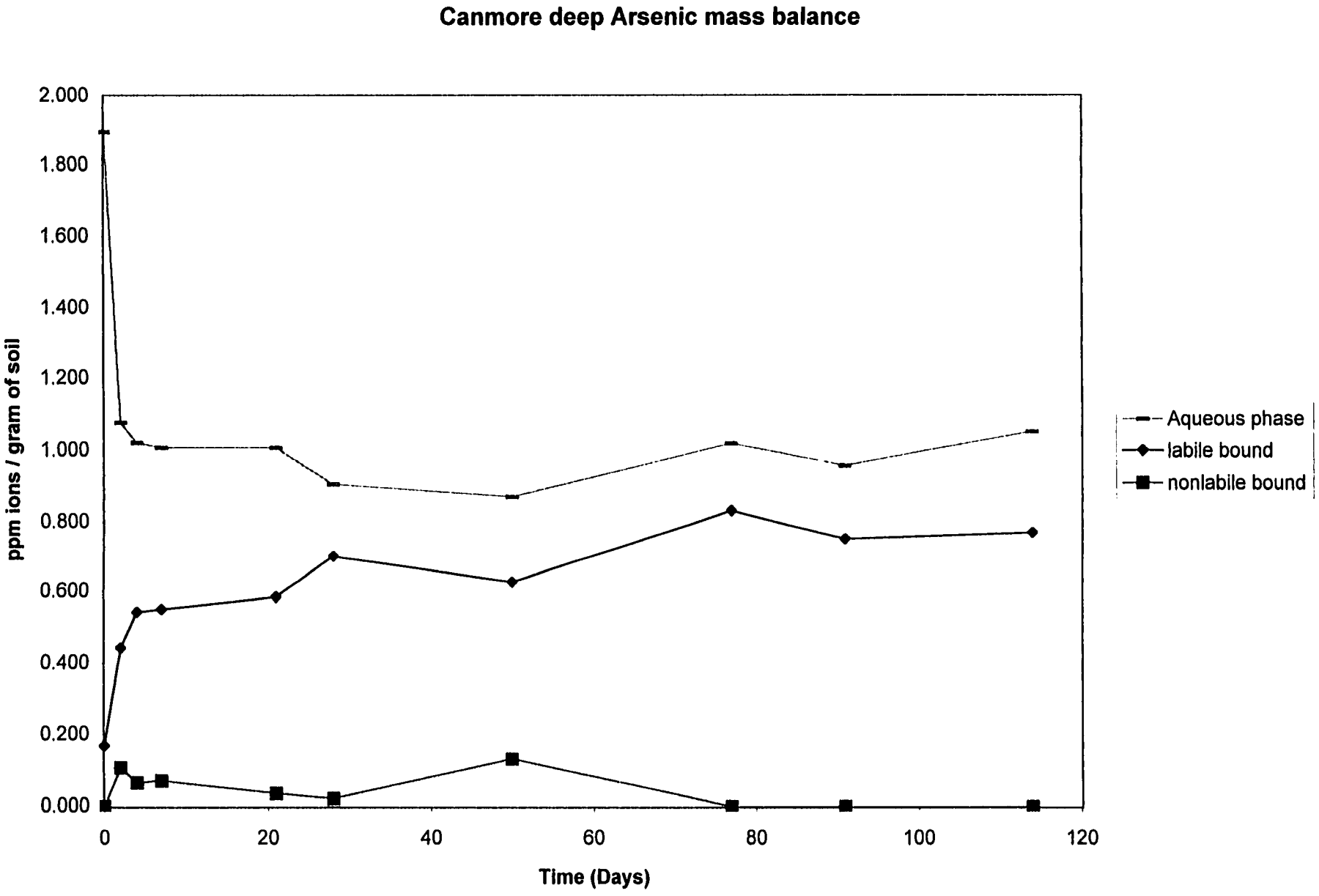

Brooks Surface - Mass Balance Arsenic
ppm ions / gram of soil
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
0
20
40
60
80
100
120
Time (Days)
Aqueous phase
Labile bound
Non-labile bound

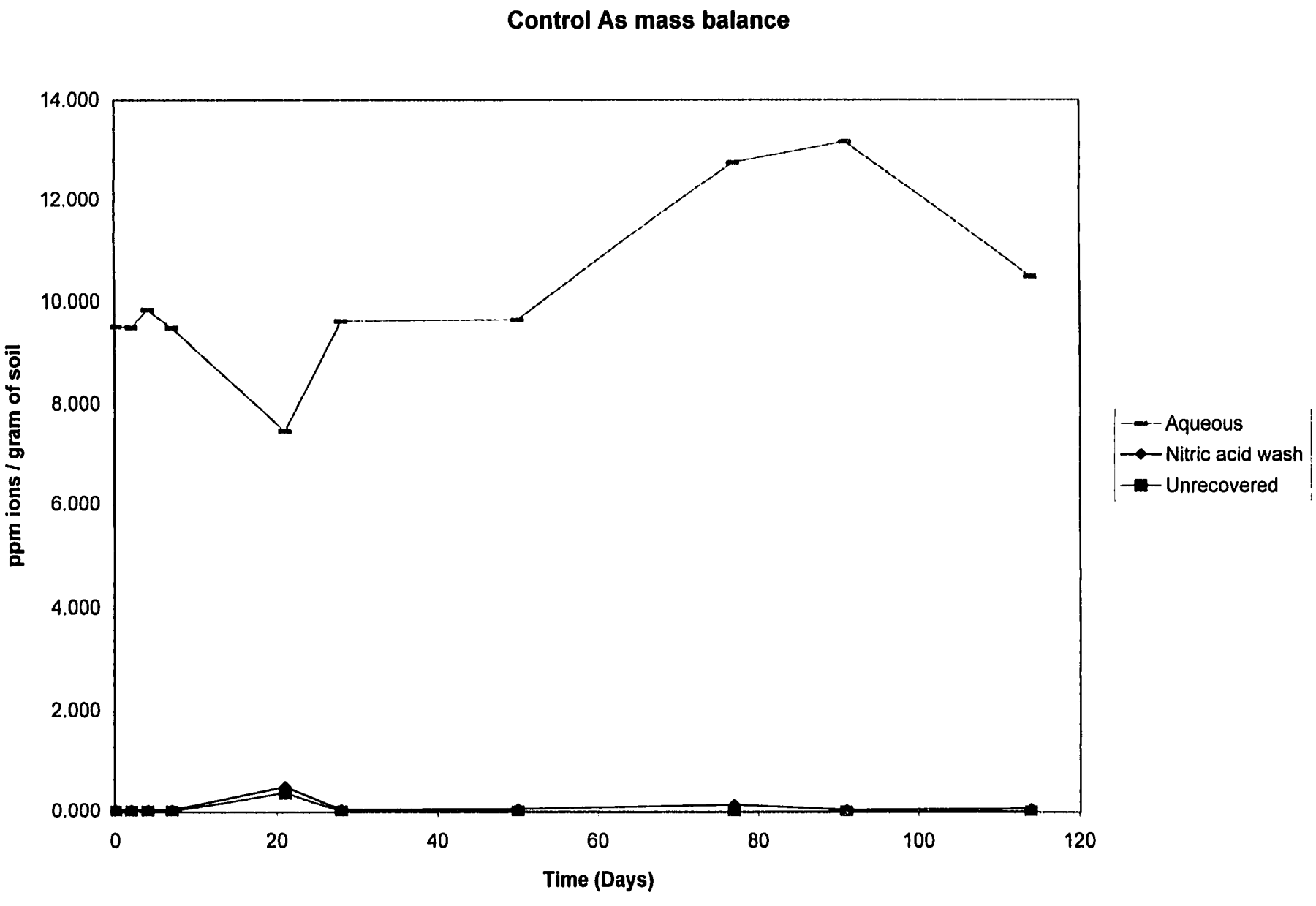

Brooks Medium - Arsenic mass balance
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
Aqueous phase
labile bound
nonlabile bound

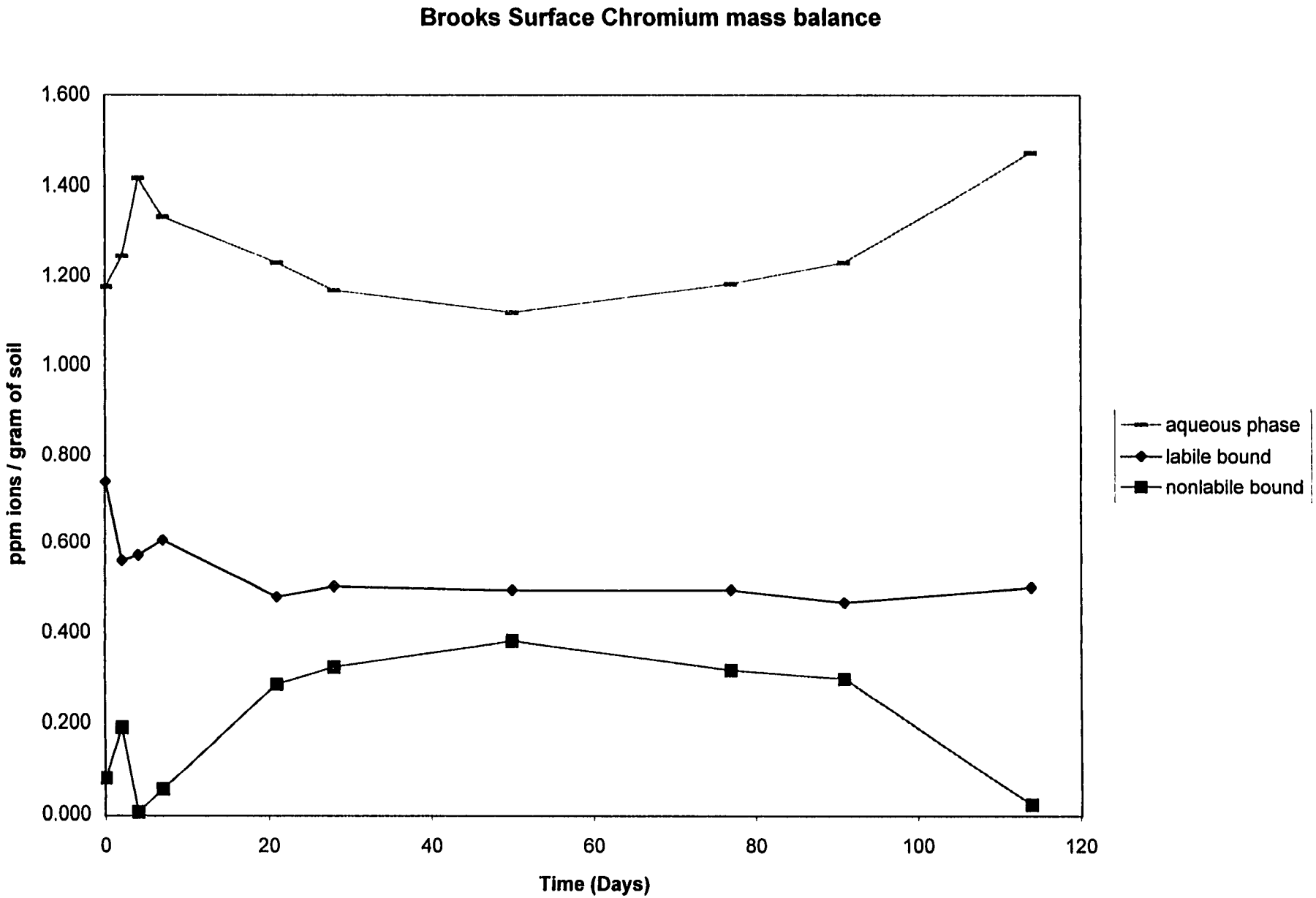

Brooks Deep - Arsenic Mass Balance
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
Aqueous phase
labile bound
nonlabile bound

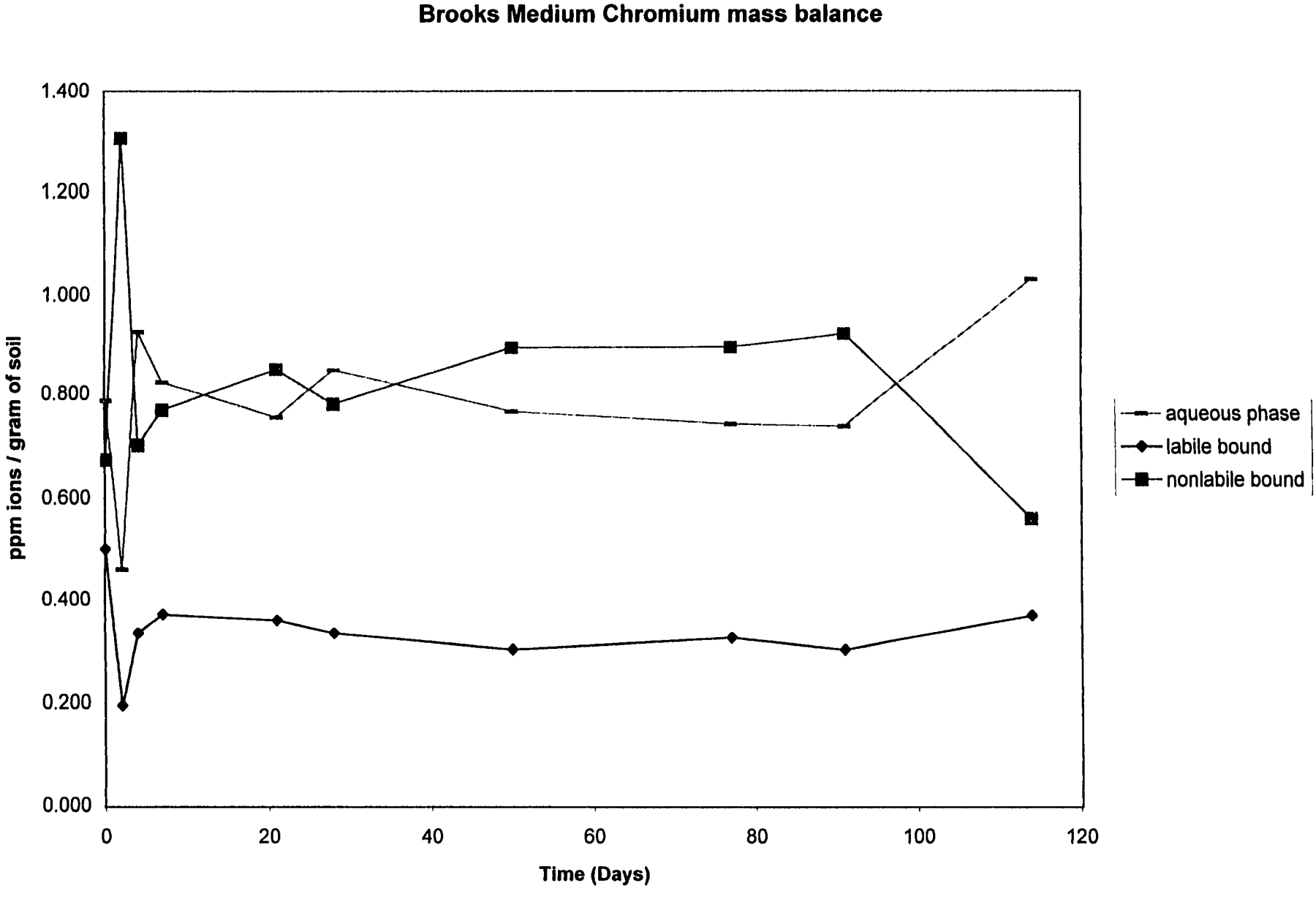

Canmore Surface - Arsenic mass balance
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
Aqueous phase
labile bound
nonlabile bound

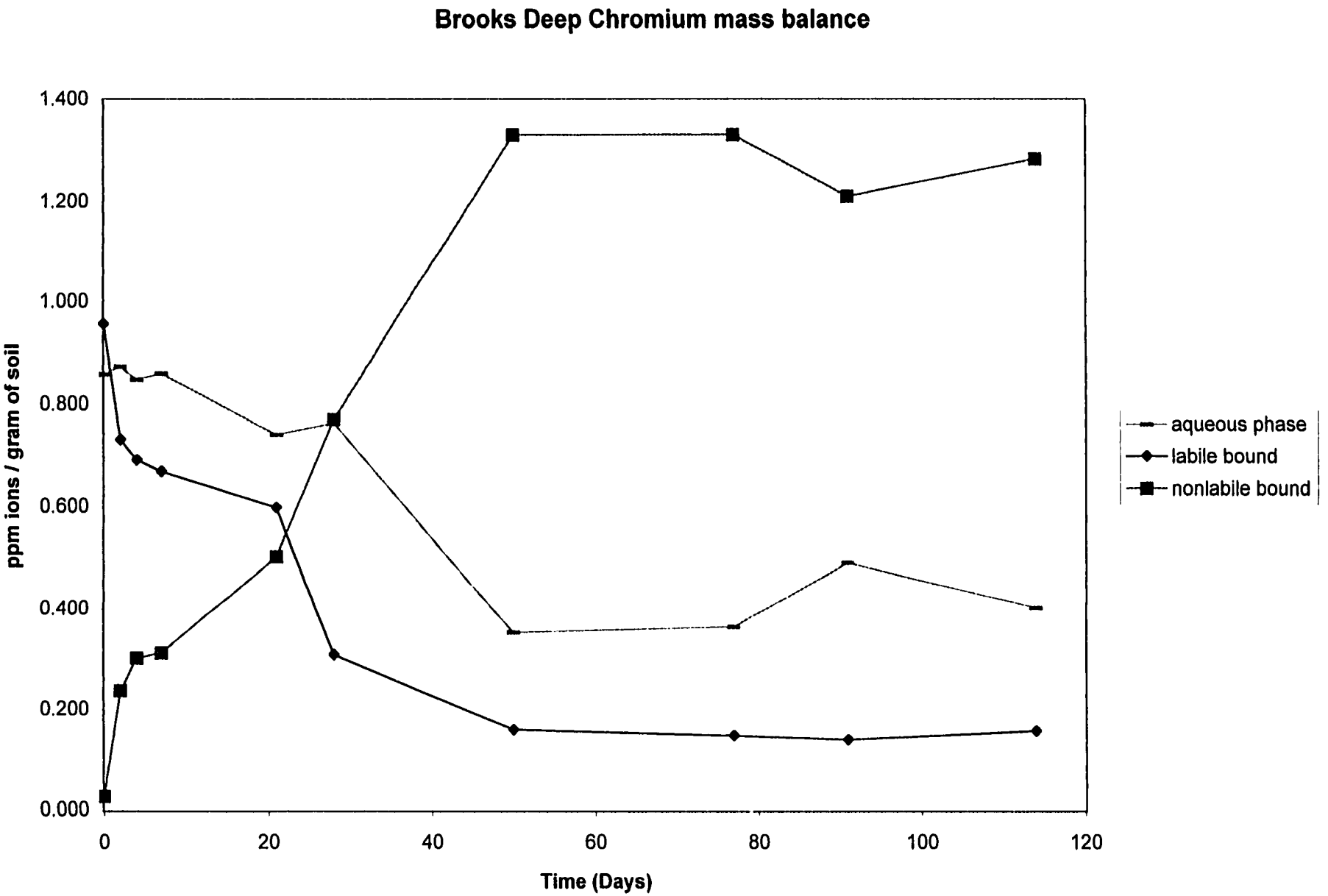

Canmore medium Arsenic mass balance
ppm ions / gram of soil
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
0
20
40
60
80
100
120
Time (Days)
Aqueous phase
labile bound
nonlabile bound

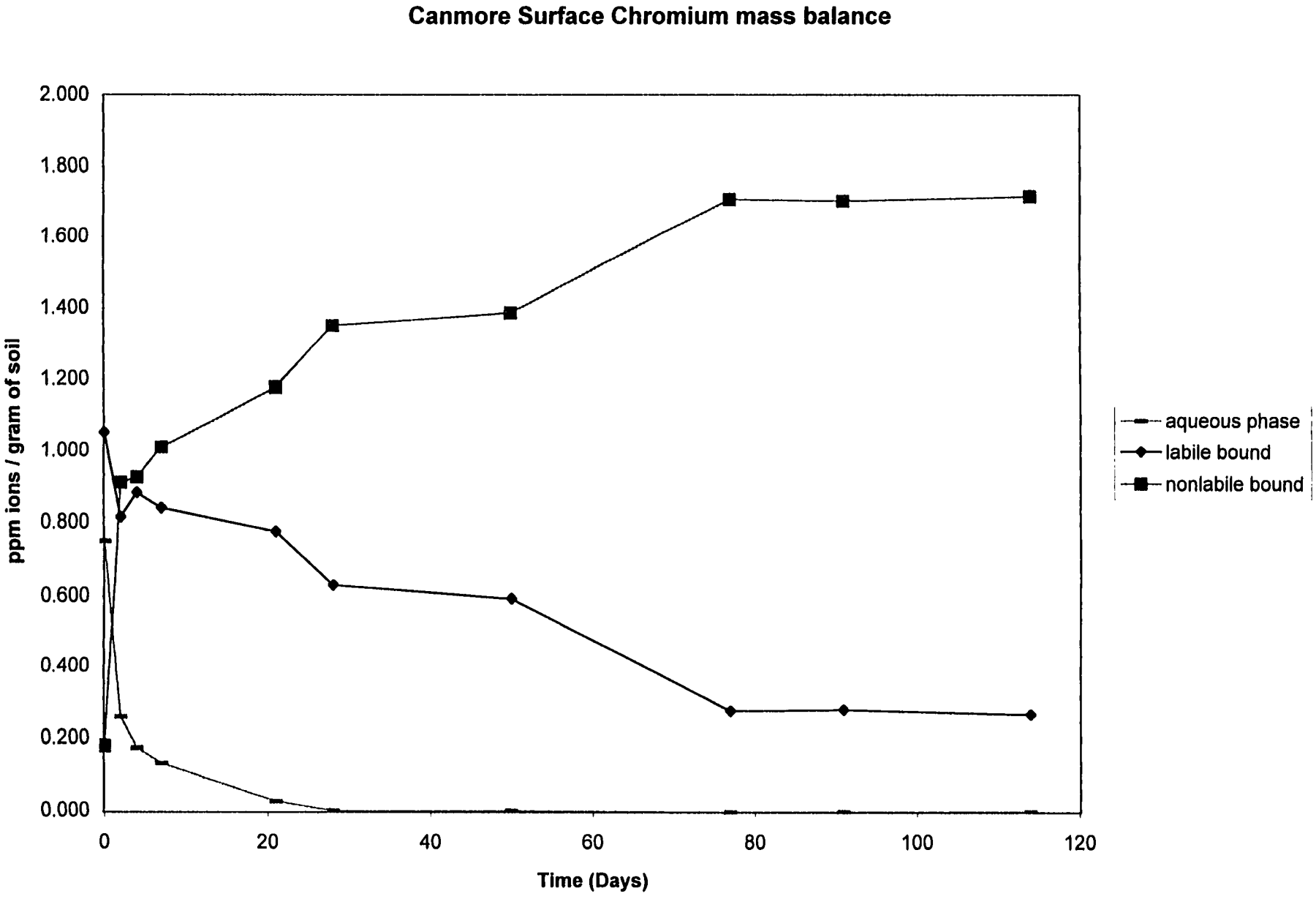

Canmore deep Arsenic mass balance
2.000
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
Aqueous phase
labile bound
nonlabile bound

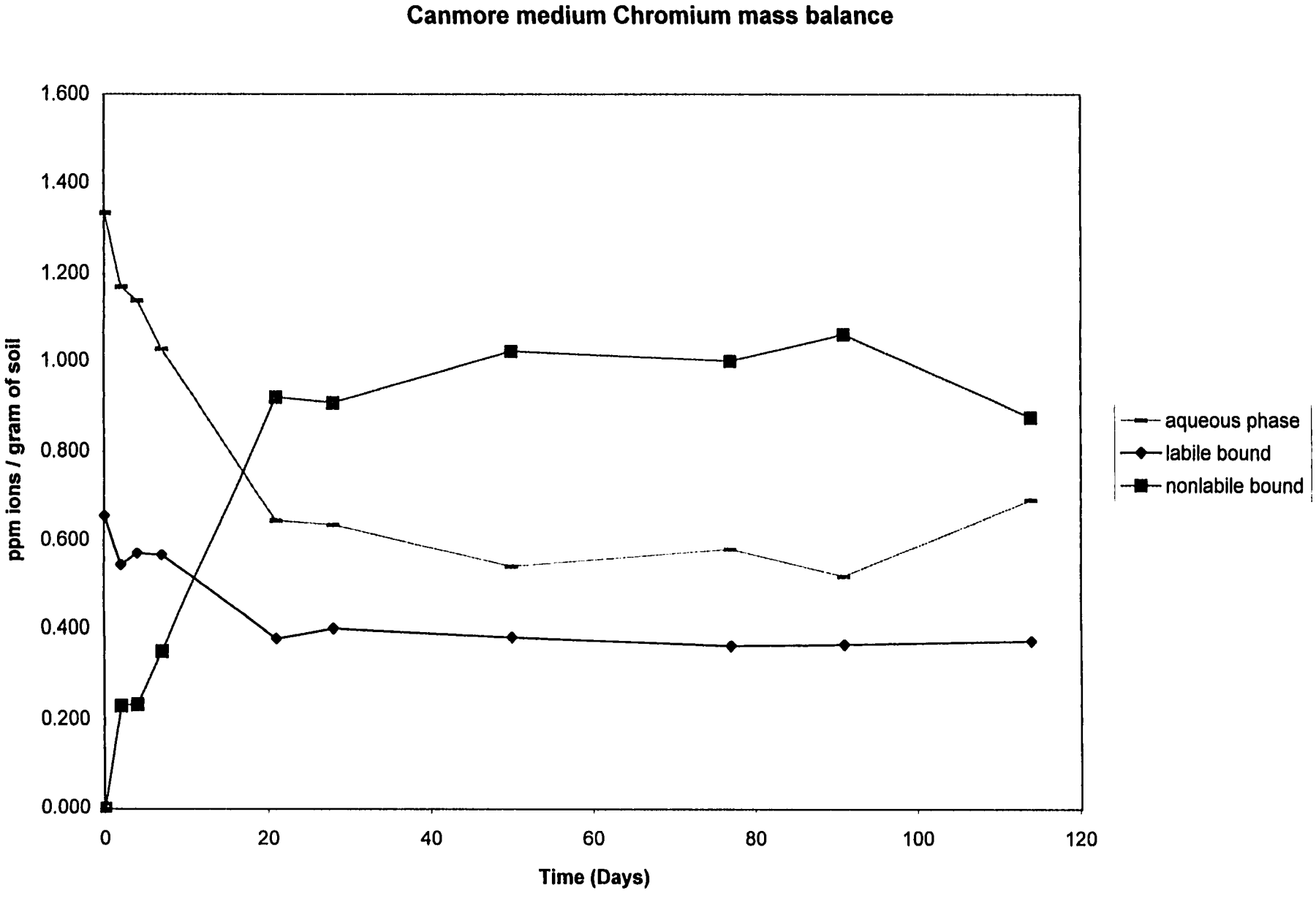

Control As mass balance
14.000
12.000
10.000
8.000
6.000
4.000
2.000
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
Aqueous
Nitric acid wash
Unrecovered

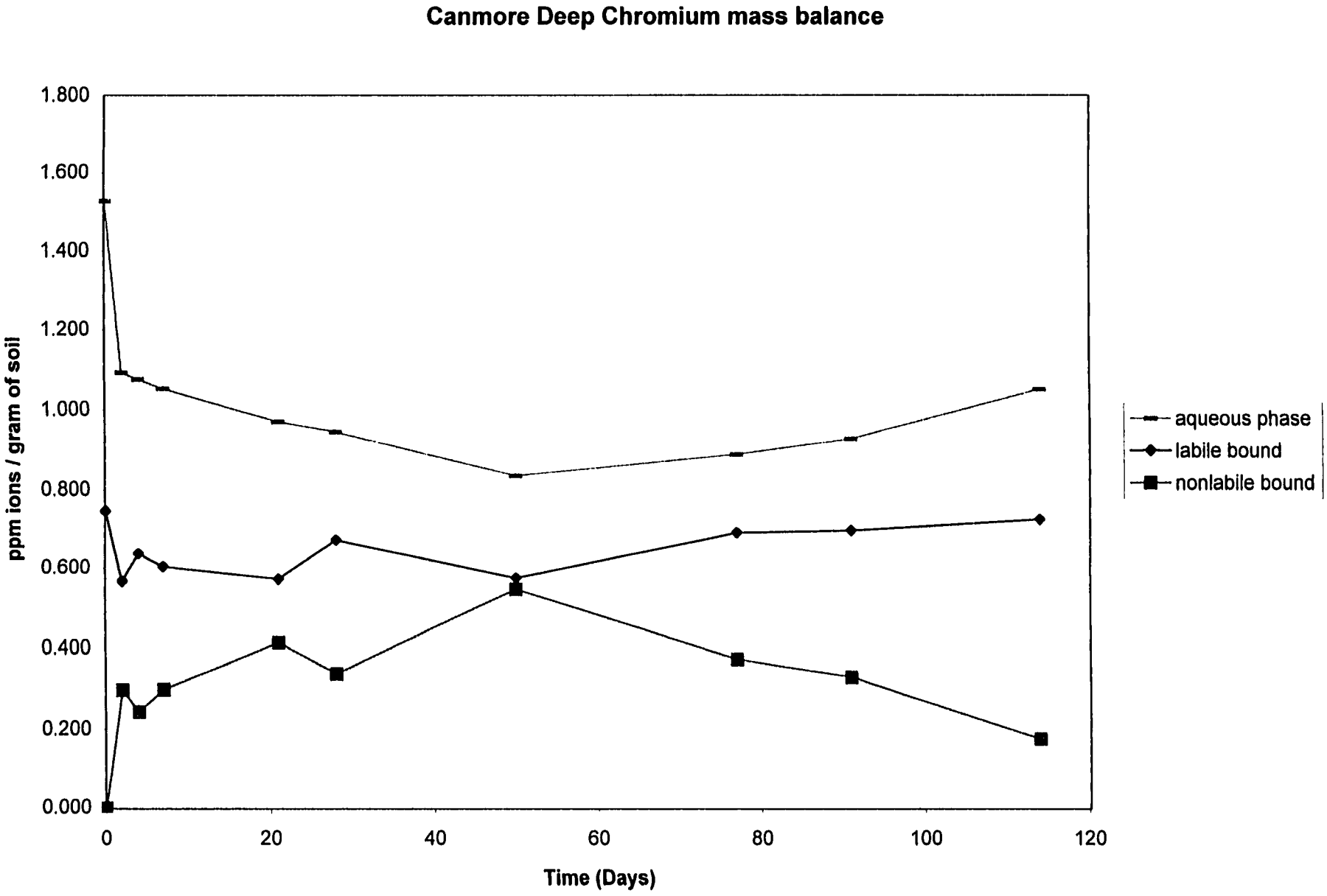

Brooks Surface Chromium mass balance
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
aqueous phase
labile bound
nonlabile bound

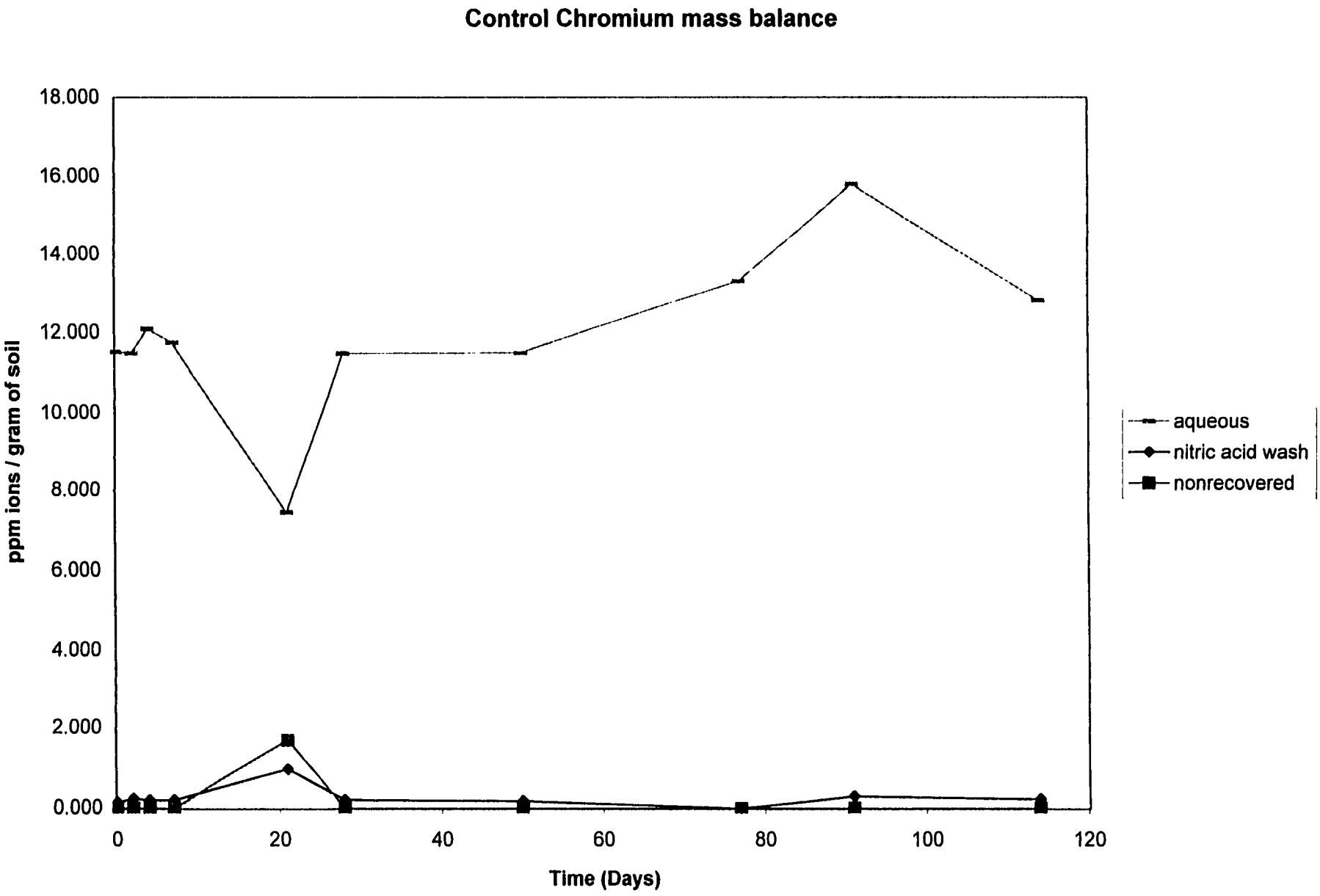

Brooks Medium Chromium mass balance
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
aqueous phase
labile bound
nonlabile bound

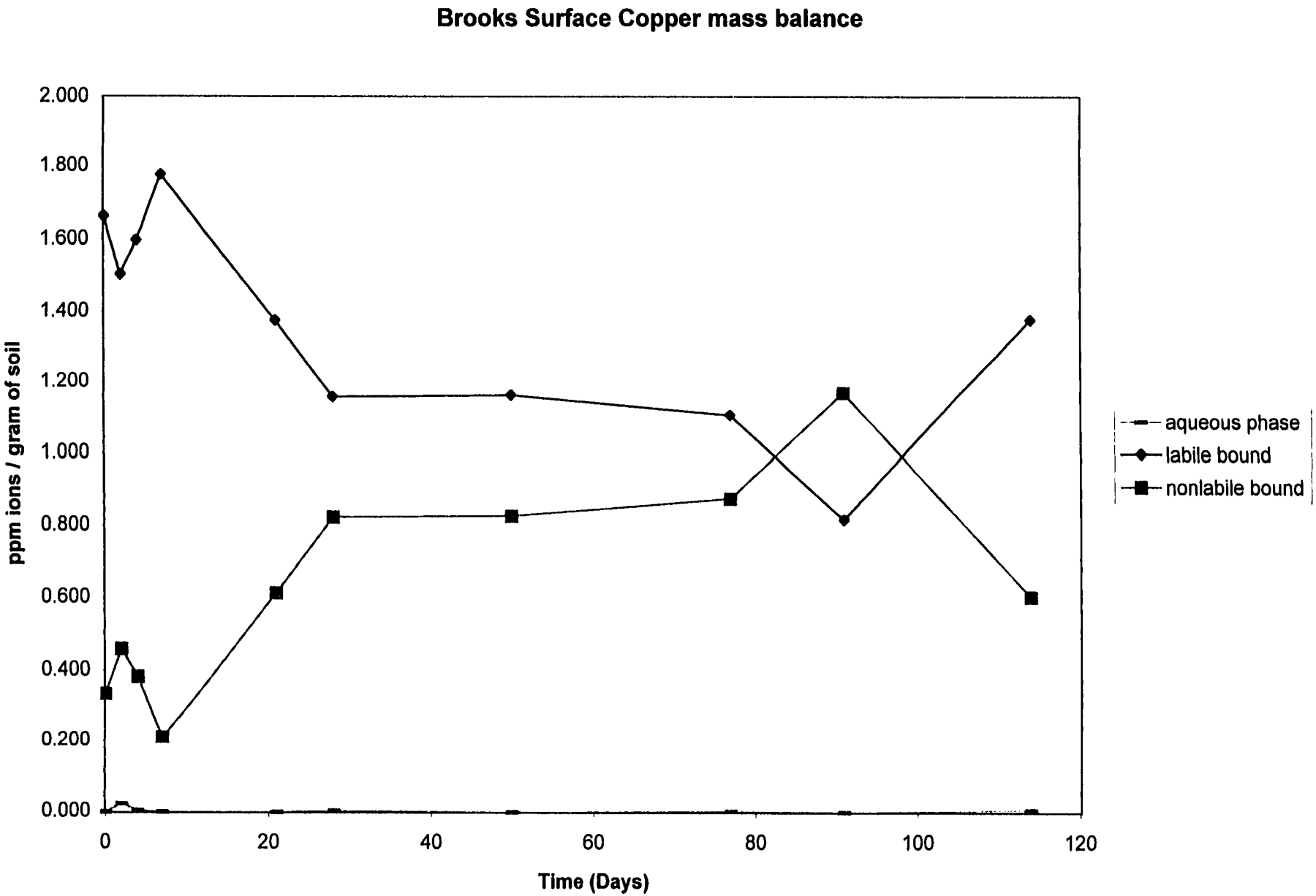

Brooks Deep Chromium mass balance
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
aqueous phase
labile bound
nonlabile bound

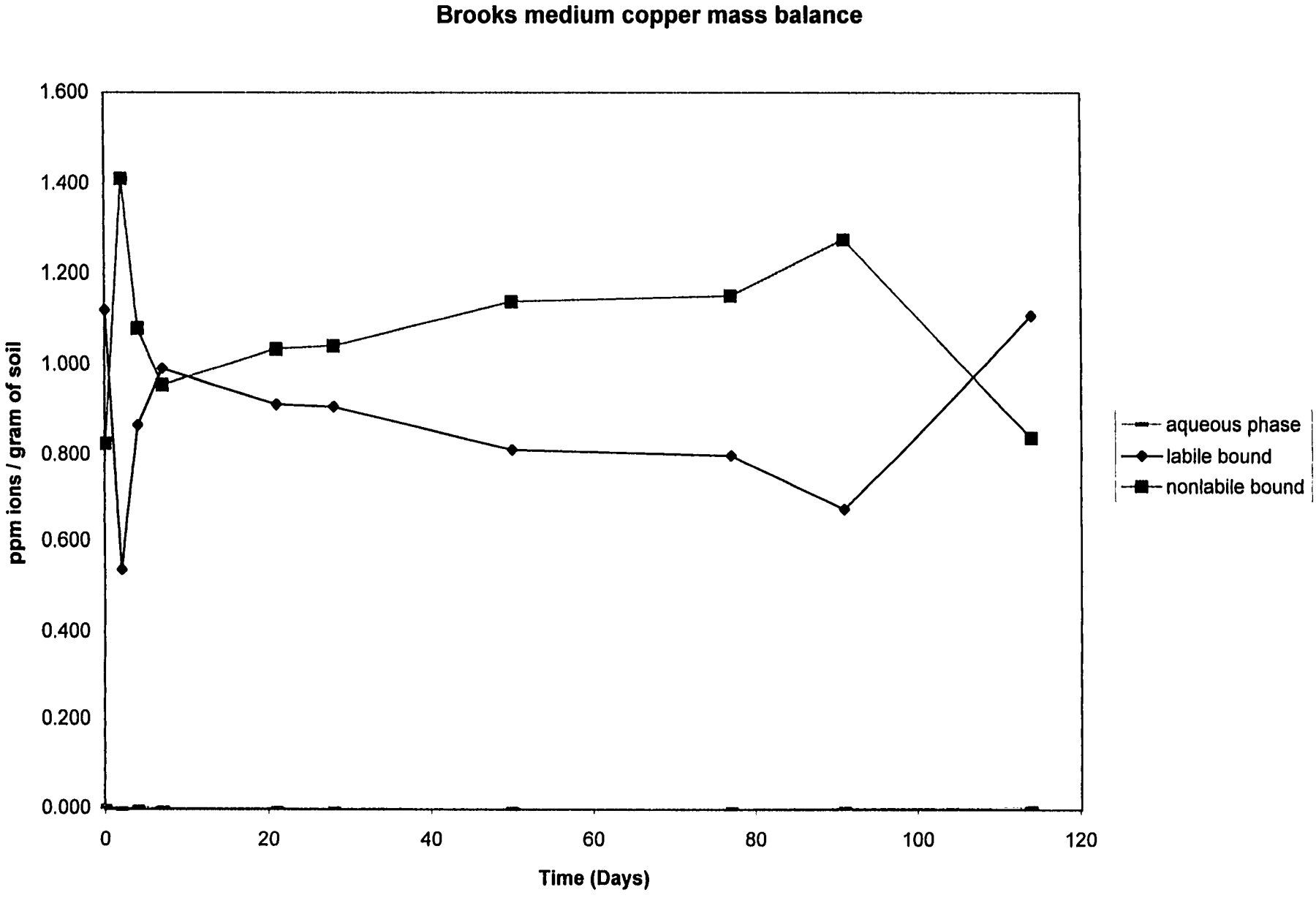

Canmore Surface Chromium mass balance
2.000
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
aqueous phase
labile bound
nonlabile bound

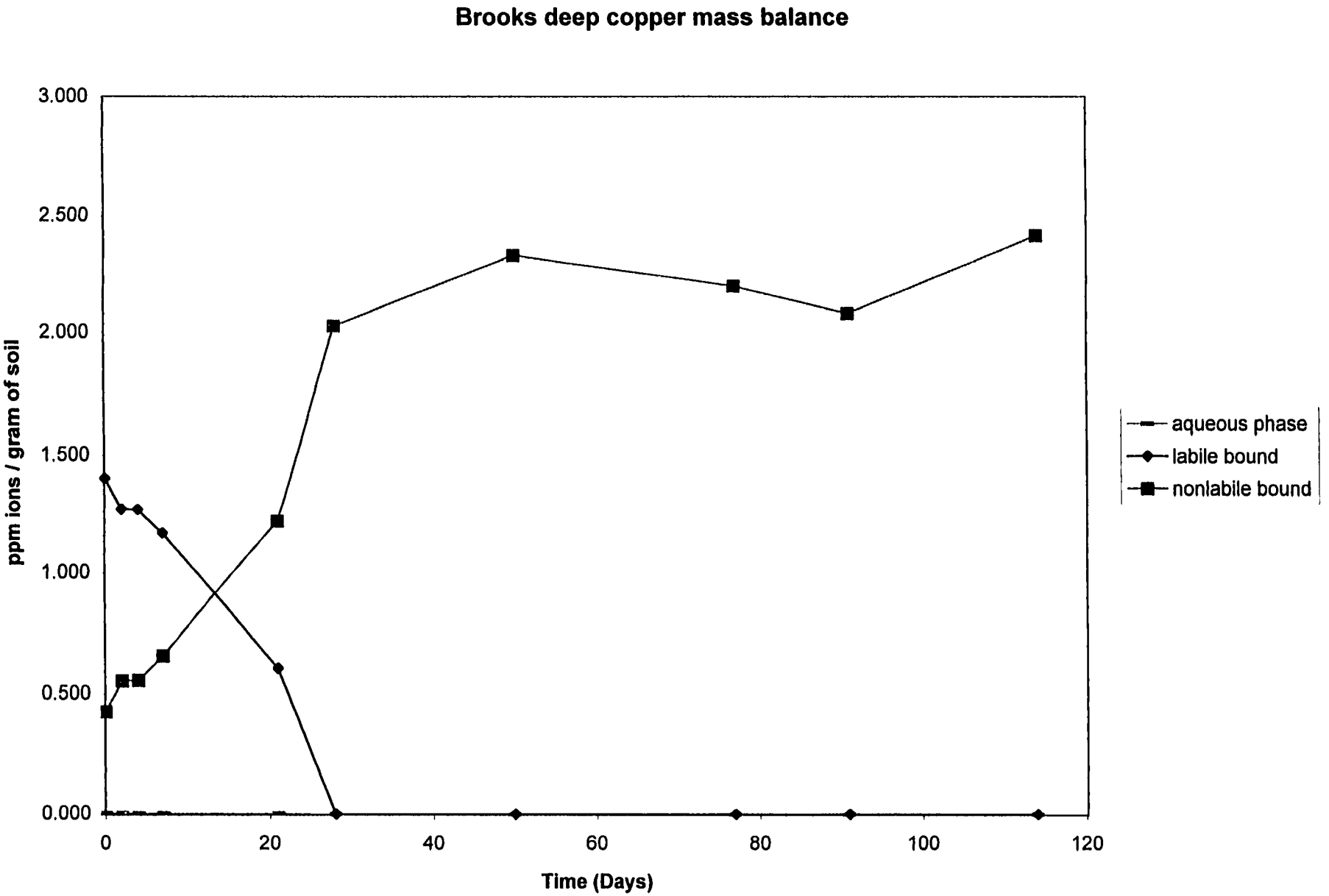

Canmore medium Chromium mass balance
ppm ions / gram of soil
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
0
20
40
60
80
100
120
Time (Days)
aqueous phase
labile bound
nonlabile bound

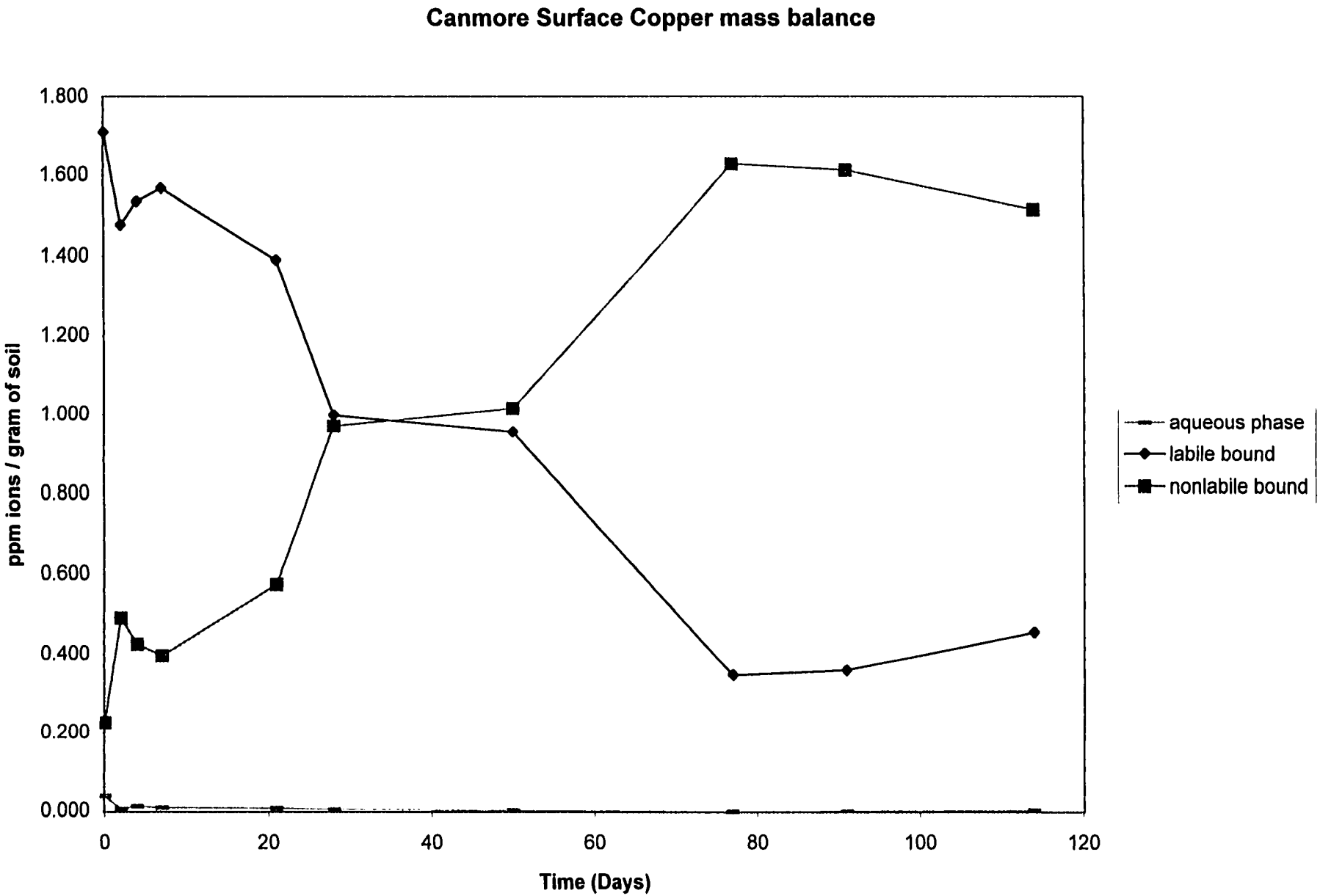

Canmore Deep Chromium mass balance
ppm ions / gram of soil
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
0
20
40
60
80
100
120
Time (Days)
aqueous phase
labile bound
nonlabile bound

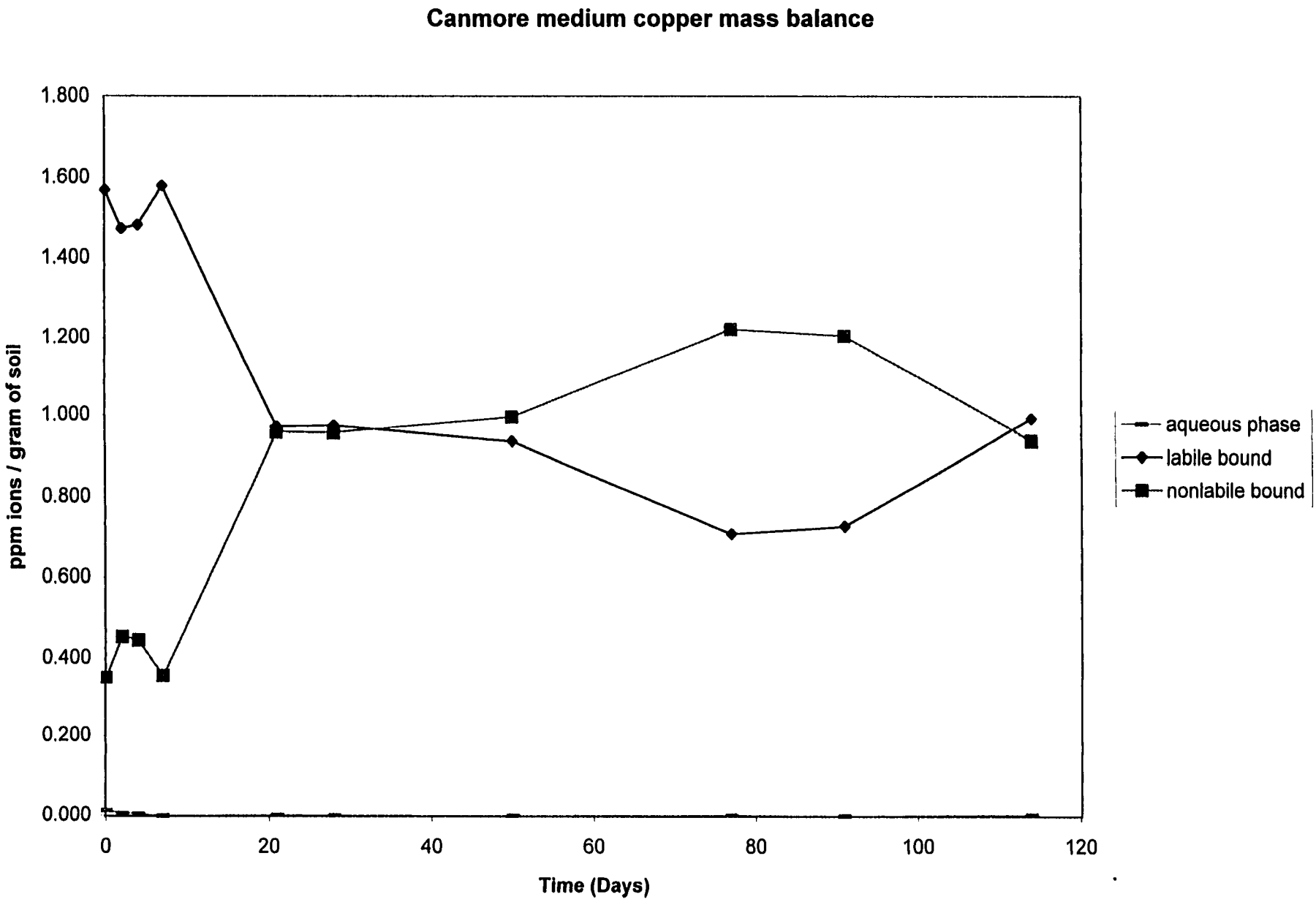

Control Chromium mass balance
18.000
16.000
14.000
12.000
10.000
8.000
6.000
4.000
2.000
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
aqueous
nitric acid wash
nonrecovered

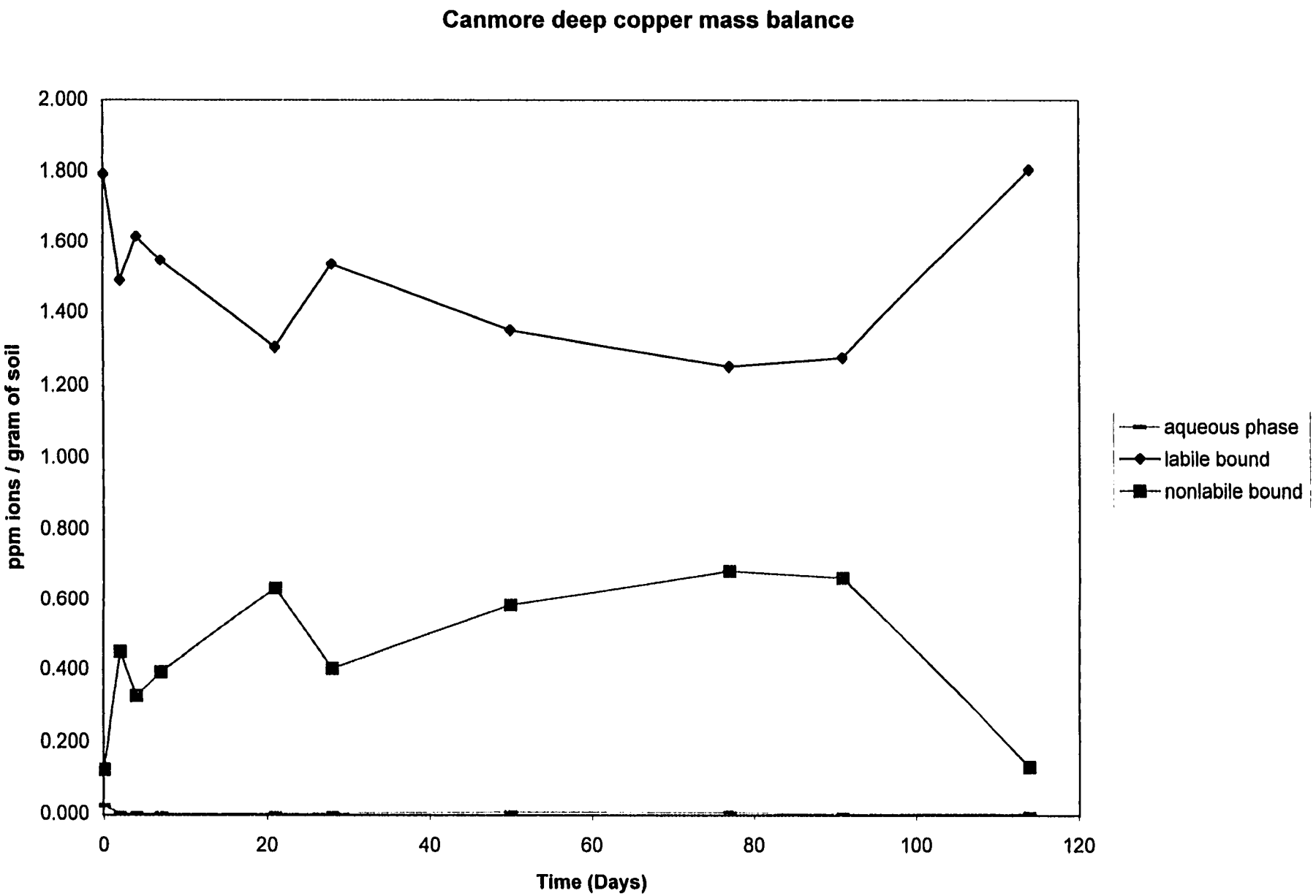

Brooks Surface Copper mass balance
2.000
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
aqueous phase
labile bound
nonlabile bound

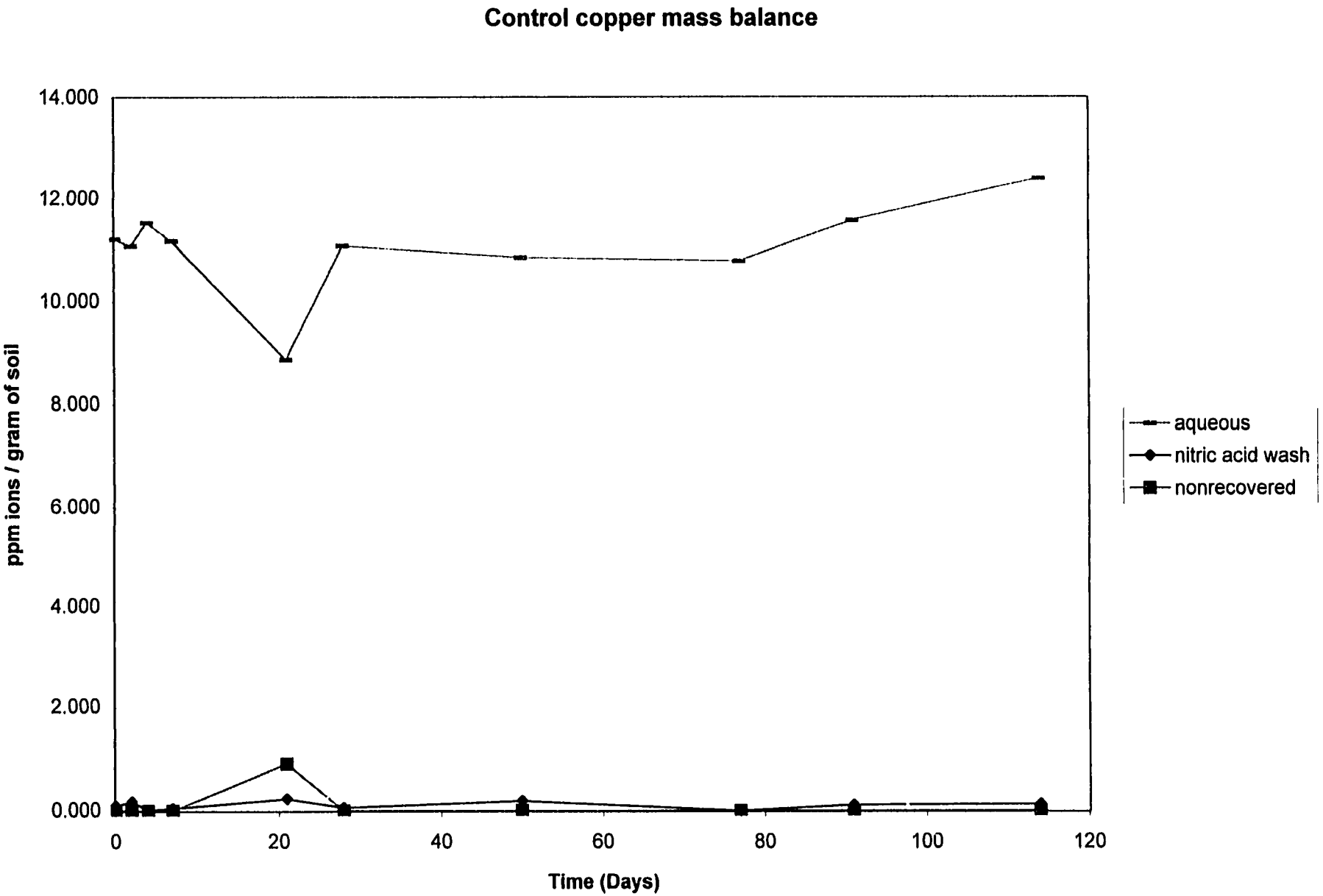

Brooks medium copper mass balance
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
aqueous phase
labile bound
nonlabile bound

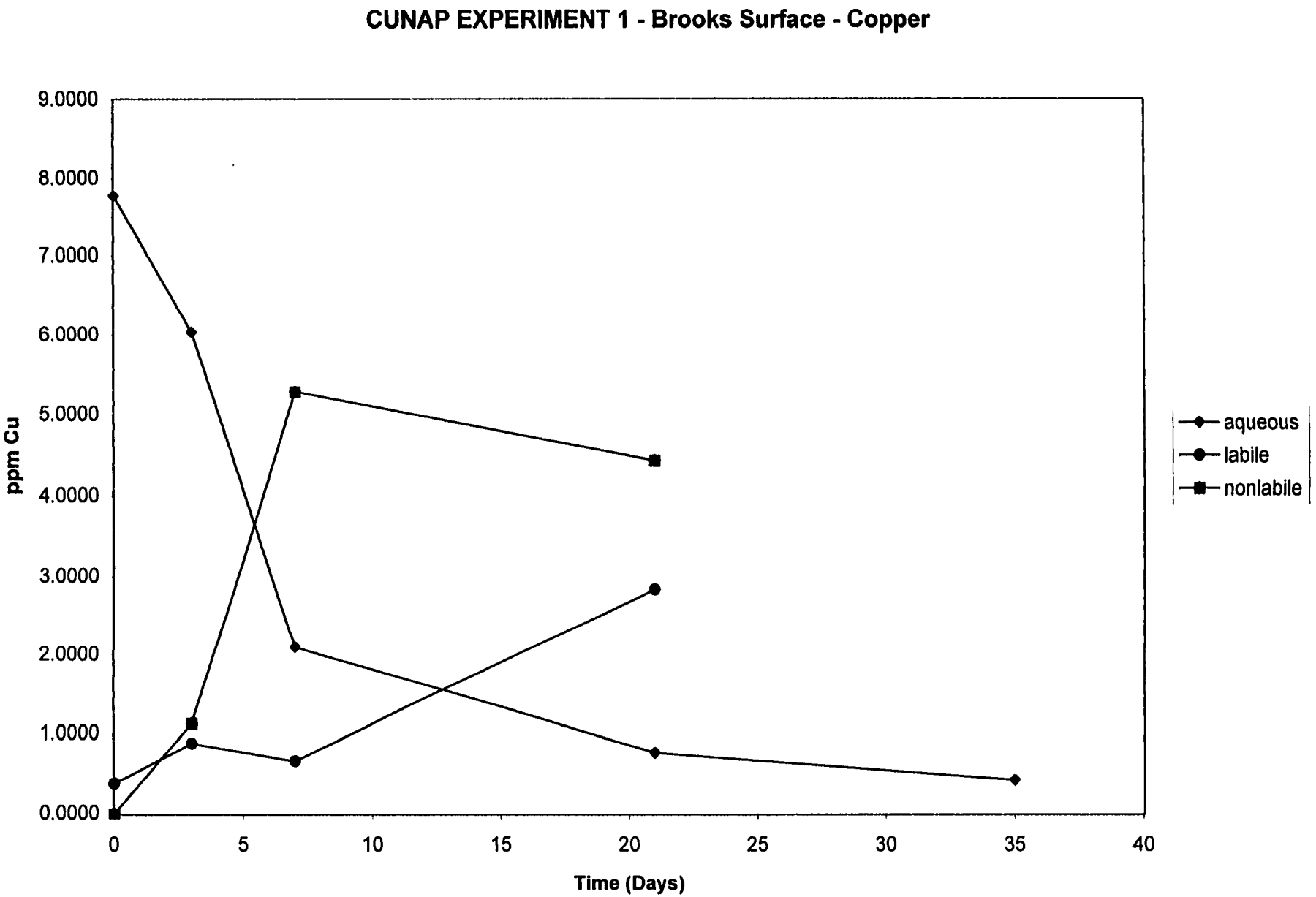

Brooks deep copper mass balance
3.000
2.500
2.000
1.500
1.000
0.500
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
aqueous phase
labile bound
nonlabile bound

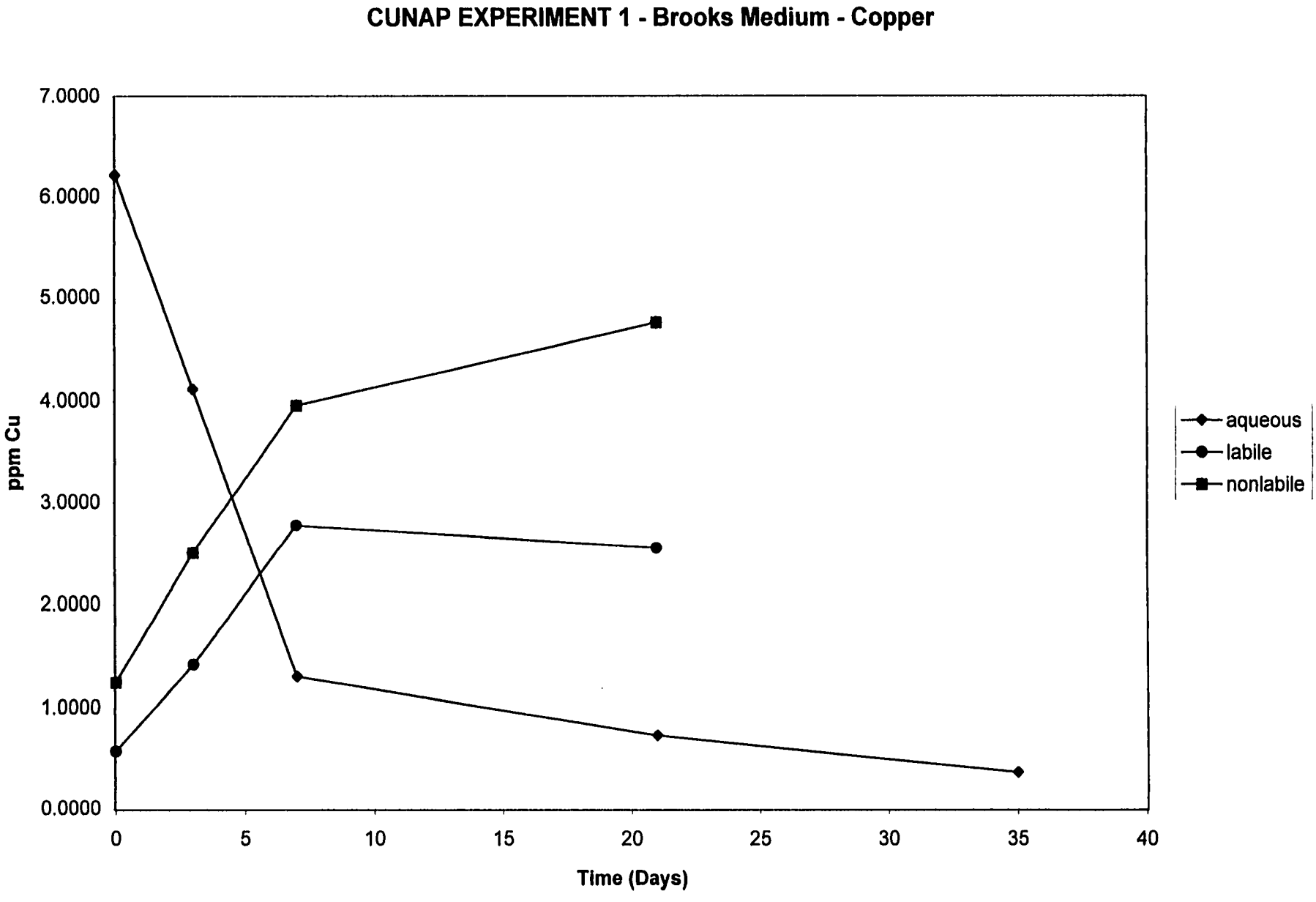

Canmore Surface Copper mass balance
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
aqueous phase
labile bound
nonlabile bound

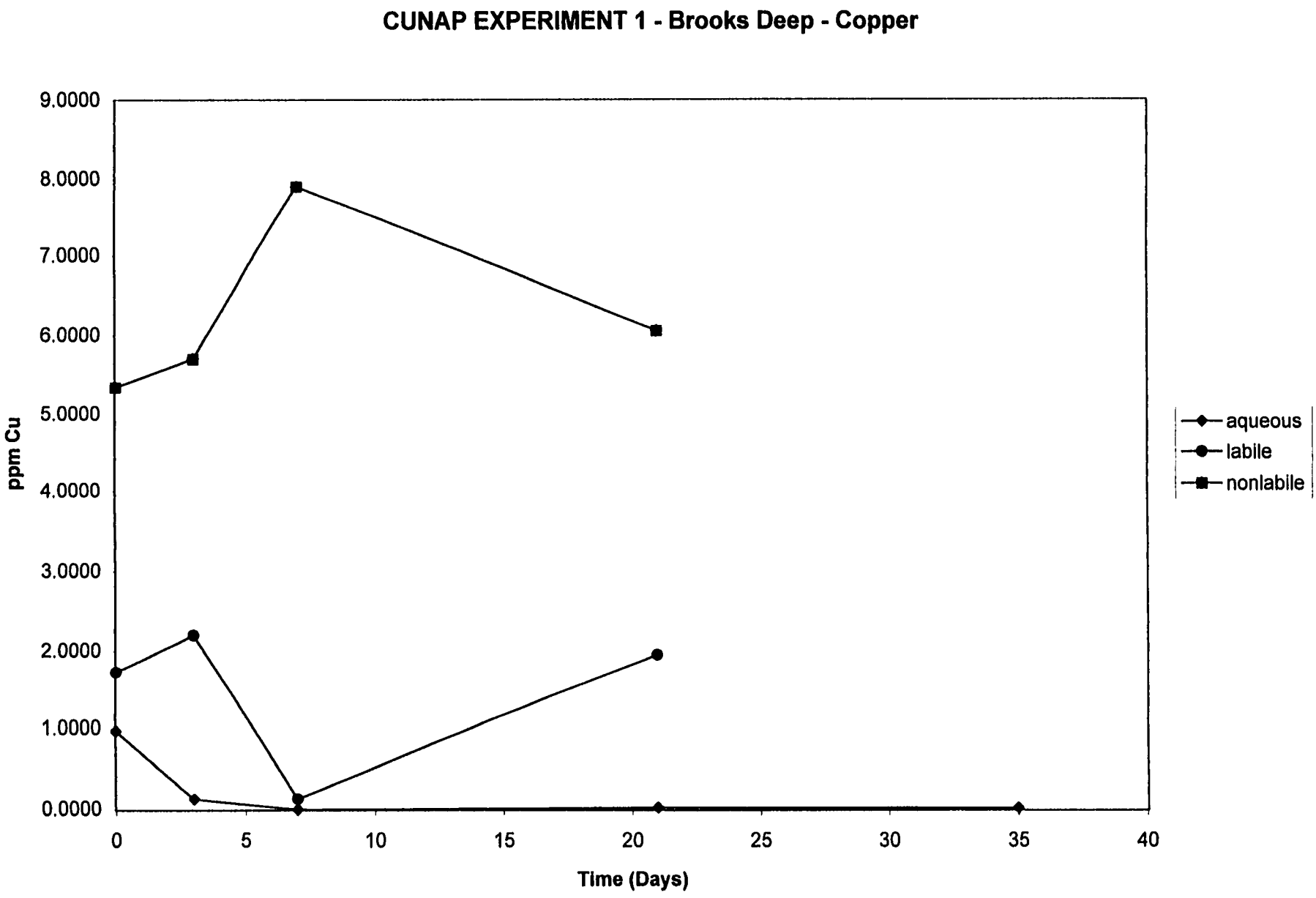

Canmore medium copper mass balance
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
aqueous phase
labile bound
nonlabile bound

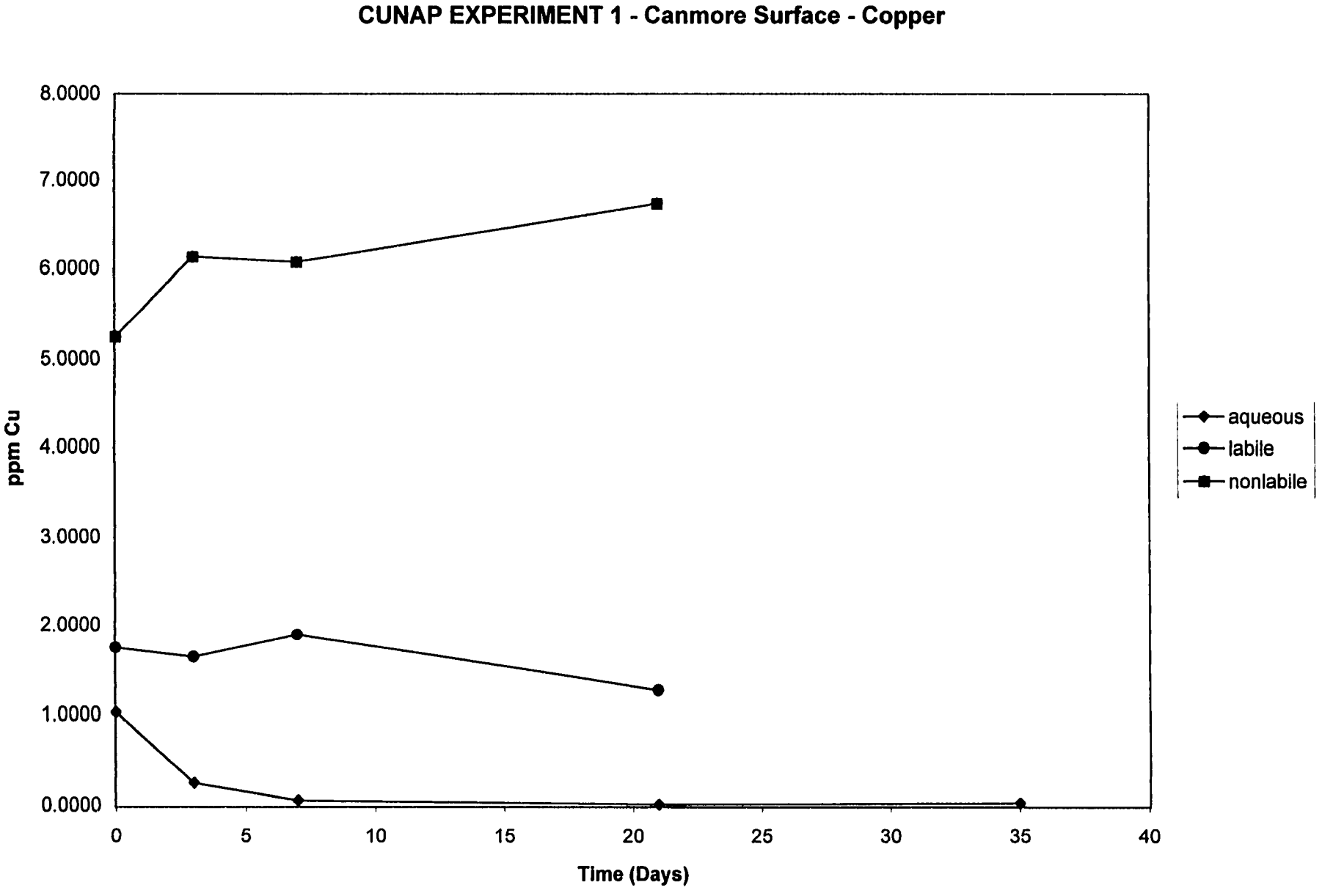

Canmore deep copper mass balance
2.000
1.800
1.600
1.400
1.200
1.000
0.800
0.600
0.400
0.200
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
aqueous phase
labile bound
nonlabile bound

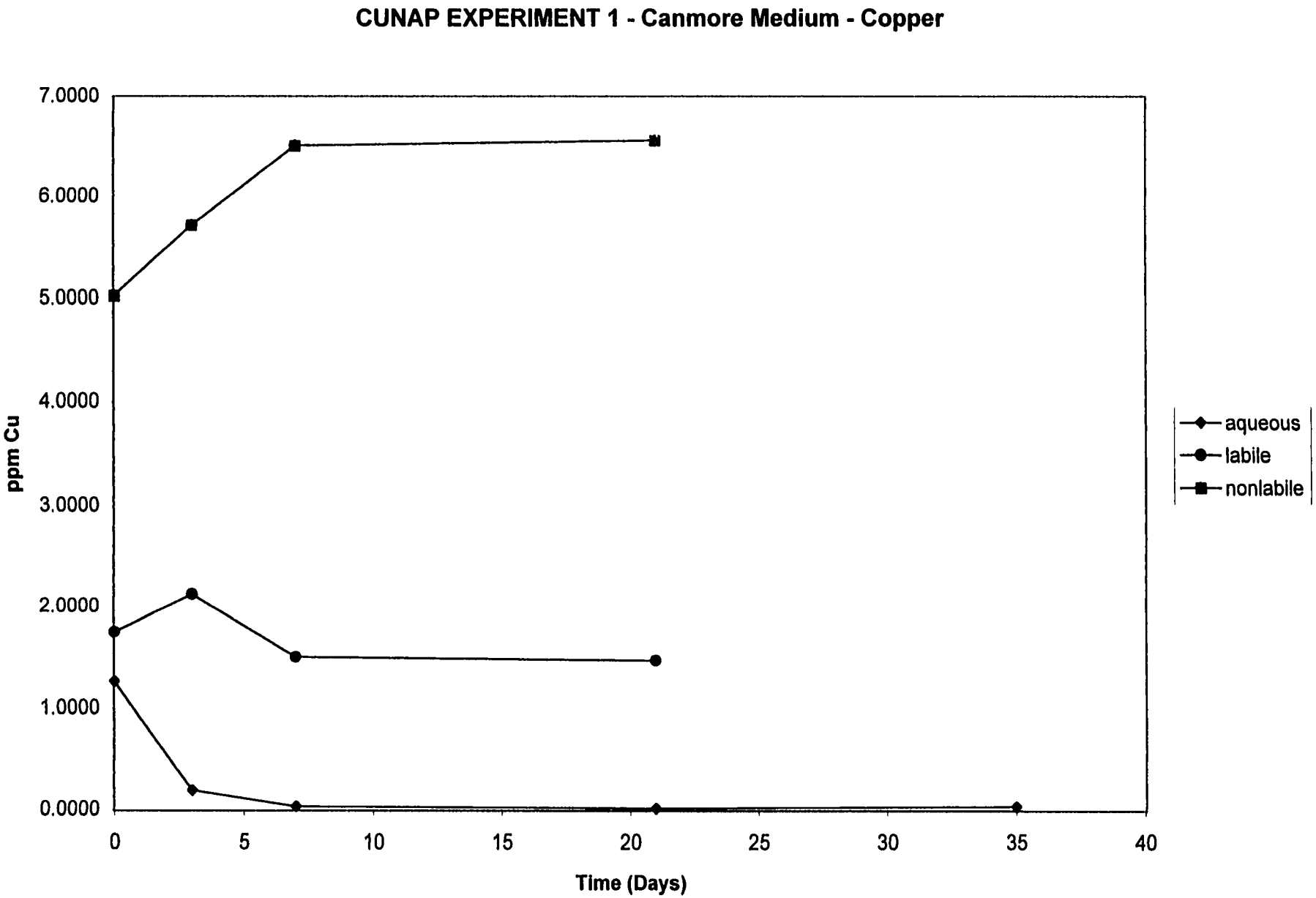

Control copper mass balance
14.000
12.000
10.000
8.000
6.000
4.000
2.000
0.000
ppm ions / gram of soil
0
20
40
60
80
100
120
Time (Days)
aqueous
nitric acid wash
nonrecovered

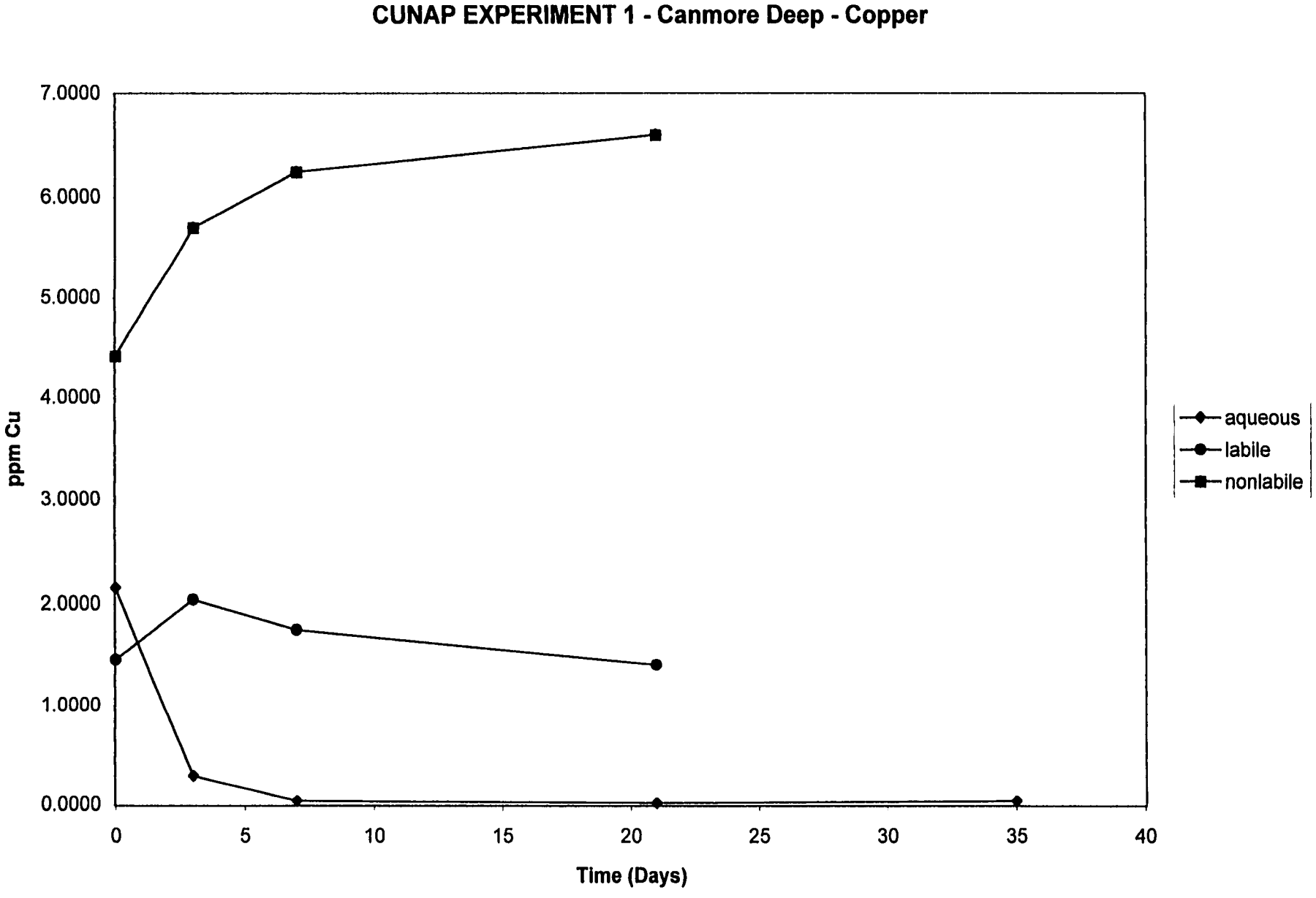

CUNAP EXPERIMENT 1 - Brooks Surface - Copper
9.0000
8.0000
7.0000
6.0000
5.0000
4.0000
3.0000
2.0000
1.0000
0.0000
ppm Cu
0
5
10
15
20
25
30
35
40
Time (Days)
aqueous
labile
nonlabile

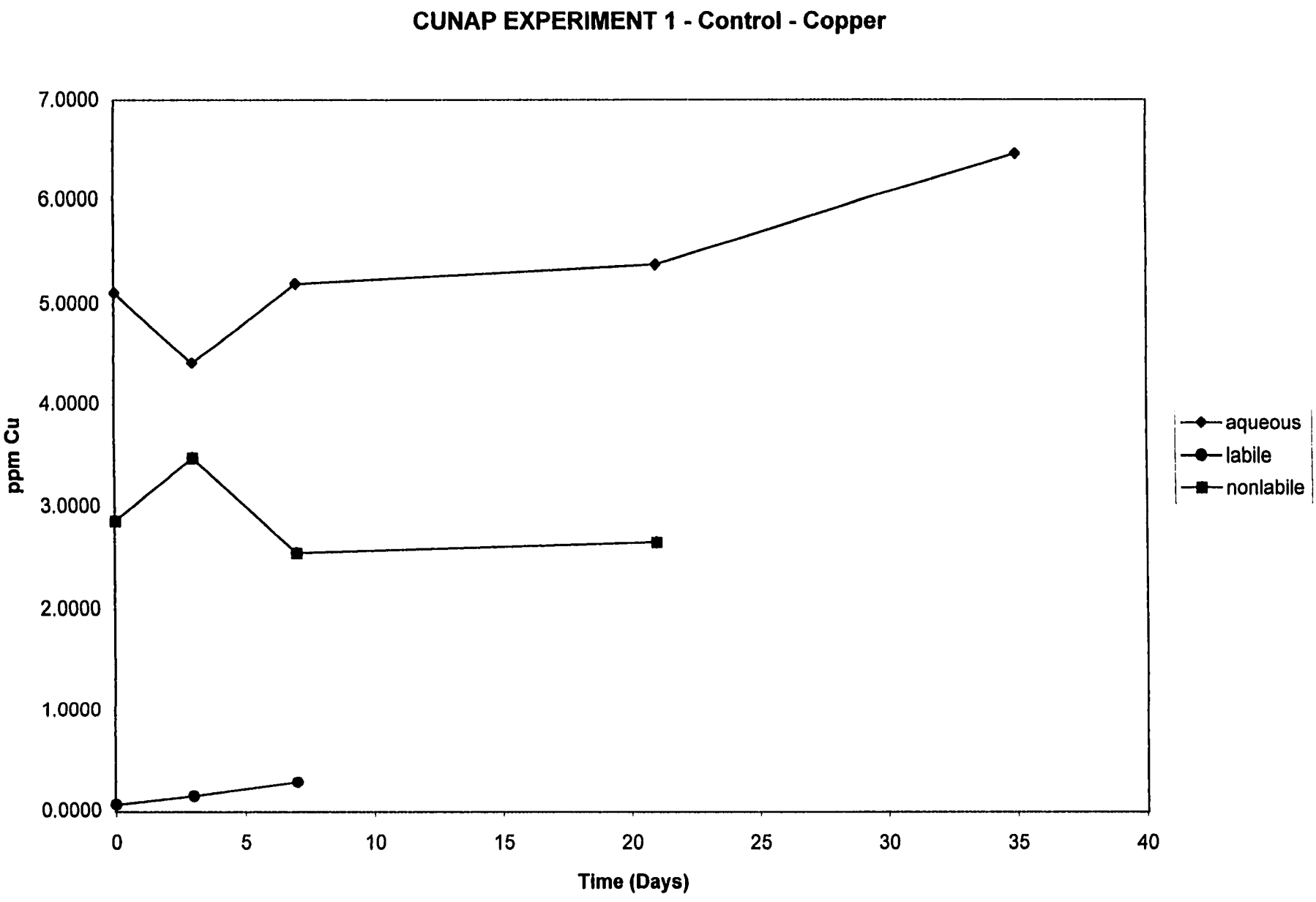

CUNAP EXPERIMENT 1 - Brooks Medium - Copper
7.0000
6.0000
5.0000
4.0000
3.0000
2.0000
1.0000
0.0000
ppm Cu
0
5
10
15
20
25
30
35
40
Time (Days)
aqueous
labile
nonlabile


CUNAP EXPERIMENT 1 - Brooks Deep - Copper
9.0000
8.0000
7.0000
6.0000
5.0000
4.0000
3.0000
2.0000
1.0000
0.0000
ppm Cu
0
5
10
15
20
25
30
35
40
Time (Days)
aqueous
labile
nonlabile

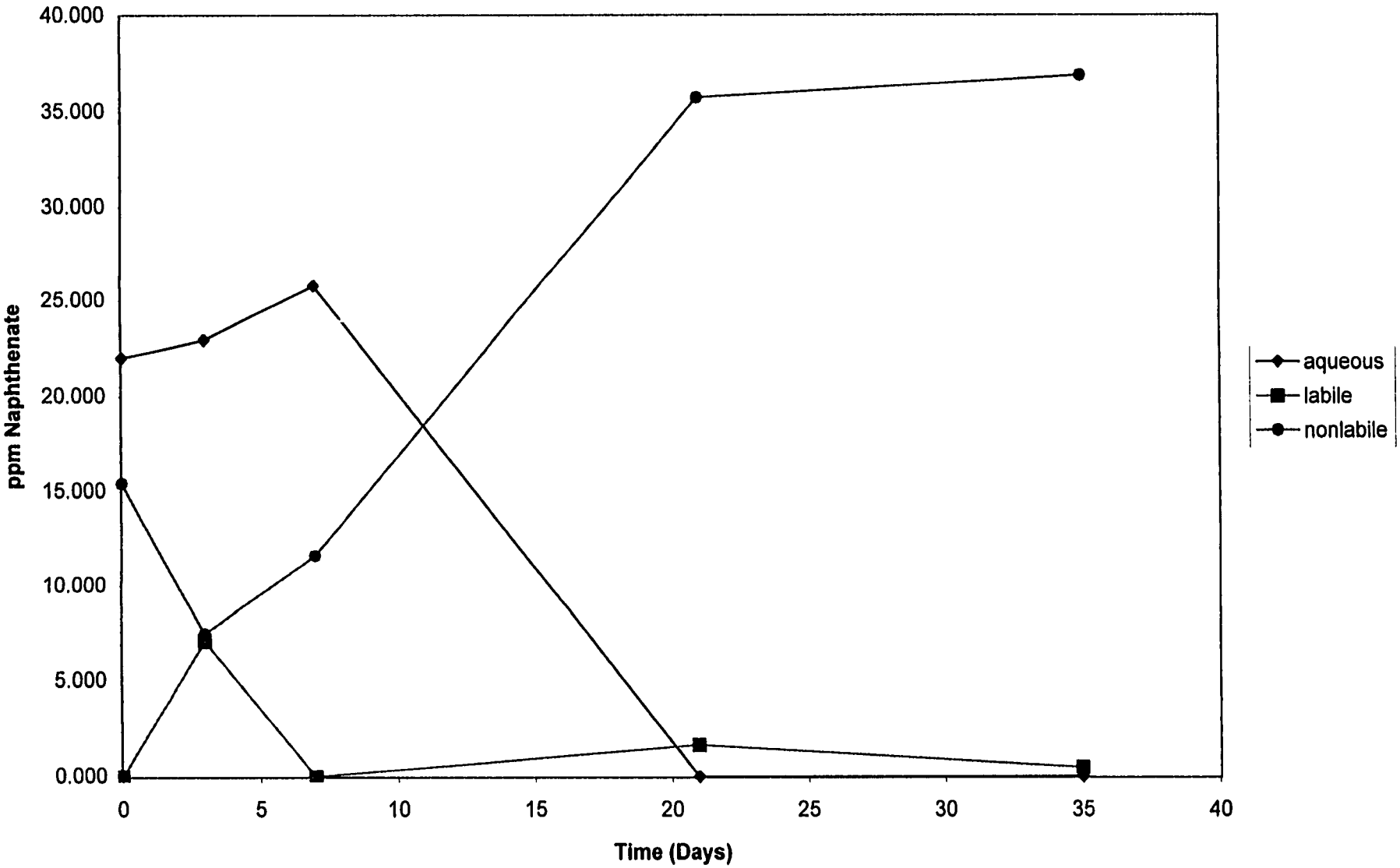

CUNAP EXPERIMENT 1 - Canmore Surface - Copper
8.0000
7.0000
6.0000
5.0000
4.0000
3.0000
2.0000
1.0000
0.0000
ppm Cu
0
5
10
15
20
25
30
35
40
Time (Days)
aqueous
labile
nonlabile

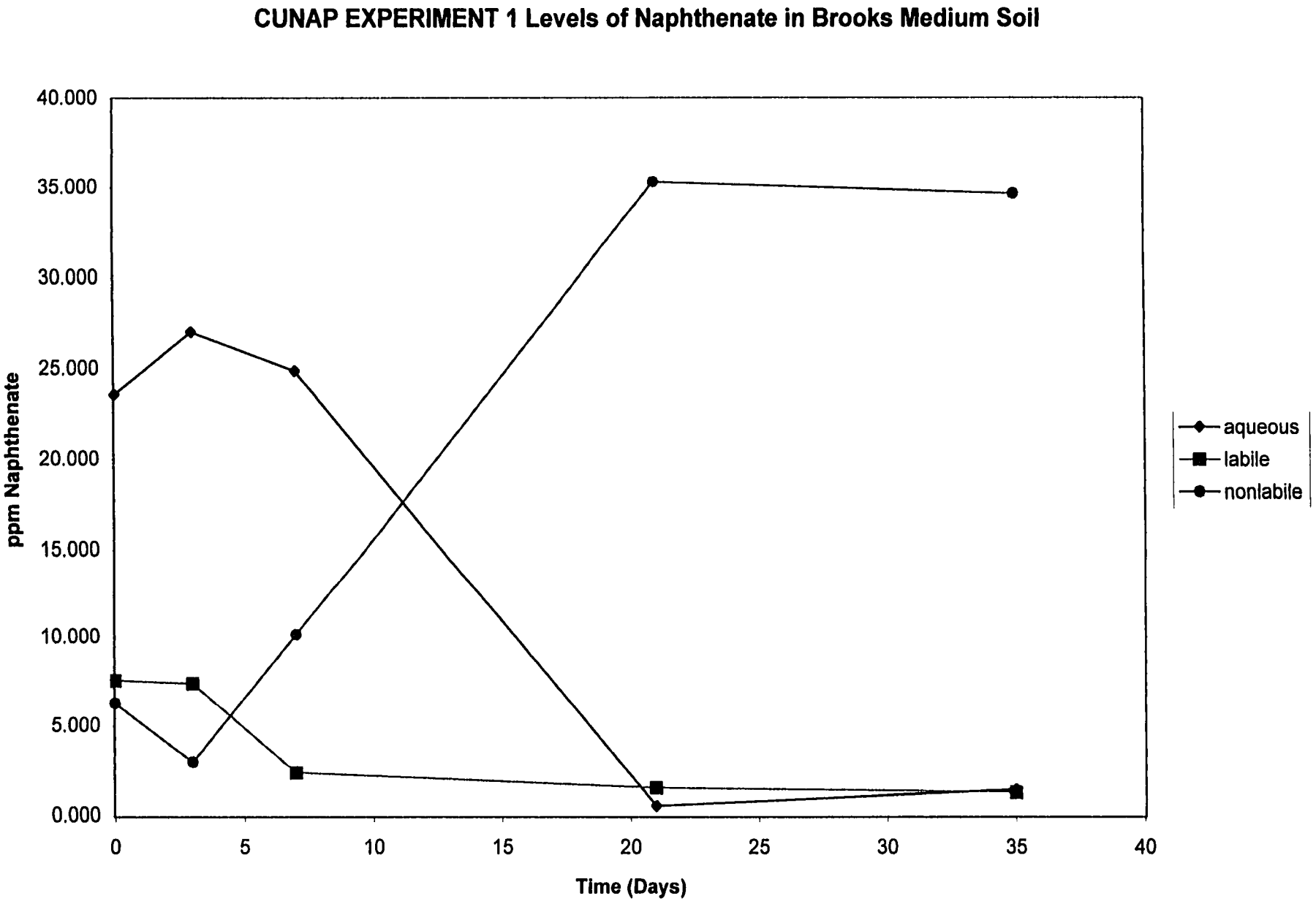

CUNAP EXPERIMENT 1 - Canmore Medium - Copper
7.0000
6.0000
5.0000
4.0000
3.0000
2.0000
1.0000
0.0000
ppm Cu
0
5
10
15
20
25
30
35
40
Time (Days)
aqueous
labile
nonlabile

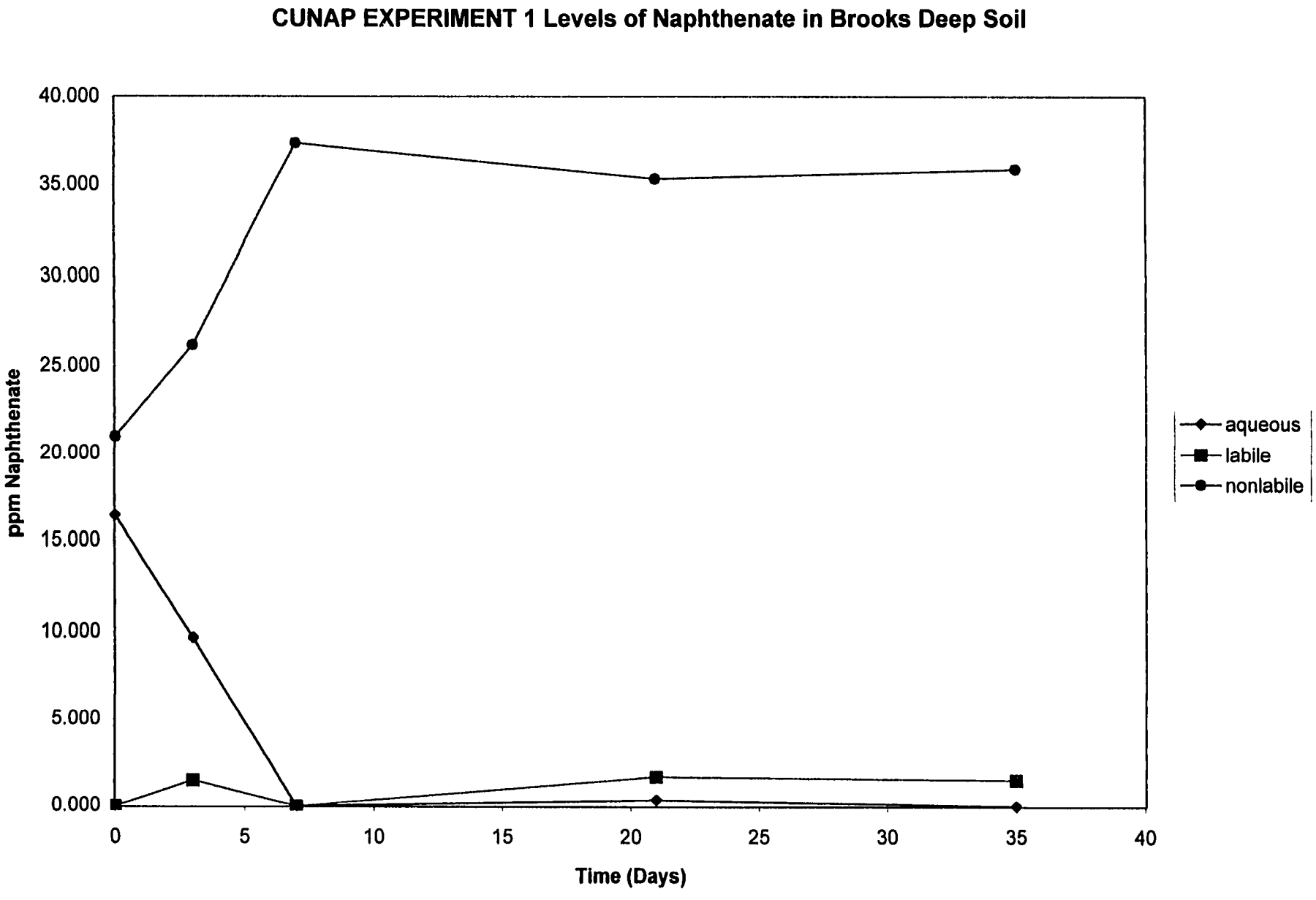

CUNAP EXPERIMENT 1 - Canmore Deep - Copper
7.0000
6.0000
5.0000
4.0000
3.0000
2.0000
1.0000
0.0000
ppm Cu
0
5
10
15
20
25
30
35
40
Time (Days)
aqueous
labile
nonlabile

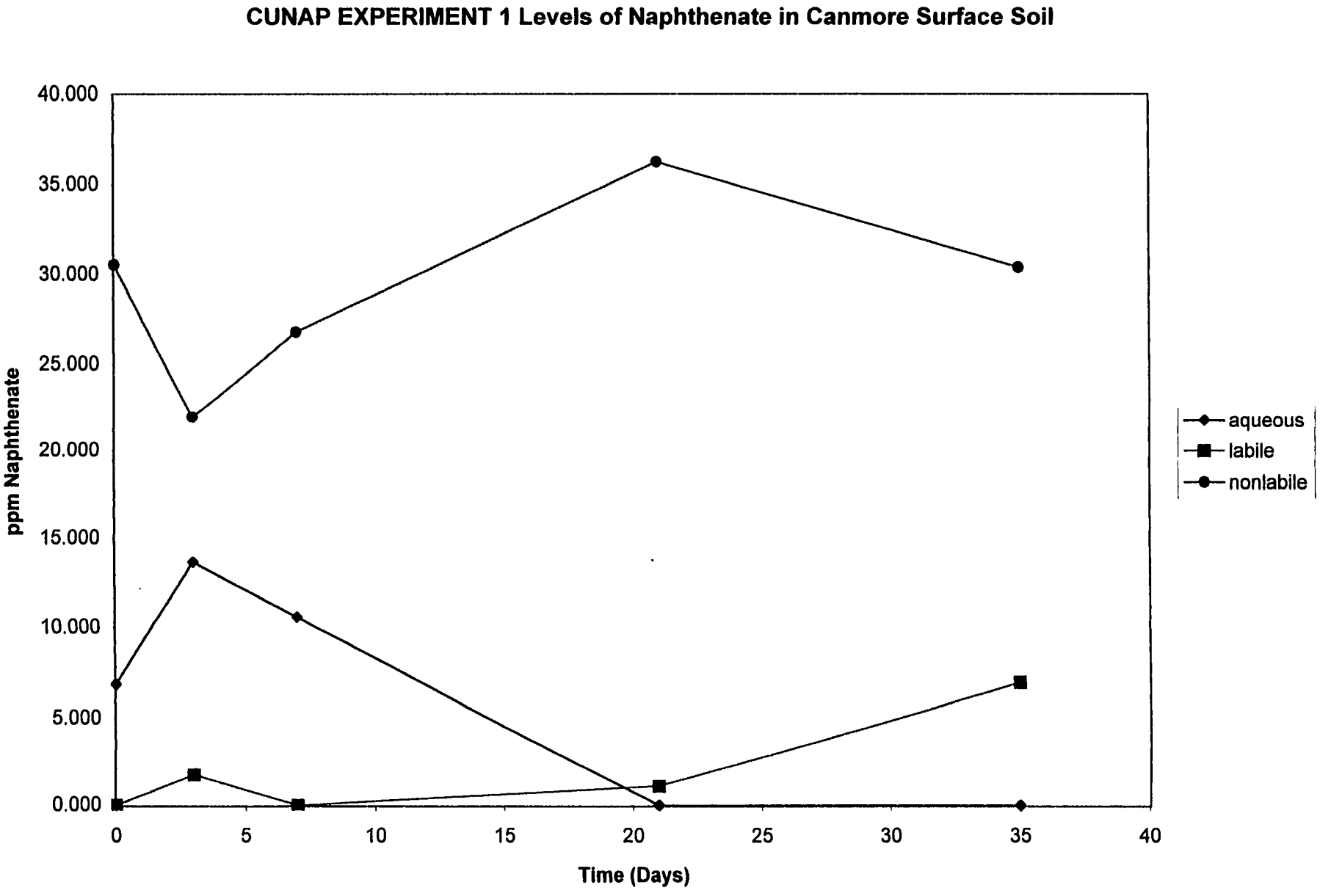

CUNAP EXPERIMENT 1 - Control - Copper
7.0000
6.0000
5.0000
4.0000
3.0000
2.0000
1.0000
0.0000
ppm Cu
0
5
10
15
20
25
30
35
40
Time (Days)
aqueous
labile
nonlabile

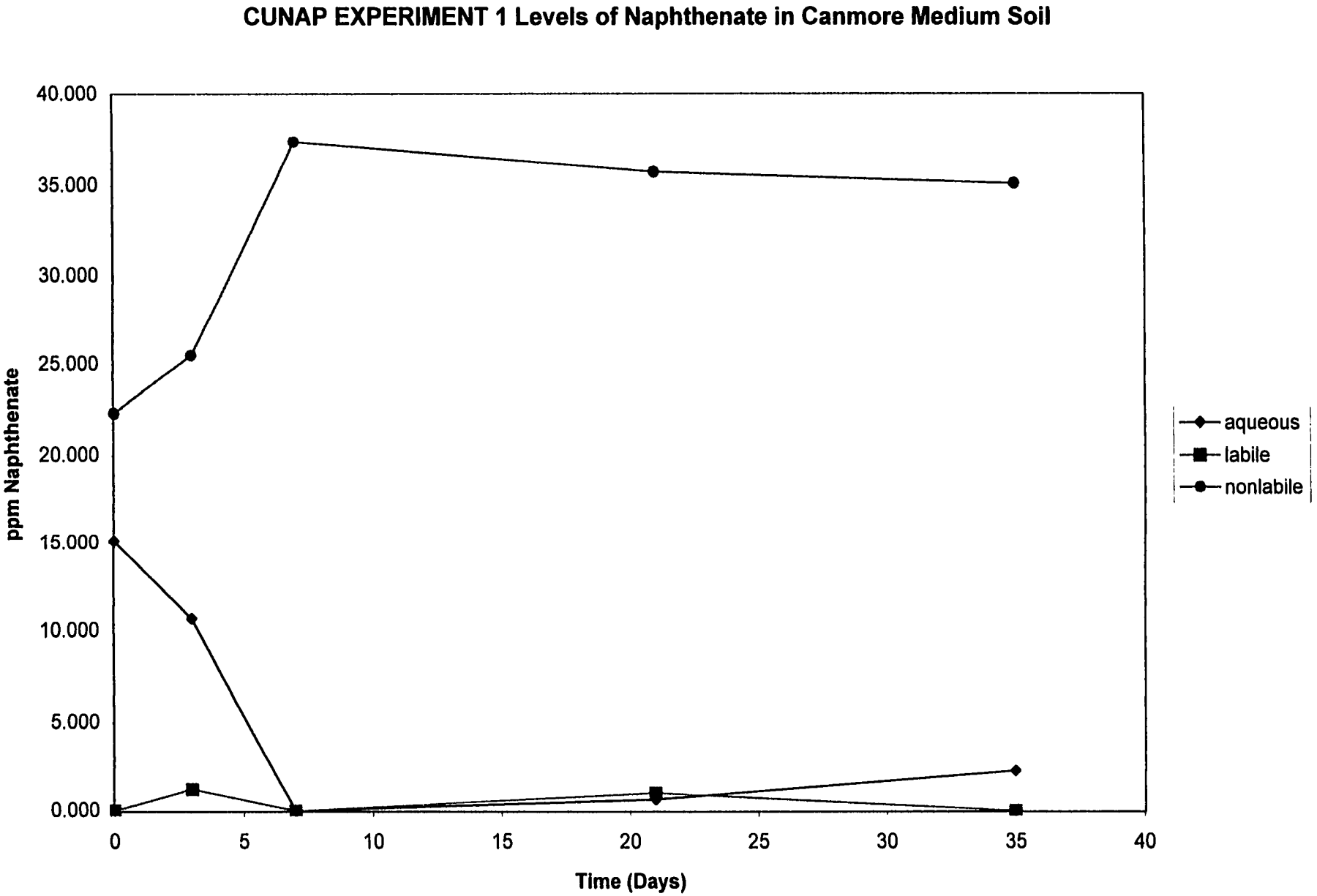
CUNAP EXPERIMENT 1 Levels of Naphthenate in Brooks Surface Soil

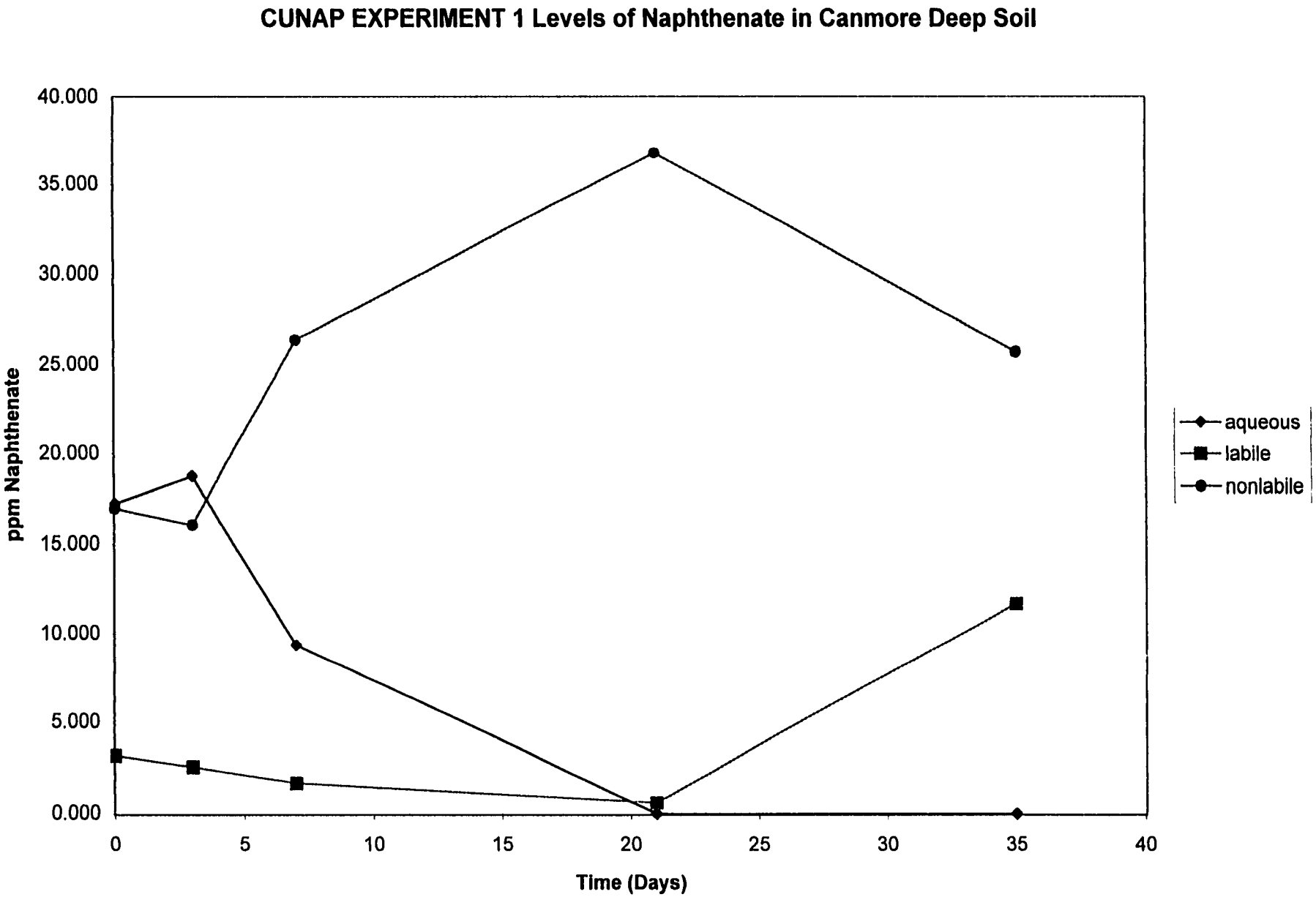



CUNAP EXPERIMENT 1 Levels of Naphthenate in Brooks Medium Soil
ppm Naphthenate
40.000
35.000
30.000
25.000
20.000
15.000
10.000
5.000
0.000
0
5
10
15
20
25
30
35
40
Time (Days)
aqueous
labile
nonlabile


CUNAP EXPERIMENT 1 Levels of Naphthenate in Brooks Deep Soil
40.000
35.000
30.000
25.000
20.000
15.000
10.000
5.000
0.000
ppm Naphthenate
0
5
10
15
20
25
30
35
40
Time (Days)
aqueous
labile
nonlabile


CUNAP EXPERIMENT 1 Levels of Naphthenate in Canmore Surface Soil
40.000
35.000
30.000
25.000
20.000
15.000
10.000
5.000
0.000
ppm Naphthenate
0
5
10
15
20
25
30
35
40
Time (Days)
aqueous
labile
nonlabile


CUNAP EXPERIMENT 1 Levels of Naphthenate in Canmore Medium Soil
40.000
35.000
30.000
25.000
20.000
15.000
10.000
5.000
0.000
ppm Naphthenate
0
5
10
15
20
25
30
35
40
Time (Days)
aqueous
labile
nonlabile


CUNAP EXPERIMENT 1 Levels of Naphthenate in Canmore Deep Soil
ppm Naphthenate
40.000
35.000
30.000
25.000
20.000
15.000
10.000
5.000
0.000
0
5
10
15
20
25
30
35
40
Time (Days)
aqueous
labile
nonlabile

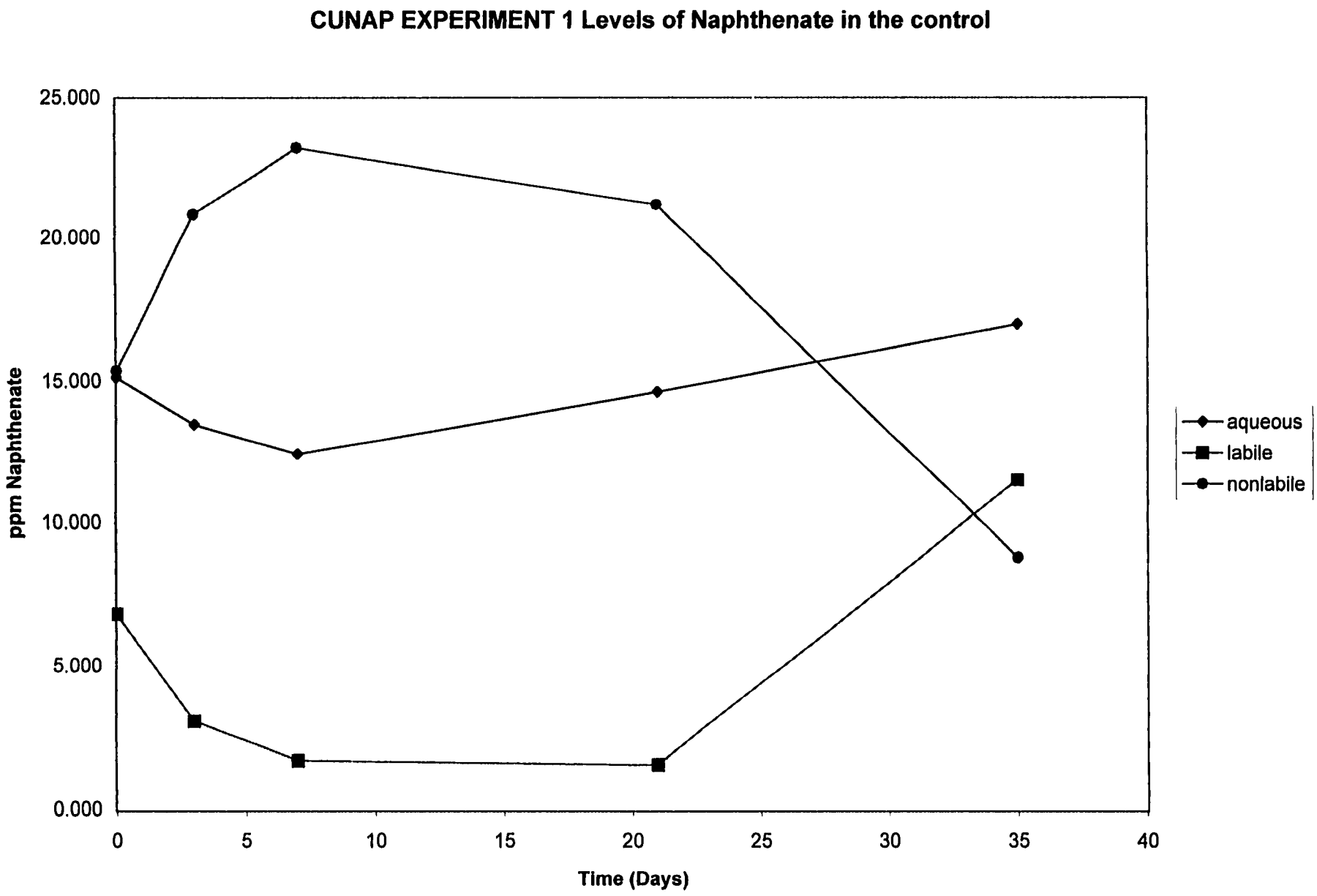

CUNAP EXPERIMENT 1 Levels of Naphthenate in the control
25.000
20.000
15.000
10.000
5.000
0.000
ppm Naphthenate
0
5
10
15
20
25
30
35
40
Time (Days)
aqueous
labile
nonlabile

IMAGE EVALUATION TEST TARGET (QA-3)

150mm

6"

APPLIED IMAGE, Inc
1653 East Main Street
Rochester, NY 14609 USA
Phone: 716/482-0300
Fax: 716/288-5989