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New Technique for Soil Reclamation and Conservation: In Situ Stabilization of Trace Elements in Contaminated Soils

Osama Negim

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THÈSE

PRÉSENTÉE A

L'UNIVERSITÉ BORDEAUX 1
ÉCOLE DOCTORALE DES SCIENCES ET ENVIRONNEMENTS

Par **Osama NEGIM**

POUR OBTENIR LE GRADE DE

DOCTEUR

SPÉCIALITÉ : SCIENCE DES SOLS

New Technique for Soil Reclamation and Conservation: In Situ Stabilization of Trace Elements in Contaminated Soils

Soutenue le 17 juillet 2009

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RÉSUMÉ

Les sols sous contraintes que ce soit du point de vue charges polluantes comme avec les Métaux Traces (MT) ou bien du point de vue stress hydrique (perte des capacités de rétention menant à la désertification des sols) concernent de nombreux espaces du territoire national, de même que la région du pourtour Méditerranéen. Le nombre de sites pollués par des substances inorganiques affectant de larges espaces est en constante augmentation. Les stratégies pour leur rémédiation sont variées mais très peu envisagent la dépollution tout en restaurant les propriétés pédologiques des sols concernés. La rémédiation comme la restauration des capacités fertilisantes de sols pollués sont un enjeu international. Pour cela, la stratégie de cette étude porte sur le développement d'outils technologiques innovants basée sur la phytoremédiation assistée par des matrices duales de sols contaminés par des MT (Cuivre, Chrome, Arsenic). Ces matrices duales ont une action double concomitante en permettant une immobilisation ou un piégeage des MT tout en favorisant la repousse végétale ou la catalyse de la croissance végétale. Le piégeage peut se faire par l'apport d'amendement ayant des capacités d'échanges (généralement liées à l'existence de phase allophane et/ou d'un réseau poral important) et de rétention (liées au réseau poral et à l'existence de phases minérales type phosphates, silice amorphe, oxydes hydroxydes de fer-manganèse). L'élaboration, à partir de laitiers d'aciéries, d'une matrice susceptible d'adsorber des MT (aspect dépollution) tout en favorisant la pousse végétale (aspect amendement) nous a permis de tester ce produit de synthèse. La seconde originalité de cette étude est d'analyser le potentiel de ces matrices, non seulement à différentes échelles (du pot en passant par le stade mésocosme et jusqu'au champ), du point de vue impact écotoxique – dépollution de sols associé à une re-végétalisation. Cette dernière participe également au transfert des charges polluantes (MT) depuis l'amendement de synthèse ou du sol vers, et dans le réseau racinaire des radicelles et ainsi favoriser la réhabilitation des propriétés hydriques des sols par le développement d'un couvert végétale pérenne. On conjugue ainsi un apport dépolluant à celui de maintien de la potentielle anti-désertification grâce au développement de solutions innovantes respectueuses de l'environnement sur la base de technologie douce valorisant les co produits de l'industrie.

Mots clés : CCA, Cuivre, Chrome, Arsenic, rémédiation, scories, re-végétalisation

ABSTRACT

Soil contamination by trace elements is a widespread problem in many parts of the world. The accumulation of toxic metals in soil is mainly inherited from parent materials or inputs through human activities. In fact, one of the sources of soil contaminations is very important resulting from chemical widely used wood preservative industries in aquatic environments and storing the wood after treatment by chromated copper arsenate (CCA). Elements such as As, Cu, Cr, and Zn can be found in excess in contaminated soils at wood treatment facilities, especially when Cu sulphates and chromated copper arsenate (CCA) were used as a preservative against insects and fungi, which may result in soil phytotoxicity as well as toxic to plants, animals and humans. New techniques are being developed to remediate trace elements in contaminated soils such as phytoremediation and *in situ* stabilization. *In situ* stabilization technique or *in situ* immobilisation is one of the common practices for reducing negative effects of metals and metalloids such as As, Cr, Cu, Pb, Cd and Zn in contaminated soils by adding amendments. Alkaline materials are usually added to acidic soils to improve soil chemical and physical properties and also to reduce the mobility and bioavailability of contaminant. Slag, which consists of calcium oxide, phosphorus oxide, silicon oxide, iron oxide, and other metal oxides, is an alkaline by-product of metallurgical processes or a residue of incineration processes. Slags have been successfully used to soil reclamation and soil fertiliser. It has been used as a soil additive to reduce various metals contaminated soil by precipitation and adsorption on the surface of metal oxide. The objectives of this Ph.D study were to evaluate the physical, chemical soil properties and the distribution of trace elements in contaminated soil. Also to evaluate the characteristics of two different slags samples, a basic slag (BS) and a basic slag phosphate (BSP) which are alkaline by-products of the French steel industry and which used as a soil amendments to improve soil properties and for the *in situ* immobilisation of copper and metals in chromated copper arsenate (CCA) contaminated soil.

Key words: CCA, soil reclamation, stabilisation, slag, soil properties, bean plants

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CHAPTER 1: General Introduction

Soil contamination by trace elements is a widespread problem in many parts of the world. The accumulation of toxic metals in soil is mainly inherited from parent rock materials or inputs through human activities (He *et al.*, 2005). One of the sources of soil contamination which is very important results from the chemical widely used wood preservative industries in aquatic environments and storing the wood after treatment by chromated copper arsenate (CCA). Elements such as As, Cu, Cr, and Zn can be found in excess in contaminated soils at wood treatment facilities, especially when Cu sulphates and chromated copper arsenate (CCA) were used as a preservative against insects and fungi, which may result in soil phytotoxicity (Kumpiene *et al.*, 2008). The rain is playing a key-role in leaching these metals from the recently treated timber and lumber stored at the treatment facility. Under conditions of storage the timber, the soils contain high concentrations of CCA (Buchireddy *et al.*, 2008). Therefore, it is very important to reduce or immobilise these metals in contaminated soils. Currently there are several technologies that can be used to clean up or remove the soils and the mining wastes contaminated by toxic metals, such as thermal treatments, biological and physical/chemical procedures. These removal technologies are generally costly to practice and destructive to the application sites and only partially effective for the total removal (efficient clean up) of toxic metals or for the sufficient reduction of their mobility and bioavailability (Raicevic *et al.*, 2005).

In the past few decades, new techniques are being developed to remediate trace elements in contaminated soil, sediments and groundwaters such as phytoremediation and *in situ* stabilization. The stabilization techniques or *in situ* immobilisation aim at decreased the labile pool of metals and metalloids such as As, Cr, Cu, Pb, Cd and Zn by the incorporation of amendments. This technique is also able to enhance one or several processes such as metal adsorption through increased surface charge, formation of organic and inorganic metal complexes, sorption on Fe, Mn, and Al oxides, and precipitation. It is considered as a simple and cost-effective approach for the treatment

of metals in contaminated soils, particularly when these soils are difficult or costly to be removed or treated *ex situ*. It can be used for *in situ* and *ex situ* applications to reclaim and re-vegetate industrially devastated areas and mine-spoils and restore the physical, chemical and biological soil properties and also reduce the contaminant mobility and bioavailability with various chemical and mineralogical agents such as industrial by-products (Mench *et al.*, 2000; Oste *et al.*, 2002; Bolan and Duraisamy, 2003; Adriano *et al.*, 2004; Pérez de Mora *et al.*, 2005; Raicevic *et al.*, 2005 ; Kumpiene *et al.*, 2006; Kumpiene *et al.*, 2008). Alkaline materials are usually added to acidic soils to ameliorate the soil chemical and physical properties and reduce the mobility and bioavailability of metallic contaminants. Several application studies have demonstrated the *in situ* immobilisation of contaminated soils and groundwaters by using inexpensive soil amendments. The amendments can significantly reduce the mobility of metals in soil, metal uptake by plants and metal phytotoxicity.

Several alkaline slags have been used for amending acid soils. Slag, which consists of calcium oxide, phosphorus oxide, silicon oxide, iron oxide and other metal oxides, is an alkaline by-product of metallurgical processes or a residue of incineration processes. Slag have been successfully used in different fields of application such as fertiliser (phosphatic fertiliser), road construction (e.g. asphaltic or unbound layers), civil engineering work, and production of metallic iron and iron concentrate, soil reclamation and water refinement (Geiseler, 1996; Shen Li, 1999; Ortiz *et al.*, 2000; Motz and Geiseler, 2001; Shen and Forsberg, 2003; Charles and Nemmer, 2006). It has been used as a soil additive to remove various metals contaminated soil by precipitation and adsorption on the surface metal oxide (Mench *et al.*, 1994a,b; Besga *et al.*, 1996; Dimitrova, 1996; Dimitrova and Mehandjiev, 1998; Mench *et al.*, 1998; Barbosa Filho *et al.*, 2004; Carvalho-Pupatto *et al.*, 2004; Bes and Mench, 2008; Kim *et al.*, 2008).

The submitted Ph.D studies the following parts:

First, to study physico-chemical soil properties and the distribution of trace elements in soil, to evaluate the relationship between the metals in contaminated soils and several soil parameters such as the particle size distribution, the organic matter content, the soil pH and the cation exchange capacity.

Second, to evaluate two different slag samples used as soil additives, basic slag (BS) and basic slag phosphate (BSP) which were obtained from the French steel industry. The chemical and mineralogical properties of both slags were investigated by using several analytical techniques: the chemical composition was determined by an atomic adsorption spectrophotometer, mineralogical analysis was performed by X-ray diffraction (XRD), the microstructure was observed by optical microscope, scanning electron microscope (SEM) coupled with energy dispersive (EDX) and electron microprobe analysis (EMPA).

Third, BS compounds may influence the composition of soil solution through acid-base, precipitation and sorption reactions and also the foliar concentrations through changes in soil solution, competition for root uptake and root-to-shoot transfer. The compounds contents in BS make it a potential liming agent to increase the precipitation and sorption of trace elements such as Cu and a potential fertilizer promoting plant growth and improving the physico-chemical properties of the soil such as soil electrical conductivity (EC) and pH soil. Therefore this study aimed at investigating BS addition into a soil mainly Cu-contaminated from a wood treatment facility in which the addition of BS may improve soil characteristics such as pH and EC and reduce the labile pool of trace elements in soil for root-to-shoot transfer in beans plants.

Fourth, BSP is used as a soil remediation technique for improve physico-chemical soil properties and also for *in situ* immobilisation of copper and CCA in contaminated soils by increased the precipitation and adsorption on the surface metal oxide of the BSP thus changing the availability and mobility of these trace elements. The objectives of this study were (1) to determine the influence of the addition of BSP into a strongly Cu-contaminated soil to improve the soil properties such as soil pH and EC (2) to evaluate the effect of different BSP addition rates on the plant yield production and the foliar elemental concentrations of both nutrients and trace elements of primary leaves, (3) to determine the potential of BSP to reduce copper and CCA in contaminated soils as well as to reduce the metal toxicity uptake by beans plants, (4) to study the mineralogical form of copper in particle size fractions of the soil treatments were determined by X – ray powder diffraction analysis (XRD).

CHAPTER 2: Review of Literature

2.1. Trace elements in soil-plant systems

2.1.1. Definition

The major elements O, H, Si, Al, Fe, Ca, Na, K, Mg, Ti and P constitute over 99% of the total elements content of the earth's crust (Alloway, 1995; Baize, 1997). A trace element is an element present at a level $< 0.1\%$ in natural materials. Trace elements include metals and metalloids (both metallic and non-metallic properties, e.g., As and B), micronutrients (chemical elements needed in small quantities for plant growth, *i.e.*, < 50 mg/g in the plant) and trace inorganic (Sparks, 2003). Heavy metals is the generic name given to the group of elements with an atomic density greater than 6 g/cm³; their concentration in soil and water varies from less than 1000 ppm to a few ppb with the exception of manganese which is found in soils from 20 to 10000 ppm (Alloway, 1995). In general, trace elements which are present at very low concentrations in agroecosystems include copper (Cu), zinc (Zn), manganese (Mn), iron (Fe), molybdenum (Mo) and boron (B); they are essential metals in small concentrations to plant growth. Some trace elements, such as cobalt (Co) and selenium (Se) are not essential to plant growth but are required by animals and human beings (He *et al.*, 2005). Other trace elements such as cadmium (Cd), lead (Pb), chromium (Cr), nickel (Ni), mercury (Hg), and arsenic (As) have toxic effects on living organisms and are often considered as contaminants. In addition trace elements are toxic to plants, animals and humans due to extremely high concentrations in the parent materials and anthropogenic inputs (Bolan *et al.*, 2003; He *et al.*, 2005).

2.1.2. Geochemistry of trace elements

The earth crust is made up of 95% igneous rocks and 5% sedimentary rocks (80% are shales, 15% sandstones and 5% limestone). Sedimentary rocks are more important than igneous rocks as soil parent materials. They are formed by the

lithification of sediments comprising rock fragments or resistant primary and secondary minerals such as clays or chemical precipitates including calcium carbonates. The concentration of trace elements in sedimentary rocks is depending on the mineralogy and adsorptive properties of the sedimentary material (Alloway, 1995; He *et al.*, 2005). The biochemical weathering processes leads to the destruction of parent materials and to the transfer of elements from the minerals into solutions. These processes include dissolution, hydration, hydrolysis, oxidation, reduction and carbonatisation of minerals (Kabata-Pendias, 2001). Trace elements occur as trace constituents of primary minerals in igneous rocks which crystallize from molten magma. They become incorporated into these minerals by isomorphously substituting in the crystal lattice for ions of one of the major element at the time of crystallisation. This substitution is governed by the ionic charge, ionic radius and electronegativity of the major element and of the trace element replacing it (Alloway, 1995).

In general, trace metals, including Cu, Zn, Cr, Co and Mn occur mainly in the weathered processes constituents of igneous rocks such as augite, hornblende and olivine. Also the sedimentary rock and sandstones are composed of minerals that are resistant to weathering and usually have little amounts of trace elements. The high amount of trace elements including Cu, Zn, Mn, Pb, and Cd occur from shales, which are derived from fine sediments of inorganic and organic origin. In addition, soils derived from the weathering of coarse-grained materials such as sands and sandstones and also from acid igneous rocks including rhyolites and granites tend to contain smaller amounts of nutritionally essential metals such as (Cu, Zn, and Co) than those derived from fine-grained sedimentary rocks such as clays and shales, and from basic igneous rocks. This is possibly due to their ability to adsorb metal ions (He *et al.*, 2005). The main concentration of metals in igneous and sedimentary rocks is given in Table 2.1. Trace metals such as Cu, Zn, Cd, and Pb are often associated with sulfur and sulfides. Under superficial environmental conditions, sulfites are quickly oxidized and Cu, Zn, Cd, and Pb are released and separated from sulfur at an early stage of mineral weathering (He *et al.*, 2005). During soil development, Cu, Zn and Cd tend to concentrate in Mn oxides, whereas Pb is more likely enriched in the oxides and hydroxides of Fe. While under reducing conditions, Fe and Mn oxides are slowly

dissolved and sulfides of these elements are formed if there is sufficient sulfur available. In general, trace metals are presented in the form of carbonates, oxides, sulfides, or salts in most soils (He *et al.*, 2005).

Table 2.1: Trace elements concentrations in rocks (mg/kg)

Trace elements	Earth's crust	Igneous rock	Sedimentary rock
As	1.5	1-1.5	1-13
Cd	0.1	0.09-0.13	0.02- 0.22
Co	20	1-110	0.1-19
Cr	100	4-2980	11-90
Cu	50	13-90	5.5-39
Mn	950	400-1500	460-850
Ni	80	0.5-2000	7-68
Pb	14	3-24	5.7-23
Zn	75	52-100	20-120

Source: Alloway (1995)

2.1.3. Pedogenesis and translocation of trace elements in soils

Pedogenesis or soil formations are the processes resulting from the interaction of environmental conditions and biological activity on the surface of weathered rock material (Alloway, 1995). Several factors cause soil formation such as climate, vegetation, parent material, topography, time and anthropogenic activity (recultivation, degradation) (Kabata-Pendias, 2001). Pedogenesis processes relating to the behaviour of trace elements in the soil are those affecting:

- (a) Trace elements composition of the soil inherited from the parent material by weathering.
- (b) The translocation and accumulation of soil constituents which absorb metals such as clays, hydrous oxides and organic matter.

Other pedogenesis processes which are very important in relation to the behaviour of trace metals in soil include processes such as leaching, eluviations, salinisation, calcification, podzolisation and ferralitisation. The concentration of ions in the soil solution is determined by the interacting processes of oxidation, reduction, adsorption, desorption and precipitation. The concentrations of many contaminants tend to accumulate in the soil surface. Then, they are either adsorbed with varying strengths on the colloids in soil porewaters at the surface of the topsoil or are washed down through the surface layer into the soil profile. This can possibly reduce their bioavailability to plants (Alloway and Ayres, 1997). In addition trace elements such as Ag, As, Cd, Cu, Hg, Pb, Sb and Zn are found concentrated in the surface layers as a result of cycling through vegetation, atmospheric deposition and adsorption by the soil organic matter. On the other hand, the elements are concentrated in the deepest layers of the soil profiles such as, Al, Fe, Mg, Ni, Ti, V and Zr tend to associated with accumulations of translocated clays and hydrous oxides (Alloway, 1995).

2.2. Soil contamination

2.2.1. Source of contaminants

Soil contamination by trace elements is a widespread problem in many parts of the world. The accumulation of toxic metals in soil is mainly inherited from parent materials or inputs through human activities (anthropogenic inputs) (He *et al.*, 2005). The sources of anthropogenic inputs of trace metals to the soils and the environment include several processes such as metalliferous mining and smelting, agricultural and horticultural materials, sewage sludges, fossil fuel combustion, metallurgical industries, use and disposal of metal commodities, electronics- manufacture, use and disposal of electronic commodities, chemical and other manufacturing industries, waste disposal, sports shooting and fishing, warfare and military training (Alloway, 1995). On the other hand, the concentrations of trace elements in soils can be higher than those found in the parent materials causing by the use of agricultural practices such as fertilizers, organic manures, industrial and municipal wastes, irrigation, and wet and/or dry deposits (He *et al.*, 2005). Both industrial and agricultural activities are the most important to produce

trace metals in soils in many parts of the world and also contribute to increase the concentration of these elements in the surface soil (Kabata-Pendias, 2001; He *et al.*, 2005). The main source of contaminated soil agricultural include the impurities in fertilisers which contains trace amounts of trace elements (Cd, Cr, Mo, Pb, U, V, Zn), sewage sludge(Cd, Ni, Cu, Pb, Zn), manures from intensive animal production(Cu, As, Zn), pesticides(Cu, As, Hg, Pb, Mn, Zn), refuse derived composts(Cd, Cu, Ni, Pb, Zn) and wood preservatives(As, Cu, Cr) (Alloway, 1995).

2.2.2. Soil contamination by chromated copper arsenate (CCA)

One of the important sources of soil contamination results from chemical widely used wood preservative industries in aquatic environments and storing the wood after treatment by chromated copper arsenate (CCA). CCA belongs to a group of inorganic waterborne preservatives including chromated copper boron, ammoniacal copper arsenate, acid copper chromate, ammoniacal copper zinc arsenate and ammoniacal copper quaternary. CCA is a mix of copper, chromium, and arsenic formulated as oxides or salts. Depending on the proportions of metals, there are three waterborne formulations, referred to as types A, B and C (Table 2.2). In addition, Type C is the most commercially popular and used almost exclusively (Cooper, 1994; Balasoiu *et al.*, 2001; Hingston *et al.*, 2001).

Table 2.2: Chromated copper arsenate (CCA) formulations (oxides basis %)

Type	CuO	CrO ₃	As ₂ O ₅
CCA-A	18.1	65.5	16.4
CCA-B	19.6	35.3	45.1
CCA-C	18.5	47.5	34.0

Source: (Cooper, 1994; Balasoiu *et al.*, 2001; Hingston *et al.*, 2001).

This group has largely replaced alternative organic preservative types such as creosote, coal tars and pentachlorophenol for aquatic use (Hingston *et al.*, 2001). CCA has proven ability to protect wood from damage caused by moisture, bacterial and

fungi, wood attacking insects, including termites, and marine borers (Buchireddy *et al.*, 2008). Since the 1940's, the application of CCA has been used to pressure treat lumber used for decks, playgrounds and other outdoor uses. In addition, since the 1970's, the majority of the wood used in residential settings was CCA-treated wood (US EPA, 2008).

CCA-treated wood is a widespread problem in many parts of the world and a concentrated source of toxic metals to a wide range of organisms, from single celled algae to humans (Cox, 1991). The toxicity of copper, chromium, and arsenic is highly dependent its chemical form and concentration. Hexavalent chromium is known to be carcinogenic and mutagenic but during the fixation process hexavalent chromium is reduced to trivalent chromium by organic matter and may be less harmful, while pentavalent arsenic is considered to be more prevalent and less toxic than trivalent arsenic (Hingston *et al.*, 2001). Copper is the most important fungicide and forms a major fungitoxic component of four wood preservatives: CCA, ammoniacal copper zinc arsenate, copper azole, copper naphthenate and copper quinolinolate (Kartal and Imamura, 2003; Kartal, 2003). In Europe, the amounts of CCA remaining in the wood for many years and the disposal of scrap wood are a growing problem. For example, in Germany and France, the total amount of wood waste is around 3-4 million tons per year, of which 2.1-2.4 million tons is toxic (Helsen *et al.*, 1998).

Elements such as As, Cu, Cr, and Zn can be found in excess in contaminated soils at wood treatment facilities, especially when Cu sulphates and CCA were used as a preservative against insects and fungi, which may result in soil phytotoxicity (Kumpiene *et al.*, 2008). After impregnation of the wood with a CCA solution, the metal compounds are fixed to the cell walls of the wood matrix. The rain is playing a key-role in leaching these metals from the recently treated timber and lumber stored at the treatment facility. Therefore, under conditions of storage of the timber, the soils contain high concentrations of CCA (Buchireddy *et al.*, 2008).

2.2.3. Chemical form and mobility of metals in soils

Copper

Copper (Cu) is an essential micronutrient for plants. However, it is also highly phytotoxic at higher concentrations, typically above 30 mg/kg (Alloway, 1995; Song *et al.*, 2004). Copper contamination of soils is a widespread as a result of mining, smelting, land applications of sewage sludge, use of Cu as fungicides, algicides, chromated copper arsenate (CCA) pressure treated lumber, copper pipes and other industrial activities (Evanko and Dzombak, 1997; Song *et al.*, 2004). Copper is distinctly soluble under oxidised condition than under reduced ones in the pH range 5.4-6.5 (Bhattacharya *et al.*, 2002). In addition, the cupric ion Cu^{2+} is the most common mobile metal in the surface environment below pH 6.9 (Alloway, 1995; Kabata-Pendias, 2001). Therefore, increasing pH soil caused Cu to be strongly adsorbed at the colloidal surfaces by decreasing the exchangeable form. It has also been suggested that in for a pH higher than 7, copper tend to precipitate in the form carbonate and hydroxide (Gagnon, 1998). Thus, $\text{Cu}(\text{OH})_2$ is the major solution species above pH 7 (Alloway, 1995). In addition, in aerobic conditions, the form CuCO_3 is the dominant soluble copper species followed by cupric ion, Cu^{2+} , and hydroxide complexes, CuOH and $\text{Cu}(\text{OH})_2$, while in anaerobic environments, when sulfide is present the form CuS is the dominant soluble species (Evanko and Dzombak, 1997).

Copper mobility in soils depends on several factors, including the Cu-complexing ability of the solid phase, the Cu-complexing ability of the dissolved organic matter (DOM) and the molecular weight of the DOM fractions (Han and Thompson, 2003). Cu-DOM complexation increases approximately 10-fold per pH unit (Lu and Allen, 2002). Organic matter is the most important factors controlling the mobility and availability of copper. Adamo *et al.* (1996) suggested that copper was strongly associated with organic matter and was homogeneously distributed on the clay fraction surface. Copper, however, has a high affinity for soluble organic ligands and the formation of these complexes may greatly increase the Cu mobility in the soils. In addition, copper forms are strong solution complexes with humic acids. Thus, the affinity of Cu for humates increases as the pH increases and the ionic strength decreases (McLean and Bledsoe, 1992).

Copper is retained in soils through exchange and specific adsorption mechanisms (McLean and Bledsoe, 1992). The adsorption of Cu ion species is depending on the surface charge of the adsorbents. High amounts of adsorbed Cu were found for Fe and Mn oxide, amorphous Fe and Al hydroxides and clay. In addition, the Cu ions can also readily precipitate with various anions such as sulfide, carbonate, phosphates and Al and Fe hydroxide which have a great affinity to bind a part of the soil Cu (Kabata-Pendias, 2001). Kumpiene *et al.*, (2008) reported that the mechanism of copper retention were precipitation of Cu carbonates and oxy-hydroxides, ion exchange and the formation of ternary cation-anion(SO_4 , PO_4) complexes on the surface of Fe and Al oxy-hydroxides.

Chromium

Chromium (Cr) is one of the less common elements and does not occur naturally in the elemental native form but only in compounds (Evanko and Dzombak, 1997). Chromium exists in two states depending on pH and redox conditions of the soil: the trivalent chromium, Cr(III) and the hexavalent chromium, Cr(VI) (McLean and Bledsoe, 1992). Most of trivalent chromium is present in the mineral chromate (FeCr_2O_4) (Kabata-Pendias, 2001). Cr(VI) is the form commonly found at contaminated sites and it is more toxic and mobile than Cr(III) ions (McLean and Bledsoe, 1992; Evanko and Dzombak, 1997). In soils, Cr(VI) is as chromate ion, HCrO_4^- predominant at pH under 6.5, or CrO_4^{2-} , predominant at pH above 6.5, and as dichromate, $\text{Cr}_2\text{O}_7^{2-}$ predominant at higher concentrations (higher than 10mM) and at pH 2-6 (McLean and Bledsoe, 1992). In addition, Cr(III) is slightly mobile only in very acid media and at above pH 5.5, it is completely precipitated, while Cr(VI) (HCrO_4^- and CrO_4^{2-}) is very unstable in soils and is easily mobilised in both acid and alkaline soils (Kabata-Pendias, 2001).

Chromium mobility in the soil is depends on the sorption properties of the soil, including the clay content, iron oxide content and the amount of organic matter present. Under aerobic conditions Cr (VI) is the dominant form of chromium in shallow aquifers while, under anaerobic conditions Cr (VI) is reduced to Cr(III) by soil organic matter, sulfide and Fe^{2+} ions (Evanko and Dzombak, 1997). Thus the reduction of Cr in soils is

accelerated by the presence of organic matter and divalent iron (Kumpiene *et al.*, 2008). In addition, the decreased of Cr in contaminated soil may be caused by the presence of iron oxide which reduced Cr (VI) to Cr,Fe(OH) by precipitation (Fendorf, 1995). In general, the application of liming, phosphate and organic matter can be effective in reducing chromate toxicity in chromium contaminated soils (Kabata-Pendias, 2001). Cr(III) forms solution complexes with NH_3 , OH^- , Cl^- , F^- , CN^- , SO_4^{2-} , and soluble organic ligands (Evanko and Dzombak, 1997). Chromate and dichromate also adsorb on soil surfaces, especially iron and aluminum oxides. Moreover CrO_4^{2-} is easily sorbed by clays and hydrous oxides (Kabata-Pendias, 2001).

Arsenic

Arsenic (As) is an element that occurs in a wide variety of minerals, mainly as As_2O_3 , and can be recovered from processing of ores containing mostly copper, lead, zinc, silver and gold (Evanko and Dzombak, 1997). The form of arsenic in the soil is arsenate, As(V) (AsO_4^{3-}), or as arsenite, As(III) (AsO_2^-), depending on the pH and redox conditions. The pH and the oxidation-reduction are the most important processes affecting the fate of arsenic in soils. Thus, at high redox levels, As(V) is dominant, usually in the form of arsenate (AsO_4^{3-}) in various compounds: H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , AsO_4^{3-} and arsenic mobility is low (McLean and Bledsoe, 1992; Evanko and Dzombak, 1997). The complex anions AsO_2^- , AsO_4^{3-} , HAsO_4^{2-} and H_2AsO_4^- are the most common mobile forms of As, being sorbed at the pH range from 7 to 9 (Kabata-Pendias, 2001). Under reducing conditions, As(III) dominates, existing as arsenite (AsO_3^{3-}) and its various forms: H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-} depending on the pH (McLean and Bledsoe, 1992; Evanko and Dzombak, 1997).

Arsenic mobility in soils is mainly controlled by adsorption/desorption processes and co-precipitation with metal oxides such as Fe and Al (Kumpiene *et al.*, 2008). As minerals and compounds are readily soluble; however As migration is limited due to the strong sorption by clays, hydroxides, and organic matter (Kabata-Pendias, 2001). The most common As mineral is a sulfo-arsenopyrite (Kabata-Pendias, 2001). Therefore arsenite As(III) can adsorb or co-precipitate with metal sulfides and has a high affinity

for other sulfur compounds (Evanko and Dzombak, 1997). Arsenate form As(V) is insoluble and precipitates with iron, aluminum, and calcium which are important in controlling arsenate mobility (McLean and Bledsoe, 1992). In addition As(V) can also co-precipitate with or adsorb onto iron oxyhydroxides under acidic and moderately reducing conditions (Evanko and Dzombak, 1997). Adsorption of arsenate by $\text{Al}(\text{OH})_3$ was reported by Xu *et al.* (2008) and who found that both the amount of arsenate adsorbed by the amorphous $\text{Al}(\text{OH})_3$ and the mole fraction of arsenate remaining adsorbed on the amorphous $\text{Al}(\text{OH})_3$ after desorption were substantially greater than those in the crystalline $\text{Al}(\text{OH})_3$ system.

2.3. Soil remediation

2.3.1. Introduction

The mobility and exchangeable fraction of trace elements in soils are the most important associated parameters to toxicity and bioavailability in contaminated soils. Therefore it is very important to remove or reduce trace metals in contaminated soils by the application of assisted natural remediation processes. Currently there are several technologies that can be used to clean up or remove metals from contaminated soils and mining wastes, such as thermal treatments, biological and physical/chemical procedures. These removal technologies generally require the removal of contaminated soil, its subsequent treatment and either replacement it *on-site*, or disposal in specific landfills which is costly to practice and destructive to the application sites and only partially effective for the total removal of toxic metals or for the sufficient reduction of their mobility and bioavailability (Raicevic *et al.*, 2005).

2.3.2. Remediation of trace elements contaminated soils using stabilization technique

In the past few decades, stabilization techniques for the *in situ* immobilisation of trace metals in contaminated soils are being developed to improve the quality of contaminated soils. These techniques can be used *in situ* and *ex situ* to reclaim and re-

vegetate industrially devastated areas and mine-spoils, restore the physical, chemical, and biological soil properties, and reduce the contaminant mobility and bioavailability with various chemical and mineralogical agents. *In situ* stabilization of trace metals in contaminated soil by adding amendment is one of the common practices for reducing negative effects of contaminants such as As, Cr, Cu, Pb, Cd and Zn in contaminated soils.

In situ remediation techniques or *in situ* immobilisation which is generally non-disruptive for the natural landscape, hydrology and ecosystems are excavation, treatment, and disposal methods. It is considered as a simple and cost-effective approach for the treatment of metals in contaminated soils, when these soils are difficult or costly to be removed and treated *ex situ*. *In situ* immobilisation aim at enhancing natural attenuation mechanisms such as (ad)sorption, through increased surface charge, precipitation, complexation and redox reactions that occur naturally in the soils to reduce the mobility and bioavailability of the toxic elements in contaminated soils. In addition the main goal of this technique is not to reduce the total content of contaminants but help to lowers the fraction of toxic elements or compounds, which are potentially mobile or bioavailable (Mench *et al.*, 2000; Oste *et al.*, 2002; Bolan and Duraisamy, 2003; Adriano *et al.*, 2004; Pérez de Mora *et al.*, 2005; Raicevic *et al.*, 2005; Kumpiene *et al.*, 2006; Kumpiene *et al.*, 2008). On the other hand, the main advantage of the application of stabilization techniques is the simple mixing of several amendments with soil to reduce the mobility and bioavailability of trace elements in contaminated soils while the disadvantage of this approach is that the final product of remediation, which contains the immobilized contaminant, although existing in inactive form, still remains in the soil (Raicevic *et al.*, 2005).

2.3.3. Dynamics of trace elements in soils

The soil is a dynamic system with various soil properties. In soils, trace metals interact with soil minerals and its organic constituents. However the fate of metals in the soil environment is dependent on both soil properties and environmental factors (Bolan

et al., 2003; Adriano *et al.*, 2004). The dynamics of trace metals in soils depend on the physico-chemical and biological interactions with inorganic and organic soil constituents (Adriano, 2001). The physico-chemical processes aim at retaining trace metals in soil largely by (ad)sorption, precipitation and complexation reactions. Sorption is defined as the accumulation of matter at the interface between the solid adsorbent and the aqueous phase. This can include ion exchange, formation of surface complexes, precipitation and diffusion into the solid (Adriano *et al.*, 2004). In many situations, the adsorption is believed to be the precursor for subsequent precipitation and it is difficult to separate the boundary between adsorption and precipitation processes (Bolan *et al.*, 2003).

2.3.4. Factors affecting the immobilisation technique

Several factors affect the bioavailability and immobilisation of trace metals in soils. The main following factors controlling the mobility of trace metals in soils will be discussed in detail.

Effect of the soil pH

The soil pH is an indication of the acidity or alkalinity of the soils. The soil pH is affected by the changes in redox potential which occurs when soils become waterlogged under periodically-reducing conditions causing a pH increase whereas oxidation brings a decrease in pH. The soil pH usually increases with depth in humid regions where bases are leached down the soil profile and also decreases with depth in arid environments causing by the evaporation of salts and accumulates in the surface horizon (Alloway, 1995). The effect of soil pH is important on the solubility of minerals or nutrients. Most minerals and nutrients are more soluble or available in acid soils than in neutral or slightly alkaline soils. Thus, extremely and strongly acid soils (pH 4.0-5.0) can have high concentrations of soluble aluminum, iron and manganese which may be toxic towards the growth of some plants. Generally, the pH range of approximately 6 to 7 promotes the most ready availability of plant nutrients. In addition, the pH of the soil

system is a very important parameter, directly influencing sorption/desorption, precipitation / dissolution, complex formation and oxidation-reduction reactions. Maximum retention of cationic metals occurs at pH above 7 and maximum retention of anionic metals occurs at pH below 7 (McLean and Bledsoe, 1992).

Several studies on adsorption and immobilisation of metals by soil and soil additives have shown that the pH is a master variable. The pH affects several mechanisms of metal retention by soils either directly or indirectly. Many adsorption sites in soils are pH dependent, *i.e.* Fe and Mn (hydro)oxides, organic matter, carbonates and the edges of clay minerals (McLean and Bledsoe, 1992). As the pH decreases, the number of negative sites for cation adsorption decreases, while the number of sites for anion adsorption increases. Also as the pH becomes more acidic, metal cations also face competition for available permanent charged sites with Al^{3+} and H^+ (McLean and Bledsoe, 1992). Under alkaline conditions, all trace metals whether under hydroxide, oxide, carbonate, and phosphate form precipitate (Lindsay, 1979). The dissolution of lead, copper, nickel, and zinc precipitates are strongly dependent on the pH and with retention dramatically increasing above pH 7.0 to 7.5 (Harter, 1983). The sorption of Cu, Zn, and Cd as a function of pH was examined in acid soils. Copper sorption increased with increasing pH and Cu was preferentially sorbed over Zn and Cd (Kuo and Baker, 1980).

The stability of metal complexes is pH-dependent with little association in acidic media. The adsorption of Cu by montmorillonite is reduced in the presence of water-soluble ligands extracted from sludges and various other organic materials (Baham and Sposito, 1986). This behaviour is the opposite of the typical relationship between metal adsorption and pH (McLean and Bledsoe, 1992). McBride and Blasiak (1979) studied the effect of pH on Zn^{2+} and Cu^{2+} solubility in an acid mineral soil and results indicate the probable involvement of hydrous oxides of iron, aluminum, or manganese in the adsorption process; the authors also found that the adsorption on permanent charge sites of clays or complexation with organic matter could not account for the

apparent fixation of Zn^{2+} in a non-exchangeable form in the pH range of 5 to 7, while Cu^{2+} showed more evidence of being controlled by organic complexation mechanisms.

The soil pH dependence of adsorption reactions of cationic metals is due, in part, to the preferential adsorption of the hydrolysed metal species in comparison to the free metal ion. The proportion of hydrolysed metal species increases with pH. Cavallaro and McBride (1980) found that copper adsorption by soils showed stronger pH dependence than Cd. This result is consistent with the hypothesis that hydrolysis of Cu at pH 6 increases its retention by soil, while cadmium does not hydrolyse until pH 8. Stahl and James (1991) also showed that zinc was retained in an exchangeable form at low pH in soil materials with varied mineralogy and sesquioxide contents (Fe and Mn oxide) but the non-exchangeable as the pH was increased above 5.5. These changes in mechanism of sorption are due to the hydrolysis of Zn and the adsorption of the hydrolysed species by the oxide surfaces. Barrown and Whelan (1998) studied the effects of soil pH on sorption of cadmium, zinc, nickel and cobalt by changing the pH of a soil and measuring sorption and observed that when the metal ions were incubated with the soil, an unit increase in pH decreased the concentration of metal ions about 10-fold for zinc, about 7-fold for nickel, about 6-fold for cobalt, and about 4-fold for cadmium; however when the soil was mixed with a large volume of solution, the effects were similar for zinc and cadmium but slightly smaller for cobalt and slightly larger for nickel. Metal sorption depended more on metal type than soil composition. Sorption characteristics of two metals, Cd and Pb, in three tropical soils (Mollisol, Oxisol, and Ultisol) were investigated by Appel and Ma (2002) who found that all soils sorbed more Pb than Cd. Cd was probably sorbed via electrostatic surface reactions and/or possible inner-sphere complexation at pH above 3.7. However, the amount of Pb sorbed by the Oxisol was greater than the amount of negative surface charge.

Effect of redox reactions

The redox potential of a soil system is a measure of the electrochemical potential or availability of electrons within a system. A measure of the redox potential indicates whether the metals are in oxidised or reduced state (McLean and Bledsoe, 1992).

Metals or elements which gain electrons and lose in valence are undergoing reduction, while those losing electrons and gaining in valence are becoming oxidized. In soils, reducing conditions are brought by the absence of oxygen (anaerobic). This is caused by the oxygen being consumed by the oxidation of organic matter at a greater rate that it can be transported into the soil system. This can be caused by water-logged soils or soils containing oxygen consuming compounds. Oxidising conditions are normally found in well-drained soils as well as soils that have not been subjected to contamination by spills or leaks (McLean and Bledsoe, 1992).

Soil redox potential can influence the solubility of metals in soils. In reducing conditions, the solubility of Zn, Cu, Cd, and Pb is higher in alkaline soil as a result of the formation of stable soluble organomineral complexes. However in oxidised conditions, the solubility of metals increases with decreasing pH (Silveira *et al.*, 2003). Chuan *et al.* (1996) reported that the mobilities of Pb, Cd, and Zn from a contaminated soil increased when the redox potential decreased. Generally acidic and reducing conditions were most favorable for metal solubilization and mobility. The dissolution of Fe-Mn oxyhydroxides under reducing conditions results in the remobilisation of adsorbed heavy metals from soils (Chuan *et al.*, 1996). In contrast, under soil flooding conditions, exchangeable Cd decreases and Cd increases in the complexed fraction, while under in upland conditions, Cd uptake would be more favourable rather than flooded conditions (Xiong and Lu, 1993). For instance in submerged paddy rice, the higher solubility of Fe maintained by $\text{Fe}_3(\text{OH})_8$ may depress Zn^{2+} solubility through the formation of ZnFe_2O_4 or a franklinite-like solid material (Sajwan and Lindsay, 1986). The behaviour of chromium and selenium also illustrates the importance of redox conditions to metals mobility in soils. Hexavalent Cr (VI) is toxic and a relatively mobile anion while trivalent Cr(III) is less toxic, relatively insoluble and strongly adsorbs to surfaces. Selenate Se(VI) is mobile but less toxic than selenite Se(IV) which is more toxic, but less mobile (McLean and Bledsoe, 1992).

In general, oxidising conditions help to immobilize metals in soils while reducing conditions contribute to an accelerated migration. Redox reactions can greatly

affect the transport of contaminants; in slightly acidic to alkaline environments, Fe(III) precipitates as a highly adsorptive solid phase (ferric hydroxide), while Fe(II) is very soluble and does not retain other metals. The reduction of Fe (III) to Fe (II) will bring the release of ferrous iron to the pore waters and also any metals that were adsorbed to the ferric hydroxide surfaces (McLean and Bledsoe, 1992). In addition, redox conditions may change as a result of fluctuating soil moisture content or decaying organic matter or due to biological activity, particularly in the rhizosphere. Staunton and Wang (2005) found that the change in redox conditions induced by soil moisture conditions did have some effect on the solubility of Cu and Zn and these changes could be partially related to changing pH and the solubility of soil metal oxides.

Effect of adsorption

A charged solute ion is attracted to a charged soil surface by electrostatic attraction and/or through the formation of specific bonds. Retention of charged solutes by charged surfaces can be broadly grouped into specific and nonspecific retention (Bolan *et al.*, 2003). The nonspecific adsorption is a process in which the charge of the solute ions balances the charge on the soil particles through electrostatic attraction, while the specific adsorption involves the formation of a chemical bond between the ions and the sorption sites on the soil surface (Bolan *et al.*, 2003; Adriano *et al.*, 2004). Therefore, the amount of metal sorbed exceeds the cation /anion exchange capacity of the soils (Bolan *et al.*, 2003). This infers that the nonspecific adsorption and other processes such as specific adsorption, precipitation and complex formation also contribute to the retention of metals in soils (Bolan *et al.*, 2003; Adriano *et al.*, 2004).

In general, both soil properties and soil solution composition determine the equilibrium between metals in the soil solution and the soil solid phases. The concentration of metals in soil solution is largely influenced by the pH and the nature of both organic and inorganic anions (Shuman, 1986; Naidu *et al.*, 1994; Adriano, 2001; Bolan *et al.*, 2003). The effect of pH values higher than 6 in lowering free metal ion activities in soils can be attributed to the increase in the pH-dependent surface charge on

oxides of Fe, Al and Mn, chelation by organic matter, or precipitation of metal hydroxides (Adriano, 2001). Naidu *et al.* (1994) studied the effect of pH and ionic strength on the surface charge of soil and sorption of cadmium and who observed that Cd is adsorbed when the potential of adsorption is either positive or negative providing evidence for both specific and non-specific adsorption of Cd.

Effect of competitive major cations

Metal adsorption reactions, in a competitive system, are important to determine the metals availability to plants and their mobility throughout the soil. For specific adsorption sites, trace cationic metals are preferentially adsorbed over the major cations (Na, Ca, Mg), while trace anionic metals are preferentially adsorbed over the major anions (SO₄, NO₃, soluble ionized organic acids). However, when the specific adsorption sites of the soil solid phase become saturated, exchange reactions dominate and competition for these sites with soil major ions becomes important (McLean and Bledsoe, 1992). Cavallaro and McBride, (1978) reported that in the presence of 0.01M CaCl₂, adsorption of Cu and Cd were much reduced, suggesting that Ca²⁺ compete for adsorption sites. The adsorption of Pb from Pb(NO₃)₂ solutions by Ca-montmorillonite is depends on the Pb/Ca ratio. Thus, the adsorption of Pb from 0.1M Ca (ClO₄)₂ solutions were considerably lower and were not sensitive to the weight of the clay (Griffin and Au, 1977).

The complex formation inhibits the sorption of metals on the clay, with an increasing influence in the order: Mn ≤ Pb ≤ Cd ≤ Zn < Ni < Cu < Cr. The Na-montmorillonite clay shows that it is a good sorbent towards all these metals (Abollino *et al.*, 2003). Ma (1996) studied the effects of Ca, K and Na on Pb immobilisation by hydroxyapatite [Ca₁₀ (PO₄)₆(OH)₂] and found that neither Na nor K affected Pb immobilisation. However aqueous Ca slightly inhibited Pb immobilisation. In addition, Pb(OH)₂ precipitate was present as positively charged Pb polymers (Janssen *et al.*, 2007). In acid contaminated soils, copper sorption increased with increasing pH and Cu was preferentially sorbed over Zn and Cd (Kuo and Baker, 1980). In addition, the influence of Ni and Cu on Zn sorption was significant only when metal concentration in

the soil solution was in excess of the sorbing capacity of the soil. Thus Cu was more effective than Ni in decreasing Zn sorption (Elrashidi and O'Connor, 1982). The effects of aqueous Al, Cd, Cu, Fe, Ni and Zn on Pb immobilisation by hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] was reported by Ma *et al.* (1994b) who found that these metals inhibited Pb immobilisation by hydroxyapatite in the order of: $\text{Al} > \text{Cu} > \text{Fe} > \text{Cd} > \text{Zn} > \text{Ni}$ and $\text{Cu} > \text{Fe} > \text{Cd} > \text{Zn} > \text{Al} > \text{Ni}$ at high and low initial Pb concentrations. This inhibition was probably through the precipitation of amorphous to poorly crystalline metal phosphates. For the competitive adsorption, Gomes *et al.* (2001) reported that the soil properties may have affected the heavy metals adsorption represented by the distribution coefficients; pH and cation-exchange capacity (CEC) for Cd, Ni, Pb and Cr while organic carbon, clay, and gibbsite contents for Cu.

Effect of complex formation

The effect of complex formation on the sorption of metals by soils is dependent on several factors: the type and amount of metal present, the type and amount of ligands present, soil surface properties, soil solution composition, pH soil and redox conditions. The decrease in positive charge on the complexed metals ions reduces adsorption to a negatively charged surface (McLean and Bledsoe, 1992). In general the formation of metal cations complexes with inorganic and organic ligands can enhance or inhibit on the adsorption metals.

a. Complexation by inorganic ligands

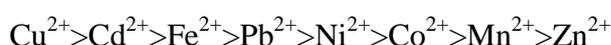
Hydrolysis and chloride complexation are important factors in the distribution and solubility of metals ions. Both the hydroxy and chloride complexes may contribute to the mobilisation of metal ions such as Hg (II), Cd (II), Zn (II), and Pb (II) in the environment (Hahne and Kroontje, 1973). In addition, chloride increases the mobility of Cd(II) and, to a lesser extent, Ni(II) and Cu(II) through soil (Doner, 1978). Elrashidi and O'Connor (1982) reported that the complexation of Zn (ZnSO_4) in the SO_4^{2-} was higher than in either the NO_3^- [$\text{Zn}(\text{NO}_3)^+$] or Cl^- [$\text{Zn}(\text{Cl})^+$] form. In an acid soil, Shuman (1986) also observed that the adsorption zinc with SO_4^{2-} complexes produced

higher adsorption than NO_3^- or Cl^- ions. Moreover increasing ionic strengths decreased the amount of Cd sorbed on the clay surfaces. Garcia-Miragaya and Page (1976) found that the sorption of Cd in the chloride form was higher than in the SO_4 form. This is due to the presence of uncharged and negatively charged complexes of Cd with Cl ligands.

The mechanisms of Cu^{2+} bond on noncrystalline aluminum hydroxide with or without various levels of pre-sorbed phosphate was reported by McBride (1985) and found that high levels of sorbed phosphate suppressed Cu^{2+} adsorption. The decrease adsorption of Cu^{2+} was a result of the weaker coordination of Cu^{2+} to the phosphate-coated surface than to the alumina surface in the absence of phosphate. In addition, the sorption of cadmium by phosphate-free and phosphate-enriched hydrous iron oxides was investigated by Kuo and Neal (1984). They found that the precipitation of these compounds was not a likely mechanism controlling the concentrations of soluble Cd for these systems. The adsorption of Zn was increased when the presence of phosphate on oxide surface (Bolland *et al.*, 1977). Ma *et al.* (1994a) also studied the effects of inorganic ligands such as (NO_3^- , Cl^- , F^- , SO_4^{2-} , and CO_3^{2-}) on Pb^{2+} immobilisation by hydroxyapatite. Results indicate that the solution concentrations of Pb^{2+} were reduced after reaction with hydroxyapatite, except in the presence of high levels of CO_3^{2-} and Pb^{2+} .

b. Complexation by organic ligands

Soil organic matter is important for cation exchange reactions and in the formation of complexes with metals. Soluble organic molecules can form stable complexes with metals which are mobile in the soil solution and bioavailable due to the protection on the metal from adsorption on soil colloid surfaces by the organic ligand (Alloway and Ayres, 1997). With increasing pH, the carboxyl, phenolic, alcoholic and carbonyl functional groups of organic matter dissociate, thereby increasing the affinity of ligand ions for metal cations. The general order of affinity for metal cations complexed by organic matter is present in the following sequence (Adriano, 2001).



The complex formation between metals and organic ligands influences the adsorption and mobility of metals. The extent of complexation between a metal and soluble organic matter depends on the competition between the metal-binding surface sites and the soluble organic ligand for the metal (McLean and Bledsoe, 1992). Interaction of Cu with dissolved organic matter (DOM) is an important physico-chemical process affecting Cu mobility in the soils. The presence of soluble organic and complexed Cu in the solution is depending on the pH soil and high amount of organic matter (McBrid *et al.*, 1997). Zhou and Wong (2001) suggested that the sorption of Cu increased with an increase in the pH for soils without the addition of DOM, while Cu sorption in the presence of DOM was decreased with an increase in pH at a pH higher than 6.8. The mobility of some micronutrients such as Mn, Zn, Cu, and Fe was investigated and found to be affected by soil organic matter and humic acid fraction (Khan *et al.*, 1997); it was also found that the soil organic matter concentration increased caused by the decreased of the metal mobility, while the increasing concentration of the humic acid fraction generated an increase in their mobility in the order Mn > Zn > Cu > Fe. In addition, the metal mobility through the soil followed the order: Ni > Mn > Cr > Cu > Pb and the higher mobility were observed in soil with decomposed organic matter than in soil with organic matter (Khan *et al.*, 1996).

The distribution of trace metals in natural aqueous systems may be controlled by surface binding on colloidal particles coated with humic compounds rather than reactions with simple oxide surface sites. In some cases metal uptake is increased by the presence of adsorbed ligands at the mineral surface. Trace metal adsorption can be significantly enhanced when a ligand is adsorbed with a strongly complexing such as thiosulfate, glutamic acid, 2,3-PDCA, ethylenediamine (Davis and Leckie, 1978; McLean and Bledsoe, 1992). Copper uptake was significantly decreased by the presence of picolinic acid. Therefore picolinic acid complexed Cu and the resulting complex were not adsorbed by the oxide surface (Davis and Leckie, 1978). In contrast, Cd(II) adsorption was not significantly affected by the presence of organic matter at the oxide surface, due to weak complex formation with the organic ligands (Davis, 1984).

2.3.5. Soil additives for physico-chemical immobilisation of metals

In situ remediation techniques or *in situ* immobilisation methods generally aim at decreasing the labile pool of metals and metalloids such as Cr, Cu, As that originate from chromated copper arsenate (CCA) used as wood impregnation and also reduce other metals such as Zn, Pb, Cd, Ni by incorporation of amendments into the contaminated soil. *In situ* immobilisation by the addition of amendments is less expensive and non-disruptive for the natural landscape, hydrology, and ecosystems as compared to the conventional excavation, treatment, and disposal methods. These techniques are able to enhance one or several sorption processes such as metal adsorption through increased surface charge, increased formation of organic and inorganic metal complexes, sorption on Fe, Mn and Al oxides, and precipitation. This technique can be used in *in situ* and *ex situ* applications to reclaim and re-vegetate industrially devastated areas and mine-spoils, restore the physical, chemical, and biological soil properties, and reduce the contaminant mobility and bioavailability with various chemical and mineralogical agents (Mench *et al.*, 2000; Oste *et al.*, 2002; Bolan and Duraisamy 2003; Adriano *et al.*, 2004; Pérez de Mora *et al.*, 2005; Raicevic *et al.*, 2005; Kumpiene *et al.*, 2006; Kumpiene *et al.*, 2008).

Several application studies have demonstrated that the *in situ* immobilisation of contaminated soils and groundwaters by using inexpensive soil amendments, such as alkaline materials (calcite, lime, dolomite and slag), phosphate minerals (phosphoric acid, phosphate rocks, synthesized apatites), aluminosilicates mineral (clay and zeolites), iron and manganese oxides and hydroxides and zerovalent iron, organic matter and alkaline biosolids (waste by-products) were found to be suitable for the remediation of metal-contaminated soils. The amendments significantly reduced the mobility of metals in soil, metal uptake by plants, and metal phytotoxicity. The following common soil additives for the *in situ* immobilisation of metals contaminated soil will be discussed in detail.

2.3.5.1. Alkaline materials

Neutralizing agents in the form of alkaline materials are usually added to acidic soils to ameliorate the chemical and physical properties of these soils (*e.g.* EC and pH) and reduce the mobility and bioavailability of metals to plants. Tylar and McBride (1982) reported that the addition of lime to an acidic soil can reduce the metals mobility. The amount of liming material required to rectify the soil acidity depends on the neutralising value of the liming material and pH buffering capacity of the soil (Brallier *et al.*, 1996; Brown *et al.* 1997; Bolan and Duraisamy, 2003; Tlustos *et al.*, 2006). A range of liming materials is available including calcite (CaCO_3), burnt lime (CaO), slaked lime [$\text{Ca}(\text{OH})_2$], dolomite [$\text{CaMg}(\text{CO}_3)_2$], and slag [CaSiO_3], with various ability to neutralise the acidity (Bolan and Duraisamy, 2003).

The lime binds H^+ ions which are sorbed to binding sites on the surface of soil particles. According to changes in the soil pH, the lime can induce metal hydrolysis reactions and/or co-precipitation with carbonates, thus acting as a precipitating agent for metals in the soil (Mench *et al.*, 1998). In general, a rise in pH decreases the mobility of metals in the soil. In contrast, under alkaline conditions in the soil the mobility of anions (*e.g.*, arsenate and chromate) (Singh and Oste, 2001) or organic contaminants can be increased by increasing the soluble organic matter fractions (Mench *et al.*, 1998). The addition of lime in acid soil does not only replace hydrogen ions and raises the soil pH, thereby eliminating most major problems associated with acid soils, but also provides two nutrients, calcium and magnesium, to the soil. Lime also makes phosphorus that is added to the soil more available for plant growth and increases the availability of nitrogen by hastening the decomposition of organic matter (SUNY-ESF, 2009).

Lime is a well known amendment in agriculture and it is used to increase the availability of essential nutrients and also to decrease the availability of elements harmful to plants, animals and humans (Singh and Oste, 2001). Liming is one of the methods commonly in soil to reduce the solubility and plant uptake of Zn and Cd (Krebs *et al.*, 1998) and decreases the soluble fraction and the concentration of Cd, Ni, Zn and Cu in plants significantly in metals rich soils (Singh and Oste, 2001).

Applications of lime combined with organic matter were already practiced more than thirty years ago to remediate the Cu phytotoxicity in French vineyard (Mench *et al.*, 1998). Derome and Saarsalmi, (1999) found that the addition of lime can decrease the Cu, Ni and Zn concentration in the soil solution sampled by a lysimeter in a contaminated soil. The addition of lime at high excess copper in a contaminated soil improved the growth of plant seedling (Fessenden and Sutherland, 1979). Bes and Mench (2008) reported that the application of lime to remediate a copper contaminated soil can increase the pH soil, improve the beans plant growth and decrease the Cu concentration in the soil solution and primary leaves. On the other hand, Mench *et al.* (1998) found that liming of contaminated soils was less effective to reduce the Cd mobility and plant Cd and Zn uptake. In addition, the application of lime in acid soils reduced the uptake of Cd, Ni and Zn to crops as well as increasing crop yield, but generally did not change Cu uptake by crops (Brallier *et al.*, 1996). Similarly, Tlustos *et al.* (2006) found that the efficiency of liming for immobilisation of Cd, Pb, and Zn in acid contaminated soil reduced these metals uptake and increase the crop production.

The addition of alkaline materials may be an effective chemical treatment for the immobilisation of cationic metals in the acid soil solution (Mench *et al.*, 1998; Singh and Oste, 2001). Limestone addition to contaminated soils can reduce the labile Zn soil fractions, increase the soybeans yield and decrease tissue metal concentration (Mench *et al.*, 1998). In addition to the effects of limestone or manure on the availability of soil Zn, Cd and Pb to soybeans grown in metal contaminated soil, the soybeans yield was significantly increased and the Zn concentration was reduced while the root tissue Cd or Pb concentration were not significantly influenced by the addition rate of limestone or manure (Pierzynski and Schwab, 1993). Similarly the application of sugar foam and dolomite residue in a metal contaminated soil reduced the availability and mobility of Cd, Cu and to a lesser extent, Pb, while the application of red gypsum and phosphogypsum in this soil proved effective in immobilizing Pb and to a lesser extent Cu and Cd (Garrido *et al.*, 2005).

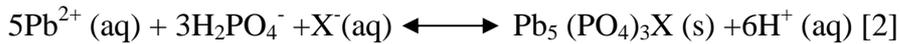
2.3.5.2. Phosphate minerals

Phosphate compounds and associated materials such as phosphoric acid, phosphate rocks, synthesized apatites have been successfully applied to stabilize Pb, Cd, Zn and Cu in contaminated soils, sediments and solid wastes, reducing their bioavailability for plant uptake and thus their mobility in soils and subsequent groundwater contamination (Bolan *et al.*, 2003; Liu and Zhao, 2007). Phosphate enhance the immobilisation of metals in soils through several processes including direct metal adsorption by the phosphate, phosphate anion-induced metal adsorption and precipitation of metals with phosphate as metal phosphates (Adriano *et al.*, 2004). Surface complexation and coprecipitation are the most important mechanisms with possibly ion exchange and solid diffusion; the major metal surface species are likely to be $\equiv\text{POZn}^+$ and $\equiv\text{POCd}^+$ (Xu *et al.*, 1994). The effects of phosphate addition on Zn sorption could be large and could either increase or decrease Zn sorption depending on the direction of the pH effect (Barrow, 1987).

Phosphates minerals have the potential to sorb and /or coprecipitate trace metals (Ma *et al.*, 1993; Pierzynski and Schwab, 1993; Xu *et al.*, 1994; Ma, 1996; Mench *et al.*, 1998). The application of phosphate minerals for the remediation of contaminated soils with *in situ* immobilisation of Pb was reported by numerous authors (Ma *et al.*, 1995; Ma 1996; Basta *et al.*, 2001; Cao *et al.*, 2003; Chen *et al.*, 2003; Geebelen *et al.*, 2003). Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; HA] is effective in immobilizing aqueous Pb in the presence of anions (NO_3^- , Cl^- , F^- , SO_4^{2-} , or CO_3^{2-}) and cations (Al^{3+} , Cd^{2+} , Cu^{2+} , Fe^{2+} , Ni^{2+} or Zn^{2+}) (Ma *et al.*, 1994a,b). The sorption of aqueous Pb was primarily through a process of dissolution of apatite followed by the precipitation of variable pyromorphite-type minerals (Wright *et al.*, 1995). The addition of hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$; (HA) in the presence of Ca, K, Na, calcite and EDTA in Pb-contaminated soils can reduce aqueous Pb by 97% in the form of hydroxypyromorphite [$\text{Pb}_{10}(\text{PO}_4)_6(\text{OH})_2$; HP] (Ma, 1996). HA was also effective at reducing the solubility of Ni, Al, Ba, U, Cd, Co, Mn, and Pb in several contaminated soils (Seaman *et al.*, 2001). In addition, the application 0.5% and 1% hydroxyapatite (HA) as a soil additive for the *in situ* remediation of metals (Zn, Pb, Cu, and Cd) in contaminated soils resulted in a decreased

of the exchangeable metal contents in soil and also a decrease of toxic metals in the plant leaves; however As mobility increased due to the phosphate-arsenate competition for the sorption complex of the solid soil phase (Boisson *et al.*, 1999a,b).

On the other hand, phosphate rock (PR) was equally or more effective than triple superphosphate (TSP) or phosphoric acid (PA) in reducing bioavailable Pb in contaminated soils. Thus, the dissolution of PR and subsequent formation of pyromorphite can be expressed as follows (Hettiarachchi *et al.*, 2001).



Where X = F⁻, OH⁻, or Cl⁻.

In Pb contaminated soils, the addition of triple superphosphate (TSP) significantly reduced bioavailable Pb, Cd, and Zn concentrations in shoot plants and did not change with the addition of phosphate rock (PR), while the combination of phosphate rock (PR) and Mn oxide significantly reduced Pb concentrations in plants (Hettiarachchi and Pierzynski, 2002). In contrast, Cao *et al.*(2004) found that PR has the highest affinity for Pb, followed by Cu and Zn in contaminated soil and also reported that the greatest stability of Pb retention by PR can be attributed to the formation of insoluble fluoropyromorphite [$\text{Pb}_{10}(\text{PO}_4)_6\text{F}_2$]. In addition, PR amendment enhanced metal uptake in the roots of St. Augustine grass (*Stenotaphrum secundatum*), it also significantly reduced metal translocation from root to shoot, especially Pb via the formation of a pyromorphite-like mineral on the membrane surface of the root (Cao *et al.*, 2003).

Thomas phosphate basic slag was used as an amendment in several contaminated soils, which affect $K_{d\text{Cd}}$ especially in acid soil, decreases Cd and Zn in shoot uptake by ryegrass, restorate dwarf beans growth and also lowers Pb

bioavailability in contaminated soils and concentration of Pb uptake by plants (Mench *et al.*, 1994a,b). The combination of Thomas phosphate basic slag and steel shots were more effective in reducing Zn and Cd mobility than when used separately for contaminated soils. This combination may also limit possible Mn phytotoxicity in sensitive plant species (Mench *et al.*, 1998). The incorporation of phosphate compounds (*e.g.* Thomas basic slag, ammonium phosphate and triple super phosphates) into a highly Cu contaminated soil from wood treatments facility was reported by Bes and Mench (2008). They also found that Thomas basic slag increased the soil pH values and foliar Ca concentration, decreased the Cu concentration in the soil solution and restored shoot and root biomass of beans plants. Additionally the effect of ammonium phosphate and triple super phosphate on plants production was consistent with high Cu concentration in the soil solution.

Vivianite minerals (iron phosphate) are a group of phosphates that have very similar structures ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$) and are used for the *in situ* immobilisation of metals in contaminated soils. Liu and Zhao (2007) reported that the use of iron phosphate as a stabilizer for the *in situ* immobilisation of Cu in contaminated soils can effectively reduce the leachability of Cu. The formation of copper phosphate minerals through precipitation and adsorption was probably responsible for the decrease of the Cu availability in soils. On the other hand, the combination of $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and CaCO_3 stabilizers in a multi-metal contaminated site containing Cd, Cu, Ni, Pb and Zn reduced the leaching extractable concentrations of these metals by more than 87% in a laboratory test, while the reduction ratios were 98% for Cd, 97% for Cu, 99% for Pb, 96% for Zn and 65% Ni for the field treatments (Wang *et al.*, 2001). In addition, the incorporation of K_2HPO_4 into a Zn contaminated soil significantly increased soybeans yields and significantly decreased the Zn concentrations in soybeans tissues (Pierzynski and Schwab, 1993).

2.3.5.3. Aluminosilicates minerals

Aluminosilicates mineral consists of natural materials like clay and zeolites, synthetic zeolites and incinerator ashes. Zeolites are naturally crystalline and highly porous materials. The framework of zeolites consists of $[\text{SiO}_4]_4^-$ and $[\text{AlO}_4]_5^-$ tetrahedral linked at all corners and creating fixed negatively charged sites through the structure. These tetrahedral are the basic building blocks for various zeolite structures, such as zeolites A and X (the most common commercial adsorbents) (Singh and Oste, 2001). While the negative charges are balanced by an equivalent number of mobile cations loosely in the crystal structure and free to exchange with other cations in solution (Mench *et al.*, 1998). Several studies were focused on the use of zeolites as immobilisation agents (Gworek, 1992; Chlopecka and Adriano, 1997; Leggo and Ledésert, 2001; Singh and Oste, 2001; Oste *et al.*, 2002; Mahabadi *et al.*, 2007). Zeolites can decrease the free metal concentrations in the soil solution, leading to a decreased metal uptake by plants. A small amount of zeolites may influence soils with a high acid buffering capacity and a pH above 6, particularly to reduce metal uptake by plants (Oste *et al.*, 2002). Zeolites were used for a long time in Japan to improve the soil quality. In general, farmers add zeolites to the soil to control the soil pH and nitrogen retention. In wastewater treatment plant, natural zeolites were used to remove ammonium ions and heavy metals (Singh and Oste, 2001). The combination of a nutrient source with a zeolite amendment is beneficial for plant growth on a heavily polluted soil as zeolite does not interfere with the action of the fertilizer by binding nutrient cations (Mench *et al.*, 1998).

Synthetic zeolites have a high capacity to bind heavy metals; moreover the alkaline character of this material can increase metal sorption to the soil. For instance a sodium-saturated zeolite can be bound high amounts of Ca and the competition of Ca in the soil can be decreased (Oste *et al.*, 2002). Oste *et al.* (2002) reported that the addition of synthetic zeolite had an effect on the immobilisation of Cd and Zn. They found that the free ionic concentration of Cd and Zn strongly decreased after the addition of zeolites which might explain the reduction in metal uptake in plant growth. The addition of zeolite reduced heavy metal concentration in the leachate, as well as inhibited heavy

metal mobility in the soil. In fact, the higher cation exchange capacity of the zeolite-soil mixtures and higher pH were responsible for stabilising Cd in soils. Lin *et al.* (1998) reported that the effect of synthesized zeolite on a Cd-contaminated acidic loamy soil reduced Cd leaching. The addition of synthetic zeolites to metal contaminated soils can reduce the soil phytotoxicity and improve the quality of plant growth (Edwards *et al.*, 1999).

Beringite, a modified alumino-silicate that originates from the fluidized bed burning of coal refuse (mine pile material) was investigated for the immobilisation metals contaminated soil. The high metal immobilisation capacity of beringite is based on chemical precipitation, ion exchange and crystal growth. The combination of these sorption mechanisms can explain its high metal sorption capacity (Mench *et al.*, 1998). Beringite has been used in several studies to reduce the metal concentration in soil solution and the metal uptake by plants (Mench *et al.*, 1994b; Oste *et al.*, 2001; Geebelen *et al.*, 2006). Beringite can be used for the fixation Zn and Cd in contaminated soils and can strongly reduce or eliminate the phytotoxicity of these metals in beans plants. Therefore the addition of 5% beringite to a Zn-contaminated sandy soil resulted in an increased shoot length and leaf area of beans plants and also reduced the Zn concentration in leaves from 350 mg kg⁻¹ to 146 mg kg⁻¹ (Mench *et al.*, 1998). Similarly, the application of beringite to immobilize Cu in metal contaminated soils of coffee gardens in Tanzania increased the plant growth of maize and beans plants (Loland and Singh, 2004). Beringite also increased concentration of Cu extracted by diethylenetriaminepentaacetic acid (DTPA) (Singh and Oste, 2001).

2.3.5.4. Iron and manganese Oxides and hydroxides

Iron and manganese oxides and hydroxides are known to play an important role in the retention, mobility and bioavailability of metals in contaminated soil (Mench *et al.*, 1994a; Silveira *et al.*, 2003). Iron oxides can be used to stabilise many trace elements in soils contaminated from industrial activities such as mining, wood impregnation in soil (Moore *et al.*, 2000; Mench *et al.*, 2003; Warren *et al.*, 2003; Kumpiene *et al.*,

2006; Mench *et al.*, 2006). Specific adsorption of copper on goethite was reported by Padmanabham, (1983) who found that the goethite has a great capacity to immobilise Cu. Hartley *et al.* (2004) studied the effect of Fe^{3+} , Fe^{2+} , iron grit, goethite and lime on immobilising soluble arsenic in contaminated soils and found that Fe-oxides formed *in situ* were more effective at immobilising soluble arsenic compared to goethite. In addition, iron oxide application for the treatment of As-contaminated garden soils resulted in a 50% reduction of water extractable As and a decrease of As accumulation in dwarf beans leaves (Mench *et al.*, 1998). On the other hand, the addition of hydrous manganese oxides (HMO) in Cd and Pb contaminated soil decreased to a maximum extent Cd in ryegrass and tobacco plants. Therefore the used of HMO reduced Pb concentrations only in ryegrass shoots and HMO exhibited a most promising potential to reduce either Cd or Pb transfer from the soil to soil solution or their entry into the food chain via plant uptake (Mench *et al.*, 1994a). In addition, the soluble and exchangeable fractions of Cd, Ni and Zn in a contaminated soil were decreased by the addition of 1% of hydrous iron oxide and to a lesser extent with hydrous manganese oxide. However, in these studies, hydrous iron oxide did not generally reduce shoot metal uptake by plants (Mench *et al.*, 1998).

Zerovalent iron (Fe^0) was also used for the stabilization of trace metals in a contaminated soil (Sastre *et al.*, 2004; Kumpiene *et al.*, 2006). The application of 1% Zerovalent iron (Fe^0) to reduce the mobility and bioavailability of Cr, Cu, As and Zn in a CCA-contaminated soil was investigated by Kumpiene *et al.* (2006). They found that both As and Cr concentrations decreased in soil leachates by 98% and 45% respectively, whereas As and Cr concentrations in soil pore water decreased by 99% and 94% respectively ; additionally As and Cr concentrations in plant shoots decreased by 84% and 95% respectively. However zerovalent iron was not effectively to stabilize Cu. Steel abrasive (SA) or oxygen scarfing granulate (OSG) may be effective amendments for CCA-contaminated soil. The application of SA or OSG to stabilization of metals from CCA-contaminated soil decreased the concentrations of As, Cr, Cu, and Zn in leachates and soil pore waters, while the effect of the mobility As was lower in the soil with higher organic matter content, probably due to dissolved organic matter competing for sorption sites on the iron oxides (Lidelöw *et al.*, 2007). The application of red mud as a

soil amendment in metal contaminated soil was reported by Friesl *et al.* (2003). These authors found that the red mud decreased the lability of Zn, Cd, and Ni in soils and the plant uptake of metals.

2.3.5.5. Coal fly ashes

Industrial by-products, like coal and biofuel combustion fly ashes (CFA), are alkaline materials with a high sorption capacity (Kumpiene *et al.*, 2007). Fly ashes are frequently composed of a ferro-aluminosilicate mineral in which Al, Si, Fe, K and Na are the predominant elements. The fine sand-silt particle size of fly ash makes it more susceptible than natural soils to detachment and transport by erosive processes. In addition, because the high content of the silt-size particles in a fly ash, the soil is more susceptible to surface crust formation, resulting in reduced infiltration and increased surface runoff and erosion (Gorman *et al.*, 2000). Fly ash is a useful ameliorant that may improve the physical, chemical and biological properties of degraded soils and mine lands (Gorman *et al.*, 2000; Jala and Goyal, 2006). As many fly ashes are highly alkaline, they have been used as amendments to neutralize highly acidic soils, decrease the bulk density, increase the water holding capacity, reduce the soil compaction and precipitate soluble metals. However the application of fly ash may also result in excessive soluble salts concentrations, excess boron, and adverse effects on the soil properties (*e.g.* cementation) and may even generate increased the concentrations of potentially toxic trace elements (Mench *et al.*, 1998). However the addition of fly ash reduced metals content in a contaminated soil (Ciccu *et al.*, 2001). Soil amendment with coal fly ash and peat reduced the leaching of Cu and Pb from a contaminated soil (Kumpiene *et al.*, 2007). This is possibly due to an increased amount of sorptive sites.

The most immediate effects of fly ash incorporation into soil are increases in both alkalinity and salinity (Mench *et al.*, 1998). The application 10 t ha⁻¹ of fly ash in combination with organic sources and chemical fertilisers increased the grain yield and nutrient uptake of rice, the pod yield of peanut compared to the application of chemical fertilisers alone. Additionally the metal contents in the plant and soil system were found

to remain below the permissible level (Mitra *et al.*, 2005). Moreover, in acid lateritic soil, the low availability of P and high content of Al and Fe generates nutritional imbalance which is generally corrected by lime materials. Alkaline fly ash can be used in such problematic soils as an amended material and also acts as a source of readily available plant macro and micronutrients (Mitra *et al.*, 2005; Jala and Goyal, 2006). Therefore the integrated use of fly ash, organic wastes and chemical fertilizers was beneficial in improving crop yield, soil pH, organic carbon and available N, P and K in sandy loam acid lateritic soil (Rautaray *et al.*, 2003). In addition the application of a combination of coal fly ash and peat increased the soil pH and decreased the metal mobility to allow the re-vegetate soil and reduce the metal uptake into plant shoots and reduced the soil toxicity to microorganisms (Kumpiene *et al.*, 2007).

2.3.5.6. Organic amendments

Organic matter is one the most important soil constituents retaining metals. Metal-organic associations can occur both in solution and in the solid surfaces of either native soil constituents or any added material (*e.g.* biosolids) (Silveira *et al.*, 2003). The application of sewage sludge or biosolids on soils has been widespread in agricultural areas; depending on their characteristics, they may cause an increase in metal concentration of the treated soils. Li *et al.* (2000) reported that the application of biosolids compost reduced soluble Zn and Cd in a highly Zn-contaminated soil. The potential for biosolids products to reduce Pb availability in a high Pb urban soil was shown by Brown *et al.*(2003). Kiikkila *et al.* (2002) studied the effect of biosolids as organic immobilizing agents in a heavy metal-polluted forest soil. They observed that the exchangeable Cu concentration decreased in the polluted soil; on the other hand, copper and lead mobility and bioavailability in soil were effectively reduced by using a combination of coal fly ash and natural organic matter (peat) as soil amendments (Kumpiene *et al.*, 2006). In addition, organic amendments such as manures were successful to immobilise Zn, Cd, and Pb in a metal- contaminated alluvial soil (Pierzynski and Schwab, 1993). The addition of a paper mill sludge, consisting mainly of carbonates, silicates and organic matter to a heavy-metal polluted soil decreased the available metal forms (Calace *et al.*, 2005).

2.3.6. Remediation of trace elements in contaminated soils using slags as soil amendments

2.3.6.1. Definition

Slag is a final waste material in steel making processes. In blast furnace iron making, limestone (as fluxes) is added to react with the gangue minerals (iron ore and coke) to form iron slags. In a basic oxygen furnace, the molten iron is converted into steel reacting with oxygen (Li, 1999). Kim *et al.* (2008) reported that slag is an alkaline by-product of metallurgical processes or a residue of incineration processes. Although slags are in fact, classified as wastes, they can currently consider as a product (Geiseler, 1996).

2.3.6.2. Production and application of slag in different fields

Slag is produced in metallurgical processes or as residues in incineration processes. The amounts of steel slag production in different countries are presented in Table 2.3 (Shen and Forsberg, 2003). Slag have been successfully used in different applications such as fertiliser (phosphates fertiliser), mainly used as aggregates for road construction (*e.g.* asphaltic or unbound layers), as armourstones for hydraulic engineering constructions (*e.g.* stabilization of shores), civil engineering work, and production of metallic iron and iron concentrate (Geiseler, 1996; Motz and Geiseler, 2001; Shen and Forsberg, 2003; Charles and Nemmer, 2006), and also used as landfill daily cover, soil reclamation and water refinement (Li, 1999; Ortiz *et al.*, 2000). In Europe, approximately 85% of basic steel slag is re-used, 42% in civil engineering, 17% for metallurgical use, 16% as fertiliser for agriculture purposes, and 10% as bulk fill material (Geiseler, 1996). The application of steel slag in the different fields is shown in Figure 2.1 (Shen and Forsberg, 2003).

Table 2.3: Production of steel slags in the different countries

Country	Steel slag (BOF+EAF) (Million tons/year)
Europe	12
USA	8
China	14.07
Japan	12.60

Source: Shen and Forsberg (2003)

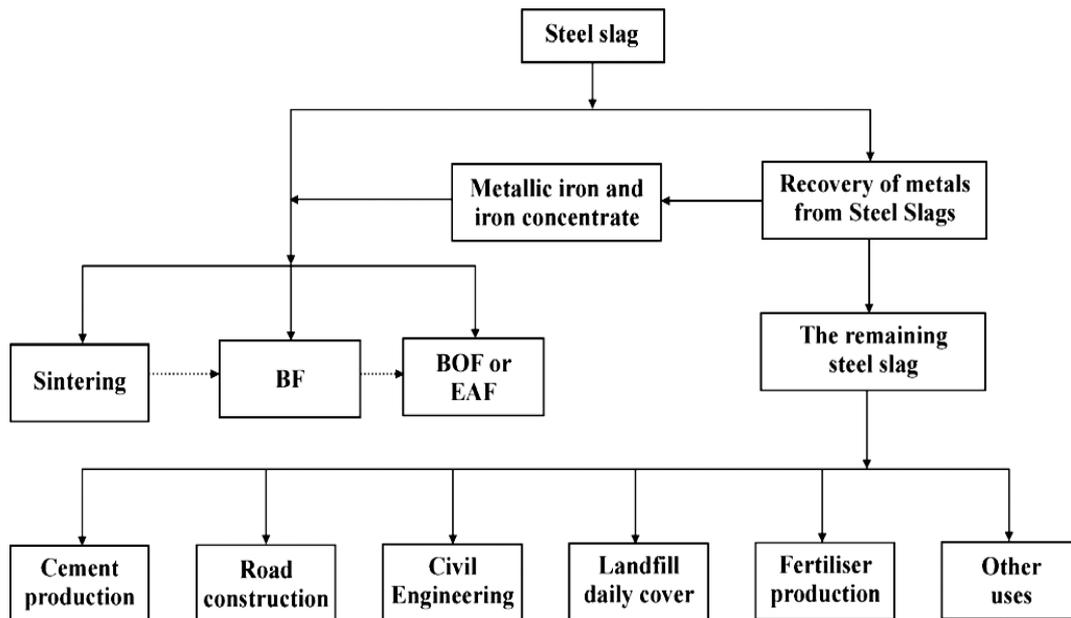


Figure 2.1: Application of steel slag in different fields

2.3.6.3. Chemical composition of various slags

A large percentage of solid wastes are the metallurgical slags containing a quantity of various metals such as CaO, MgO, SiO₂, Al₂O₃, FeO, MnO and P₂O₅ which are usually utilized as a resource material in many areas. In the steel making process, steel making slag is produced from basic oxygen furnace (BOF steel slag), electric arc furnace (EAF steel slag) and ladle furnace (LF steel slag). The chemical compositions of the various slag is presented in Table 2.4 (Motz and Geiseler, 2001; Shi, 2002; Alanyali *et al.*, 2006). In addition, Kawatra and Ripke (2002) reported that the

steelmaking slags are produced by the steel production techniques such as blast furnace (BOF), electric arc furnace (EAF), and ladle furnace (LF) and they are typically contain 20–25% iron. The mineral composition of steel slag also varies. The main mineral composition of slag may include major solid phases such as calcium-silicate (dicalciumsilicate, tricalciumsilicate and dicalciumferrite), calciowustite, magnesiowustite, calcium aluminate, free lime and free magnesium (Dimitrova, 1996; Geiseler, 1996; Dimitrova and Mehanjiev, 1998; Motz and Geiseler, 2001). The content of free lime and free MgO is the most important component for the utilisation of steel slags for different remediation applications. The free lime and free MgO in the slag occur as both precipitate from the melt, which would be associated with a more complicated mechanism of adsorbing and fixing metal ions due to the participation of different active phases (Geiseler, 1996; Motz and Geiseler, 2001). Radosavljevic *et al.* (1996) reported that the mineralogical composition of the slag is made of iron, calcium ferrite, larnite, rankinite, wustite, periclase, manganosite, Fe and Mn monticellite, Mn-cordierite, melilite and glass. Steel slag consists of CaO, Fe₂O₃, SiO₂, MgO, Al₂O₃ and MnO (Shen and Forssberg, 2003; Tsakiridis *et al.*, 2008). Olivine, merwinite, C₃S, C₂S, C₄AF, C₂F, RO phase (CaO-FeO-MnO-MgO solid solution) and free-CaO are the common minerals in the steel slag (Shi and Qiua, 2000; Shi, 2002). In addition, steel slag is mainly composed of CaO, SiO₂, Fe₂O₃, Al₂O₃, MgO, MnO and P₂O₅ (Cha *et al.*, 2006; Tossavainen *et al.*, 2007). The major mineral in ladle slag fines is γ -C₂S, C₃S, β -C₂S, 54CaO.MgO.Al₂O₃.16SiO₂, 11CaO.7Al₂O₃.CaF₂, γ -C₂S, 3CaO.MgO.3SiO₂, CaMg(CO₃)₂, CaF₂ and Ca(OH)₂ (Shi, 2002).

Table 2.4: Chemical compositions of various slags %

Slag indicates	Fe products	CaO	SiO ₂	Al ₂ O ₃	MnO	MgO
BF	<1	30-40	32-40	7-11	<1	12-18
BOF	5-35	31-55	10-22	1-4.5	0-8	2-15
EAF	10-34	1-60	6-57	2-14	0-15	0.5-15
LF	0-10	40-60	3-27	5-40	0-10	3-15

BF: Blast furnace; BOF: basic oxygen furnace; EAF: electric arc furnace; LF: ladle furnace

Some steel slags contain higher amount of P_2O_5 and S than iron concentrate. This may affect the direct recycling of the steel slags to the iron and steel making process (Shen and Forsberg, 2003). Phosphorus slag is a by-product of the production of elemental phosphorus and is composed mainly of SiO_2 and CaO, the CaO/ SiO_2 ratio of phosphorus slag usually ranges from 0.8 to 1.2. The main minor components in phosphorus slag are 2.5–5% Al_2O_3 , 0.2–2.5% Fe_2O_3 , 0.5–3% MgO, 1–5% P_2O_5 and 0–2.5% F. (Shi and Qiua, 2000). In addition, the main crystalline compounds in air-cooled phosphorus slag are $CaO \cdot SiO_2$; $3CaO \cdot 2SiO_2$ and $3CaO \cdot 2SiO_2$ (Shi and Qiua, 2000). On the other hand, in acidic soils, the phosphorus availability of Thomas slag is similar to that of other water soluble phosphorus fertilisers (Sinaj *et al.*, 1994). The Thomas slag was composed of P, Si and Ca and silicato-calcium phosphates were the prevailing form of P in the cells and a high Fe, Ca and Mn content was found in the walls (Sinaj *et al.*, 1994). In addition, Thomas basic slag consists of 37.8% CaO, 2.8% Al_2O_3 , 14.4% Fe_2O_3 , 10.6%, SiO_2 , 1.9%, MgO, 1.6% MnO_2 and 1.2% P_2O_5 (Panfili *et al.*, 2005). Also, Thomas basic slag contains some phases such as larnite, calcium silico phosphate containing P_2O_5 , calcium ferrite ($Ca_2Fe_2O_3$), wustite (FeO), lime and magnetite (Panfili *et al.*, 2005).

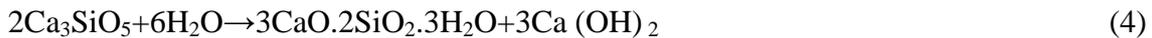
2.3.6.4. Slags sorption properties

The adsorption capacity of the slag is dependent on the pH and the hydration of the slag in aqueous solutions. The sorption of metal ions by slag from ferrous and nonferrous metallurgy is caused by various processes: ion-exchange and replacement of calcium ions from the slag by the metal ions in the solutions as chemical bonding of hydrolysis metal species with the surface. The composition of the slags (oxides, calcium silicates, aluminosilicates, etc.) is associated with a more complicated mechanism of adsorbing and fixing metal ions due to the participation of different active phases (Dimitrova, 1996; Dimitrova and Mehanjiev, 1998). These ions react with the hydrolysed silicates resulting in the formation of scarcely soluble metal silicates on the slag surface and the metal ions sorption takes place mainly in the form of $2CaO \cdot SiO_2$. Major hydration reactions may occur with calcium oxide, magnesium oxide, calcium silicates, and calcium aluminates as following (Yan *et al.*, 2000; Cha *et al.*, 2006).

For free-CaO and free-MgO



For calcium silicates and calcium aluminate



In general, slag, which consists of calcium oxide, aluminium oxide, and other metal oxides, is an abundant by-product in the steel-making process. It has been used as an adsorbent to remove various metals, the major removal mechanisms being precipitation and adsorption on the surface of metal oxide. The relative contribution of adsorption on the removal of copper using slag decreased dramatically and that of precipitation increased sharply as the initial pH increased. The mechanism of copper removal using slag is not adsorption on slag surface but rather precipitation with hydroxide dissolved from slag as most of copper was removed by slag in the form of copper hydroxide (Kim *et al.*, 2008). In addition, Ortiz *et al.* (2001) reported that magnetite which is the main component of converter slag in the steel industry can be used like an adsorber material for wastewater treatment. In fact the application of 1g of the converter slag reduced the Ni concentration from 20 to 1.57 mg/l. Moreover blast-furnace slag is an effective sorbent for Cu, Zn, Ni and Pb ions in a wide range of ion concentration and pH values (Dimitrova 1996; Dimitrova and Mehandjiev, 1998).

2.3.6.5. Effect of slags addition on soil properties

Alkaline materials are usually added to acidic soils to ameliorate soil chemical and physical properties and also to reduce the mobility and bioavailability of metals in contaminated soils (Brallier *et al.*, 1996; Brown *et al.*, 1997; Krebs *et al.*, 1998; Singh

and Oste 2001; Bolan and Duraisamy 2003; Gray *et al.*, 2006; Tlustos *et al.*, 2006). Slag has been used as a soil additive to remove various metals in contaminated soils by precipitation and adsorption on the surface of the metal oxide (Kim *et al.*, 2008). The application of Linz-Donawitz (LD) slag in acid soils managed under pastures increased the soil pH with and without NPK fertilization (Pinto *et al.*, 1995). Ali and Shahram (2007) found that the increasing rate of soil pH was proportional to the slag amount added in the soils. The application of slag treatments in the soil increased more the soil pH than converter sludge treatments (Forghani *et al.*, 2006). Calcium silicate slag can reduce the soil acidity and increase the available Ca, Mg, Si and P (Besga *et al.*, 1996; Barbosa Filho *et al.*, 2004), whereas exchangeable Al, Mn, Cu and Zn decreased (Besga *et al.*, 1996). Thomas phosphate basic slag (TBS) was used as an amendment in several contaminated soils to decrease the mobility and bioavailability of Cd, Zn and Pb (Mench *et al.*, 1994a,b). In addition, the incorporation of Thomas basic slag into an excessively Cu contaminated topsoil from a wood treatment facility increased the soil pH and decreased Cu concentration in the soil (Bes and Mench, 2008). However the combination of basic slag and steel shots was more effective in reducing Zn and Cd mobility than when used separately in contaminated soils (Mench *et al.*, 1998). In addition, the application of steel abrasive (SA) or oxygen scarfing granulate (OSG) to stabilise metals from CCA-contaminated soil can decrease the concentrations of As, Cr, Cu, and Zn in leachates and soil pore water (Lidelöw *et al.*, 2007).

2.3.6.6. Effect of slags addition on plant production

Several alkaline slags have been used in acid soils for the amelioration of plant growth and increase of the biomass production. The application of Linz-Donawitz (LD) slag in acid soils in combination with NPK fertilizers resulted in highest crop yields and nutrient concentrations in plants (Lopez *et al.*, 1995). In greenhouse studies, the application of respectively 1 % and 2 % (w/w) of slag in tea garden soil and 0.5, 1 and 2 % slag in rice field soil increased the plant shoot dry yield and also increased P and Mn uptake (Ali and Shahram, 2007). In addition Fe and K uptake increased in rice field, but K uptake decreased in tea garden soil and Fe uptake was not changed (Ali and

Shahram, 2007). In addition, the application of blast furnace slag to correct the soil acidity promotes maximum root growth and higher shoots dry matter of upland rice under sprinkler irrigation (Carvalho-Pupatto *et al.*, 2004). Both calcitic limestone and basic slag (BS) applied in Brazil sugarcane fields increased the yield of sugarcane ratoon (Prado *et al.*, 2003). A combination of converter slag and fungicide did not decrease the density of dormant spores of *Plasmodiophora brassicae* in the soil but suppressed the clubroot disease (Murakami and Goto, 2005). The combination of slag and converter sludge treatments enhanced the plant Ca and Mg concentrations (Forghani *et al.*, 2006). The application of TBS in a copper contaminated soil from a wood treatment facility increased the shoot and root biomass, and increased the foliar Ca concentration whereas foliar Cu concentration in plant decreased (Bes and Mench, 2008). In contrast, the incorporation of TBS in contaminated soil did not increase the plant biomass production but reduced shoot Pb concentrations (Mench *et al.*, 1994a).

CHAPTER 3: Research Objectives

The objectives of this study were to evaluate the physical and chemical characteristics of a contaminated soil together with the characteristics of two different slags, basic slag (BS) and basic slag phosphate (BSP) used as soil additives into a highly copper and others trace elements contaminated soil originated mainly from Cu sulphate and in a lesser extent from standard CCA type C (copper oxide 11.1 % w/w, chromium trioxide 30 % w/w, arsenic pentoxide 19.9 % w/w) (Bes and Mench, 2008; Mench and Bes, 2009). The effects of addition BS and BSP on physical, chemical and mineralogy soil properties were also investigated. Therefore the concentration and accumulation of these metals in beans plants were evaluated to change the availability and mobility of these metals in contaminated soil and metal uptake by plants. Several objectives were carried out under laboratory and pot experiments as followed.

-Soil physico-chemical properties and distribution metals in contaminated soil

The objective of this research was (1) to study the physical and chemical soil properties of a CCA-contaminated soil (2) to identify the distribution of trace elements in the contaminated soil (3) to determine the relationships between the metal concentration in the contaminated soil and the soil parameters such as particle size distribution, organic matter, soil pH and cation exchange capacity.

-Characteristics of slags used as remediation technology for contaminated soils

Two types of slag samples, a basic slag (BS) and a basic slag phosphate (BSP), were used as soil amendments to remediate trace elements contaminated soils. This study aims at evaluating the chemical and mineralogical properties of both slags by several analytical techniques. The chemical composition was analysed by an atomic adsorption spectrophotometer after acid digestion, the mineralogical analysis performed by X-ray diffraction (XRD), the microstructure was observed by optical microscope,

scanning electron microscope (SEM) coupled with energy dispersive (EDX) and electron microprobe analysis (EMPA).

-Effect of the addition basic slag on soil properties and trace elements mobility in contaminated soils

This study aimed at investigating a basic slag (BS) addition into a soil mainly Cu-contaminated from a wood treatment facility to improve the soil characteristics such as the soil pH and soil electrical conductivity (EC) and also may reduce the labile pool of trace elements in soil for root-to-shoot transfer in beans. Pot experiments were carried out on a 2-week period with (*Phaseolus vulgaris* L.) beans plants. An uncontaminated sandy soil was used as a control (CTRL). BS was added into the soil (1 kg soil/pot) to constitute four treatments in triplicates: 0 % (T1), 1 % (T2), 2 % (T3) and 4 % (T4) BS/kg air-dried soil. Changes in soil EC and pH, plant growth, biomass production and the foliar elemental concentrations of both nutrients and trace elements of primary leaves were determined.

-Effect of the addition basic slag phosphate used as in situ remediation of trace elements contaminated soils

In this study, basic slag phosphate (BSP) was used as a soil remediation technique to improve the physical and chemical soil properties and also the *in situ* immobilisation of copper and other trace elements in a CCA contaminated soil by increasing the precipitation and adsorption on the surface metal oxide of the slag thus changing the availability and mobility of metals. The objectives of this study were :(1) to determine the influence of BSP addition into a strongly Cu-contaminated soil from a wood treatment facility by solutions of Cu sulphates and chromated copper arsenate to improve soil properties such as soil pH and EC soil, (2) to evaluate the effect of BSP addition on the plant yield production and the foliar elemental concentrations of primary leaves, (3) to determine the potential of BSP to reduce copper and other trace elements in a CCA contaminated soil as well as to reduce the metal toxicity uptake by beans plants. Pot experiments were carried out with dwarf beans (*Phaseolus vulgaris* L.) grown on the contaminated soil. BSP was added into the pots (1 kg/ soil) with four

different treatments in triplicates: 0 % (T1), 1 % (T2), 2 % (T3) and 4 % (T4) BSP/kg air-dried soil. An uncontaminated sandy soil was used as a control (CTRL). After a two weeks period, soil and plant samples were collected to determine the soil pH and EC, growth and mineral analysis of plants. In addition, clay and silt fractions of soil mixed with BSP were separated by pipette methods and they were determined by X-ray powder diffraction analysis (XRD), performed on a PANanalytical X pert MPD diffractometer using Cu K α radiation of 40Kv and 40 mA with the range 2 θ secondary monochromator and counting time of one hour.

CHAPTER 4: Material and Methods

4.1. Location

The case study is a large post-industrial site (former wood treatment facility) located in south Bordeaux (France, X 1973.15; Y 376.8), France. The industrial facility goes back to 1846, with the building of a railway. Since 1913 a wood saturation factory has treated crosspieces with creosote and vineyard and telegraph posts with Cu sulphate. An autoclave to inject copper sulphate solution under vacuum and pressure was installed in 1950. After 1980, another autoclave was installed to treat wood timbers with an aqueous solution of Cu, Cr and As salts (standard CCA type C, Copper oxide 11.1% w/w, Chromium trioxide 30% w/w, Arsenic pentoxide 19.9% w/w) (Bes and Mench, 2008; Mench and Bes, 2009). About 10 ha were derelict areas and waste repositories (Figure 4.1).

The study area has been previously studied by (Mench and Bes, 2009), regarding the apparent concentrations of trace pollutants on the ground. They selected 10 plots that we conserved for the work thesis. Plots P1 to P4 were located at a former area for stacking freshly treated timbers. Plots P1, P2 and P3 formed an isoscele right-angled triangle (10 m) in a homogeneous barren area, with a similar soil type. Plot P5 corresponded to a fallow and plot P6 to a section for staking phone posts. Plot P7 was located near the former crosspiece treatment plant, and was also a barren area. At Plot P8 freshly treated vineyard posts were stacked. Plot P9 was on the side of a former railway. Plot P10 was a garden adjacent to the treatment facility with a similar sandy soil texture (Bes and Mench, 2008; Mench and Bes, 2009).

4.2. Field study and soil sampling

Four soil profiles (P1-3, P5, P7 and P9) were selected from the location under study (Figure 4.1). They are the most contaminated by Cu and other trace metals. For the remediation test, only the plot P7 has been selected. The reason of this selection is mainly due to the weak mass of slags available for this study. Soil profiles were dug to a suitable depth according to the type and nature of the soil material. In our study, soil samples (15 samples) were collected from studied soil profiles to represent various soil pedons of the location under study. Soil samples were taken from each layer of the soil profile. They were air dried, then sieved with 2- mm and finally stored in plastic containers for physical and chemical analysis.

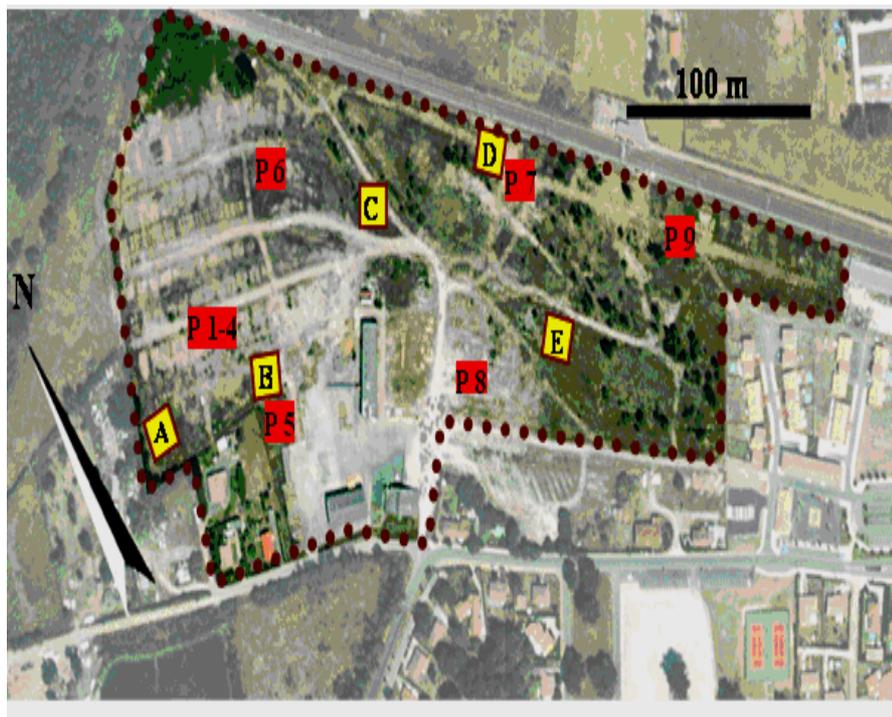


Figure 4.1: Location of the studied soil profiles

4.3. Methods of analysis

4.3.1. Soil physical and chemical analysis

The soil physical and chemical analysis of the studied soil are presented in the Tables 4.1

Table 4. 1: Physical and chemical methods in soil analysis

Soil parameters	Methods	References
Particle size distribution	Gravel percentage was measured by weight for each soil layer and soil material (50g) was used for the particle size distribution analysis. Total carbonates were removed by hydrochloric acid. Hydrogen peroxide was used to oxidise organic matter. Sodium hexameta phosphate solution (10%) was used as a dispersing agent. Sand fraction was separated from silt and clay by sieving. Clay fraction was determined in the suspension by the pipette methods. Silt content was calculated by difference.	(Richards, 1954).
Organic matter content	The organic matter content was determined by a modified Walkely-Blake method; 0.5 g soil was placed in a 500-ml conical flask and mixed with 10ml of 0.17M K ₂ Cr ₂ O ₇ , followed by the addition of 20 ml of H ₂ SO ₄ , 200 ml of water, 10 ml of H ₃ PO ₄ FeSO ₄ and one ml of diphenylamine indicator. Finally the contents were titrated with 0.5 M.7H ₂ O. The estimation of organic matter assumes that 77% of the organic carbon is oxidized by the method and that soil organic matter contains 58% C.	(Jackson, 1967).
Calcium carbonate content	Calcium carbonate content was measured gasometrically using a calibrated Collin's calcimeter method.	(Jackson, 1967).
Soil pH	The soil pH was measured in 1:1 soil: water suspension using a glass electrode pH meter.	(Jackson, 1967).
Soil electrical conductivity (EC)	The soil electrical conductivity (EC) was measured in 1:1 soil: water suspension by using the glass electrode.	(Jackson, 1967).
Cation exchange capacity (CEC)	The cation exchange capacity (CEC) was determined using cobaltihexamine chloride.	(Ciesielski and Sterckeman, 1997).
Total metal contents	Total metal content in soil were determined by ICP-AES after wet digestion in HF and HClO ₄ (AFNOR NF X 31-147).	Ciesielski et al., 1997).

4.3.2. Slag analysis

From the year 60s', slag has been used as fertilizer like the Scories Thomas (Sinaj *et al.*, 1994). These slag are mainly issued from the by products of the steel and coal industry in France. New generation of slags from electric furnace are produced and contains more trace metals (CTPL, 2008). The CTPL kindly furnished 10 kg kilogrammes of these slag called basic slag (BS). Half of the BS has modified by liquid chemical reaction to enhance the amount of phosphorus, in order to synthetize micrometric phosphates minerals (Amin, 1992). The aim of this reaserch was to evaluate the chemistry and mineralogy of the slag samples. The analysis was carried out using the following analytical techniques: chemical composition was determined by an atomic adsorption spectrophotometer after acid digestion. The mineralogy was performed by X-ray diffraction (XRD). The petrography and microstructure was observed by optical microscope for the microlitic phases and by scanning electron microscope (SEM, JEOL 2000FX) coupled with energy dispersive (EDX, TRACOR Detector) for submicrolitic and amorphous phases of the slags. Electron microprobe analysis (EMPA) is also performed to correlate the chemical composition obtained by X-EDS analysis.

-Chemical composition

The chemical compositions of slag samples were carried out with an atomic absorption spectrophotometer. Slag is digested in dilute HNO₃ after flux-fusion at 1100 °C in the presence of lithium metaborate.

-Polarized Optical Microscope (PLM)

The BS and BSP were examined by using polarized optical microscope (PLM) to identify the different mineralogical phases and their association (petrology). Polished petrography thin sections (normative thickness of 25 µm) have been prepared after impregnation of the slag samples with an epoxid resin. The analyses were performed using a Zeiss Axioskop 40A polarization microscope and a leica DM 6000 B digital microscope equipped with a digital camera. The magnification used varied from X10 up

to X100 allowing a resolution of 2 μm . The analysis has been performed at the (UMR EPOC- University of Bordeaux1).

-X – Ray Diffraction analysis (XRD)

Characterisation of the crystallized phases of both slags was carried out by X – ray powder diffraction analysis (XRD), performed on a PANalytical X` Pert MPD diffractometer using Cu K α radiation of 40Kv and 40 mA with the range 2 θ secondary monochromator and counting time of one hour. The analysis of the spectrogram allows the identification of the crystalline phases present and thus with the determination of the crystallographic composition of the main diffracted minerals. All diffraction analysis of both slag samples was performed at the (ICMCB-CNRS- University of Bordeaux1).

-Scanning Electron Microscope (SEM)

Scanning electron microscope investigations were conducted with a JEOL- JSM-840A operated at 25 kv and linked with an energy dispersive (EDS from Tracor). Image analyses have been performed on thin section made from slag samples with a 100 to 1000 nm resolution. The interest of SEM/X-EDS analysis compared to Optical microscope is to identify the submicrolitic mineral and amorphous phases but also their elemental composition. The X-EDS analysis covered a range from C up to U with a sensibility of 1% coupling with an electron probe of few micrometers (1 square μm). The analysis has been performed at the CREMEM (Microscopy facility center of University of Bordeaux1).

-Electron Microprobe Analysis

Chemical microanalysis of slag samples were carried out by using electron microprobe analysis (EMPA), CAM.ECA model SX100 which combines scanning electron microscopy (SEM) and compositional analysis using x-ray spectrometry. Both slags samples were carried out by service CECAMA (located at ICMCB- University of Bordeaux1).

4.4. Remediation techniques

4.4.1. Soil properties

The topsoil of P7 (0 - 0.25 m) of a mainly Cu-contaminated soil was sampled from a soil French wood treatment facility (Mench and Bes, 2009). This anthropogenic soil developed on an alluvial soil in terrace (Fluvisol) containing alluvial materials from the Garonne River combined with wind deposits (BRGM, 1978). Copper contamination originated mainly from Cu sulphate and to a lesser extent from standard CCA type C (copper oxide 11.1 % w/w, chromium trioxide 30 % w/w, arsenic pentoxide 19.9 % w/w) used as wood preservatives (Bes and Mench, 2008; Mench and Bes, 2009). The soil was air-dried and sieved at 2 mm. A sandy control soil from the same soil type was sampled (0-0.25 m) in an uncontaminated kitchen garden, Gradignan, France. A soil aliquot (50g) was used for particle size distribution analysis by sieving and pipette methods (Richards, 1954). The soil pH was measured in 1:1 soil: water suspension using a glass electrode pH meter (Jackson, 1967). The soil electrical conductivity (EC) was measured in 1:1 soil: water suspension by using the glass electrode (Jackson, 1967). Total nitrogen was determined at the INRA laboratoire d'Analyses des sols (LAS), Arras, France using standard methods (Inra Las, 2007). The organic matter content was determined by a modified Walkely-Blake method: 0.5 g soil was placed in a 500-ml conical flask and mixed with 10ml of 0.17M $K_2Cr_2O_7$, followed by addition of 20 ml of H_2SO_4 , 200 ml of water, 10 ml of H_3PO_4 and one ml of diphenylamine indicator. Finally the contents were titrated with 0.5 M $FeSO_4 \cdot 7H_2O$. The estimation of organic matter assumes that 77% of the organic carbon is oxidized by the method and that soil organic matter contains 58% C (Jackson, 1967). The cation exchange capacity (CEC) was determined using cobaltihexamine chloride (Ciesielski and Sterckeman, 1997). Total metal content in the soil was determined by ICP-AES after wet digestion with HF and $HClO_4$ (AFNOR NF X 31-147, Ciesielski *et al.*, 1997). The physico-chemical properties of the contaminated and control soils are presented in Table 4.2.

Table 4. 2: Physico-chemical properties of contaminated and control soils

Parameters	Contaminated soil P7	Control soil CTRL
Particle size distribution		
Sand %	88.8	66.5
Silt %	4.8	15.5
Clay %	6.4	18.0
pH	5.64	7.01
EC mS cm ⁻¹	0.11	0.62
Total nitrogen (N) g kg ⁻¹	0.693	2.94
Organic carbon g kg ⁻¹	14.8	40.4
C/N %	21.3	13.8
Organic matter g kg ⁻¹	25.6	69.9
CEC cmol ⁺ kg ⁻¹	1.94	16.1
As mg kg ⁻¹	27.4	3.6
Co mg kg ⁻¹	3.37	2.62
Cr mg kg ⁻¹	41.9	17.9
Cu mg kg ⁻¹	630	21.5
Mn mg kg ⁻¹	147	189
Ni mg kg ⁻¹	8.31	7.46
Zn mg kg ⁻¹	42.3	50.9

4.4.2. Pot experiments

4.4.2.1. Effect of basic slag addition on soil properties, growth and leaf mineral composition of beans in a Cu-contaminated soil

This study aimed at investigating a BS addition into a mainly Cu-contaminated soil from a wood treatment facility. The addition of BS may improve the soil characteristics such as pH and EC and reduce the labile pool of trace metals in soil for root-to-shoot transfer in beans plant.

-Treatments and preparation of pot experiment

Four soil treatments were prepared by mixing soil P7 (1 kg air-dried weight) with 0 %, 1 %, 2 % and 4 % of BS. Amended soils (made in triplicates) were homogenised by rotation in 2-L plastic flasks, transferred into 1.3-L plastic pots, then watered daily and maintained at 70 % of water holding capacity (WHC, 10% of soil air-dried weight) by manual irrigation with distilled water and allowed to react for four weeks at 20°C. The control soil was treated in the same way. Four dwarf beans

(*Phaseolus vulgaris* L. cv vroege Limburgs) were sown in all pots and cultivated (15 days) in controlled conditions: illumination 12 h light/12 h darkness regime, intensity $150 \mu\text{mol m}^{-2} \text{s}^{-1}$, temperature $25^{\circ}\text{C}/22^{\circ}\text{C}$, and 50% relative humidity. Pots were arranged in a fully randomised block design on a bench and watered daily with deionised water (at 50% WHC) without loss from drainage. The plant growth was monitored on a daily basis using an index based on plant development steps for two weeks and then plants were harvested.

-Plant analysis

Biometrical parameters, *i.e.* the fresh weight (FW) of roots, shoots and primary leaves were determined after the plants were harvested. Plant materials were washed with deionised water (2 times) and distilled water, oven dried at 70°C and weighted to determine the DW biomass production. Plant samples (0.5 g) were wet digested in 5 mL 14M HNO_3 , 2 mL H_2O_2 and 1 mL distilled water at 180°C in PFA (perfluoroalkoxy copolymer resin) tubes under microwaves (MarXpress, CEM). Mineral composition in the plant digests (Al, Ca, Mg, K, P, Cr, Cd, Cu and Zn) was determined by ICP-AES (Ultima, Jobin Yvon Horiba, Longjumeau, France).

-Soil-BS analysis

Soil treatments were taken from all pots experiment to measure the soil pH and the EC in the suspension soil: distilled water in the ratio 1:1 using a glass electrode pH meter and electrical conductivity respectively (Jackson, 1967).

4.4.2.2. In situ remediation of CCA - contaminated soil by basic slag phosphate (BSP)

The effect of BSP on soil pH, soil conductivity, growth and biomass of beans plants were investigated using acid, sandy topsoil (0-25cm) of P7. The soil was strongly Cu-contaminated (630 mg Cu /kg) from a wood treatment facility using solutions of Cu sulphates and chromated copper arsenate. Clay and silt fractions of the soil treatments were determined by X – ray powder diffraction analysis (XRD) to identify the mineralogical form of copper in the soil.

-Characteristics of the soil amendment

BSP is an alkaline by-product of the French steel industry using electric furnace. It has been used as a soil amendment to improve the physical and chemical soil properties and to improve the *in situ* immobilisation of copper and trace elements in a chromated copper arsenate (CCA) contaminated soil in order to change the availability and mobility of trace elements in soil and their uptake by plants. In this study the BSP consists of phosphorus slag incorporating several oxides (calcium, silicon, iron oxide and other metal oxides). They are supposed to meliorate the phytoremediation by a double effect. First one is related to the fertilizing capacity of the amendment which can help the plant growth. The second one is supposed to adsorb and trap some trace metals from the soils on the surface of the oxides and phosphates phases of the BSP slag. This hypothesis will be discussed in the chapter 8.

-Treatments and preparation of pot experiments

The top layer (0-25 cm) of a Cu contaminated soil (630 mg/kg) originating mainly from Cu sulphate and in a lesser extent from standard CCA type C was sampled. BSP treatments were applied to improve soil properties and stabilize copper and other trace elements in the contaminated soil. Four soil treatments (1 kg air-dried weight) were prepared and mixed with 0 %, 1 %, 2 % and 4 % of BSP. Three replicates of each treatment were homogenised by rotation in 2-L plastic flasks, transferred into 1.3-L plastic pots. The control soil (CTRL) was treated in the same way. After incorporation of the BSP into the soil, the moisture content was raised to 70 % of water holding capacity (WHC, 10% of soil air-dried weight) by manual irrigation with distilled water and the soil was allowed to react for four weeks at 20°C before seeds were sown. Four dwarf beans (*Phaseolus vulgaris* L. cv vroege Limburgs) were sown in all pots just below the soil surface. Plants were cultivated in the laboratory under controlled environmental conditions: illumination 12 h light/12 h darkness regime, intensity 150 $\mu\text{mol m}^{-2} \text{s}^{-1}$, temperature 25°C/22°C, and 50% relative humidity.. Pots were arranged in a fully randomised block design on a bench and watered daily with deionised water (at 50% WHC) without loss from drainage. The plant growth was monitored on a daily basis using an index based on plant development steps for two weeks and then plants were harvested.

-Plant analysis

Several biometrical parameters, *i.e.* the fresh weight (FW) of roots, shoots and primary leaves were measured after plant harvested. Plant parts were washed with deionised water (2 times) and distilled water, oven dried at 70 °C, and weighted to determine the DW biomass production. Plant samples (0.5 g) were wet digested in 5 mL 14M HNO₃, 2 mL H₂O₂ and 1 mL distilled water at 180°C in PFA (perfluoroalkoxy copolymer resin) tubes under microwaves (MarXpress, CEM). Minerals composition in the plants digests were determined by ICP-AES (Ultima, Jobin Yvon Horiba, Longjumeau, France).

-Chemical and mineralogical analysis of the soil-BSP

BSP was applied into a copper contaminated soil (P7) to change its chemical and mineralogical properties. After soil incorporation with BSP, the soil pH and electrical conductivity (EC) were measured in suspension soil: distilled water in the ration 1:1 using a glass electrode pH meter and electrical conductivity respectively (Jackson, 1967). The clay and silt fractions of the soil mixed with BSP were separated by pipette methods (Richards, 1954; Jackson, 1969). The mineralogical of soil fractions was investigated to identify the form of copper in the soil treatments using X – ray powder diffraction analysis (XRD). In fact, it is important to verify that slag addition do not increase the concentration in trace elements in the soils which signficated that BSP desorbebd or release trace metal inducing additional contamination.

-Statistical analysis

The soil and plant samples data collected from the pots experiments were tested by statistical analysis (ANOVA, Kruskal-Wallis and Tukey test) with SAS software version 9.1 to evaluate the soil properties (soil pH and EC soil), plant yield (root and shoot yield), elemental concentrations in primary leaves and the total element concentrations in primary leaves [$\mu\text{g plant}^{-1}$], so-called here element accumulation which calculated based on the foliar element concentration ($\mu\text{g kg}^{-1}$ DW) and leaf biomass production ($\mu\text{g DW plant}^{-1}$) of plants. All analytical determinations were performed in

triplicate. Statistical analysis is supposed to quantify relation between different parameter and reveal potential or supposed correlation (linear, exponential, etc.).

CHAPTER 5: Soil Physico-Chemical Properties and Trace Elements Distribution in Soil

5.1. Soil physical properties

Soil physical properties such as particle size distribution, calcium carbonate content and organic matter of the soil under study are presented in Table 5.1. The results indicates that the soils of the study are mostly coarse in texture (mainly sand and loamy sand), the sandy texture dominating in most soil samples followed by loamy sand. Additionally, all soil samples have a very low content in fine materials (silt + clay). The gravel contents of the soil study ranged between 12 to 87 % by weight. The shape and size of gravels are different from one site to another and among various layers of each profile. Very gravely soil texture (gravel content > 50%) occurs in the surface and subsurface layer of profile P7 and the deepest layer of profiles P1-3, P5 and P9. It is noticed that the high amount of gravels in soil samples could be the result of its concentration on the account of transport action and loss of fine earth materials (< 2mm) by wind, rainfall and running water from soil surface during earlier stages of soil formation.

Organic matter content in soil samples is ranges between 0.67 to 3.01%. The highest level of OM was found in the surface layer of profile P9 and the lowest level of the OM was found in the subsurface layer of profile P5. All soil samples contained OM more than 1% with the exception of the subsurface layer of profile P5 which content 0.67 % of OM. Most soil profiles show a clear decrease of OM with depth indicating that little amount of OM accumulation in the soil surface. The low amounts of OM in most soil samples are the result of poor vegetation cover and indicate a poor soil fertility. On the other hand, the relatively high values of OM in some surface and subsurface soil samples could be due to the growth of some vegetation cover and also to the addition of relatively OM rich alluvium to the soil surface in some cases.

Table 5.1: Some physical properties of the soil samples profiles in the study area

Sample No.	Transect / profile	Depth of layer cm	Gravel % by weight	Sand >100 μ	Sand 50-100 μ	Silt %	Clay %	CaCO ₃ %	OM %
1	P1-3	0-15	35.83	84.73	2.67	6.4	6.2	2.14	2.68
2		15-30	30.39	84.64	2.16	6.4	6.8	1.77	2.01
3		30-60	47.12	88.12	2.08	6.2	3.6	1.98	1.34
4		60-100	76.79	93.46	1.34	3.6	1.6	1.98	1.34
Aver.			47.53	87.73	2.06	5.65	4.55	1.96	1.84
5	P5	0-10	31.17	82.86	3.54	8.4	5.2	2.14	1.67
6		10-55	36.94	80.52	4.48	10.2	4.8	1.75	0.67
7		55-75	86.9	88.66	4.14	3.6	3.6	1.34	1.20
8		75-100	56.8	96.06	0.34	2.8	0.8	1.75	1.34
Aver.			52.95	87.02	3.12	6.25	3.6	1.74	1.22
9	P7	0-10	56.34	86.28	2.52	4.8	6.4	1.75	1.20
10		10-35	73.76	82.52	2.08	10.2	5.2	2.3	1.34
11		35-55	33.51	85.66	2.74	8.8	2.8	1.82	1.54
12		55-100	12.38	81.16	4.84	8.8	5.2	2.14	1.34
Aver.			43.99	83.90	3.04	8.15	4.9	2.00	1.35
13	P9	0-15	36.23	84.66	4.34	7.8	3.2	2.23	3.01
14		15-65	31.14	85.56	4.44	7.2	2.8	2.02	2.01
15		65-100	69.78	93.2	0.8	4.8	1.2	2.14	1.87
Aver.			45.71	87.80	3.19	6.6	2.4	2.13	2.29

The results of calcium carbonate distribution in soil samples showed that the concentration of calcium carbonate is range between 1.34 and 2.3%. The highest content of calcium carbonate was found in the subsurface layer of profile P7 and the lowest content of the calcium carbonate was occur in the deepest layer of profile P5. Generally, the decrease of calcium carbonate in soil profiles may be due to the absence of the basic cations such as (Ca, Mg, and K). In addition, in some soil profiles, calcium carbonate content slightly increases with depth probably due to the leaching soil.

5.2. Soil chemical properties

The results of the soil chemical properties such as soil pH, soil EC and cation exchange capacity (CEC) of the study area are shown in Table 5.2.

Table 5.2: Some chemical properties of the soil samples profiles in the study area

Sample No.	Transect / profile	Depth of layer Cm	pH 1:1	EC (dS/m)	CEC (cmol (+) /kg)
1	P1-3	0-15	7.05	0.13	3.36
2		15-30	4.69	0.44	1.39
3		30-60	4.04	0.39	1.17
4		60-100	4.09	0.29	1.09
Aver.			4.96	0.31	1.75
5	P5	0-10	6.95	0.15	6.87
6		10-55	7.03	0.11	3.07
7		55-75	7.05	0.11	2.49
8		75-100	7.07	0.10	1
Aver.			7.02	0.11	3.35
9	P7	0-10	6.34	0.11	1.94
10		10-35	5.73	0.12	2.37
11		35-55	5.49	0.17	1.07
12		55-100	5.78	0.10	2.01
Aver.			5.83	0.12	1.84
13	P9	0-15	7.11	0.05	10.6
14		15-65	6.44	0.05	2
15		65-100	5.96	0.02	1
Aver.			6.50	0.04	4.53

Soil pH is an indication of the acidity or alkalinity of the soils. The pH soil varied from 4.04 to 7.11 with the lowest level in the deepest layer of profile P1-3 and the highest level in the surface layer of profile P9. Few soil samples are extremely acid such as the subsurface and the deepest layer of profile P1-3, slightly acid for the subsurface layer of profile P7 and deepest layer of profiles P7 and P9. All surface layers of soil samples are slightly alkaline and the soil pH decreases with depth. Generally, pH range of approximately 6 to 7 promotes the most ready availability of plant nutrients. In fact, extremely and strongly acid soils (pH 4.0-5.0) can have high concentrations of soluble aluminum, iron and manganese which may be toxic towards the growth of some plants (McLean and Bledsoe, 1992). Moreover when the soil pH is lower than 6.0; there is a decrease of the availability of the nutrients such as phosphorus, potassium, calcium, sodium and magnesium. In addition, the availability of some metals such as zinc, manganese, aluminium, copper, zinc and iron increases as the pH decreases. Most minerals and nutrients are more soluble or available in acid soils than in neutral or

slightly alkaline soils (McLean and Bledsoe, 1992). The rainfall also influences the soil pH by leaching basic cations such as (*e.g.* Ca, Mg and K) into the drainage water. These cations are replaced by acidic cations such as (*e.g.*, Al³⁺, H⁺ and Fe). For this reason, soils formed under high rainfall conditions are more acid than those formed under arid conditions. The dissolution of lead, copper, nickel, and zinc precipitates are strongly dependent on the soil pH and their retention dramatically increasing above pH 7.0 to 7.5 (Harter, 1983). The EC values of the soil samples study ranged from 0.02 to 0.44 dS/m. All soil samples are non saline (0-4 dS/m). The much lower salinity level in the studied soil is possibly due to the effect of rainfall and leaching of the soil profiles. In most soil profiles, the EC value increases more in the subsurface layers than in the surface layer probably due to the leaching of basic cations such as (*e.g.* Ca, Mg, K) into the drainage water. The result of the CEC indicates that the soil study ranged between 1 and 10.6 cmol (+)/kg CEC. The highest value of CEC was found in the surface layer of profile P9 whereas the lowest value of CEC was found in the deepest layers of profiles P5 and P9. In general, CEC decreases with depth along the soil profiles. The low value of CEC is probably due to the coarse texture of most soil profiles. The surface layers of the soil profiles have higher values of CEC than the subsurface and deepest layers of the soil profiles. This is possibly due to the effect of organic matter contents and soil fine particle in some soil surface.

5.3. Trace elements content and distribution in soil profiles

The concentrations and distribution of different trace elements with depth in the soil profiles are shown in Table 5.3 and Figure 5.1. The result indicate that, from all soil samples studied, Cu is the dominant followed by Cr, Zn, As, Ni then Co and they ranged from 4.2 to 1970, 10.9 to 114, 15.4 to 95.7, 1.93 to 51.1, 5.22 to 14 and 1.66 to 4.81 mg/kg respectively. The accumulation of toxic metals in soil is mainly inherited from parent materials or inputs through anthropogenic (He *et al.*, 2005). The main source of metals in agricultural contaminated soils has included the impurities in fertilisers, swage sludge, manures from intensive animal production, pesticides and wood preservatives (Alloway, 1995). The concentrations of many contaminants tend to accumulate in the soil surface (Alloway and Ayres, 1997). Our study indicate that the

distribution of Cu, Cr, As and Zn increases in the surface layer of soil profiles and then decreases with depth in all soil profiles. In general, Ag, As, Cd, Cu, Hg, Pb, Sb and Zn are found concentrated in the surface layers as a result of cycling through vegetation, atmospheric deposition and adsorption by the soil organic matter (Alloway, 1995). In addition, Kumpiene *et al.* (2008) reported that As, Cu, Cr, and Zn can be found in excess in contaminated soils at wood treatment facilities, especially when Cu sulphates and chromated copper arsenate (CCA) were used as a preservative against insects and fungi, which may result in soil phytotoxicity. In contrast, Co and Ni were decreased in the surface layer of soil profiles and then increased with depth in all soil profiles. Similar results obtained by Hernandez *et al.* (2003) who found that in some French acid soil, Ni and Co increases with depth while copper and zinc decreases with depth.

Table 5.3: Trace elements contents and distribution in the soil samples profiles

Sample No.	Transect / profile	Depth of layer Cm	Cu mg/kg	Cr mg/kg	Zn mg/kg	As mg/kg	Ni mg/kg	Co mg/kg
1	P1-3	0-15	1970	34.1	54.9	15.5	5.22	1.66
2		15-30	772	16.3	30.5	3.53	5.35	1.87
3		30-60	411	18.4	28.7	4.71	7.97	2.28
4		60-100	111	22.5	29.3	6.11	10.6	2.67
Aver.			816	22.82	35.85	2.12	7.28	2.12
5	P5	0-10	152	49.8	36.8	49.4	6.1	1.83
6		10-55	11.2	18	32.1	4.48	7.45	2.4
7		55-75	8.1	21.7	29.7	6.63	11.9	2.6
8		75-100	4.25	10.9	15.4	4.36	8.42	2.03
Aver.			43.88	25.1	28.5	2.21	8.46	2.21
9	P7	0-10	630	41.9	42.3	27.4	8.31	3.37
10		10-35	120	23.8	42.9	7.38	11.5	4.12
11		35-55	752	26.7	95.7	7.85	14	4.81
12		55-100	11.3	19.4	32.1	3.04	8.35	2.53
Aver.			378	27.95	53.25	3.70	10.54	3.70
13	P9	0-15	207	114	52.3	51.1	7.15	2.18
14		15-65	9.77	19.2	27.6	3.77	7.95	2.32
15		65-100	4.97	14.5	23.4	1.93	9.1	2.86
Aver.			73.91	49.23	34.43	2.45	8.06	2.45

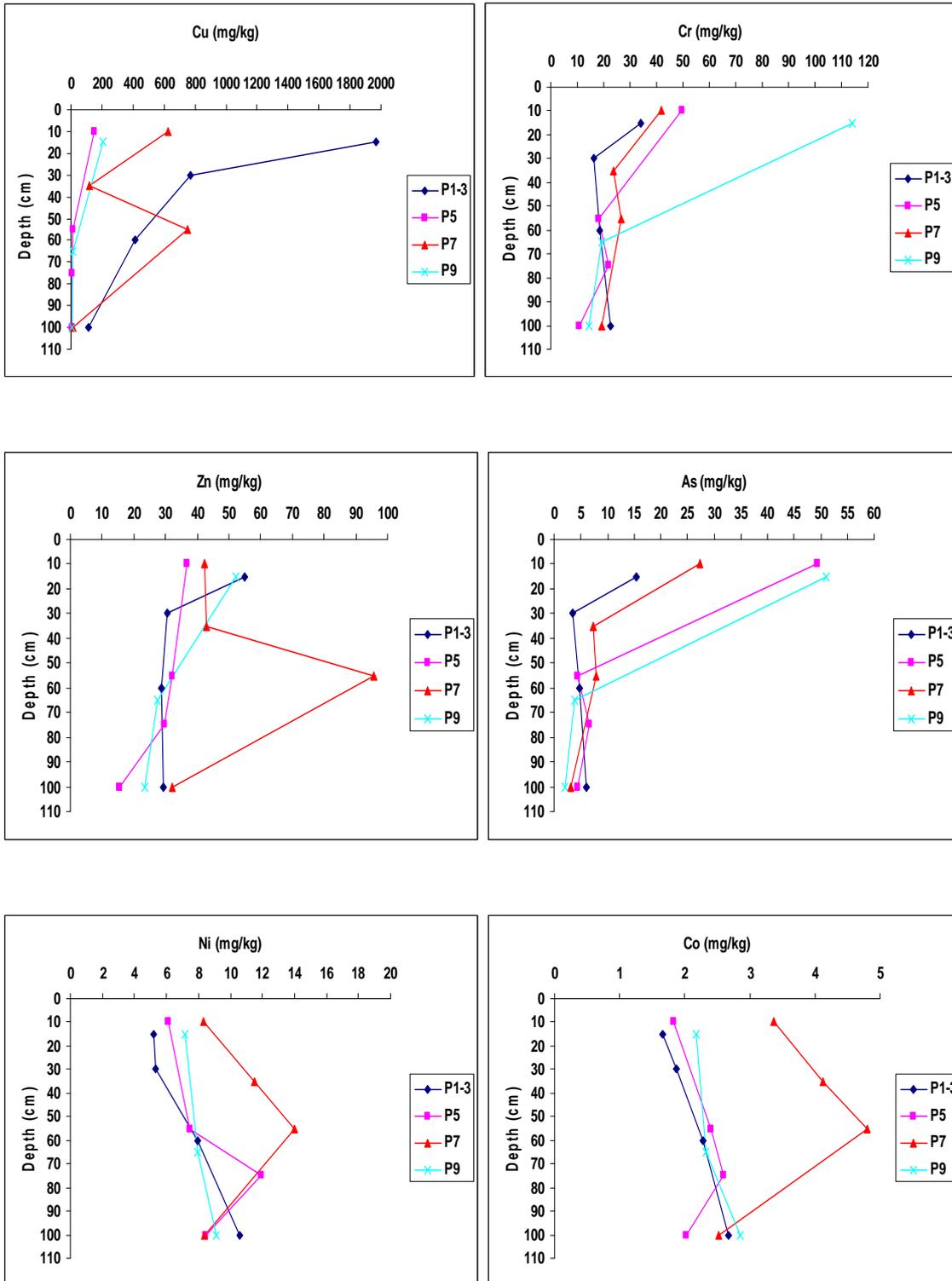


Figure 5.1: Vertical distribution of trace elements in the soil profiles

5.3.1. Copper content in the soil profiles

According to the results in Table 5.3 and Figure 5.1, the concentration of Cu in soil samples profiles ranges between 4.25 to 1970 mg/kg. Copper is highly phytotoxic at higher concentrations above 30 mg/kg (Alloway, 1995; Song *et al.*, 2004). Therefore, this is probably causing a problem of toxicity to plants then animals and humans. Copper contamination of soils is widespread as a result of mining, smelting, land applications of sewage sludge, use of Cu as fungicides, algicides, chromated copper arsenate (CCA) pressure treated lumber, copper pipes and other industrial activities (Evanko and Dzombak, 1997; Song *et al.*, 2004).

In our study, the deepest layer of profile P5 has the lowest level Cu, and the surface layer of profile P1-3 has the highest level of Cu. Higher concentration of Cu found in all surface layers of soil profiles and then decreases with depth. In some cases, copper concentration increases with depth in soil. In fact, higher concentrations of Cu occur in the subsurface and deepest layer of profiles P1-3 and P7. This is possibly due to copper mobilised under extreme acid conditions (Baize, 1997). In most cases, the retention of copper in the deepest layers of the soil is probably due by the leaching soil (Besnard *et al.*, 2001). On the other hand, it can be noticed that, in all surface soil profiles, the Cu concentration was exceeding 100 mg/kg. The exceeded levels were observed also in subsurface and deepest layers of profiles P1-3 and P7 indicating that all soil profiles were copper contaminated. This is possibly resulted from the anthropogenic contamination influence probably related to the input of CCA-C in the soil study. The top layer (0-25 cm) has been mainly contaminated by Cu originated mainly from Cu sulphate and in a lesser extent from standard CCA type C (copper oxide 11.1 % w/w, chromium trioxide 30 % w/w, arsenic pentoxide 19.9 % w/w) used as wood impregnation from an industrial site (Bes and Mench, 2008; Mench and Bes, 2009).

5.3.2. Relationships between trace elements contents and soil parameters

The aim of this study was to identify which soil parameters were the best related with copper and other trace metals content in soil profiles. The results of the principal

component analysis (PCA) which was used for all soil samples to identify the relationships between trace elements concentration in soil and physico-chemical soil parameters are presented in Figure 5.2 and Table 5.4. From the Figure 5.2 it is possible to consider two axis F1 and F2 axis which explained respectively 31% and 21% of the variance. This indicates that soil properties can explain 52% of the trace metals distribution into this kind of soils. F1 split the distribution of the metals in two domains. First one incorporates Fe, Co, Ni and Zn; while the other one integrate Cr and As. It is possible that group 1 (Fe-Co-Ni and Zn) exhibit the same fingerprint in this context while group2 (Cr and As) an another behaviour. F1 can be named soil metal chemical affinity. From this hypothesis Cu which close to the barycentre of the projection exhibit an another behaviour. The axis F2 splits the projection sphere in two distributions based on the granulometry of the soil fraction. On the right, large particles (Gravel and coarse sand), and on the left, thin one (fine sand, silt and clay). F2 can be named granulometry axis. The soil parameters EC is linked to the large granulometry indicated that this fraction assume the water tranfer by open porosity; while pH, CEC and OM could control partially the local chemistry of the Cr and As. These metals can be supposed to have a strong affinity with the OM, clay and CEC. The other metals exhibits an another behaviour more mechanistic and based on the diffusion through a media with a complex porosity. Regarding the figure 5.1 As and Cr have the same trend while the other metal show a global decrease the metal content from the surface to the bottom of the profile but with cumulation front depth around 60 cm. At this level the content of clay tends to decrease roughly compared to the surface and the depth of 100 cm. Thus trace metal accumulation of Zn, Co and Ni can be governed by a mechanism of diffusion control by the porosity of the soil. The Cr and As can be governed by a mechanism of adsorption on the surface of the fine fraction (OM or/and silt-clay fraction). Cu has a behaviour more complex in the studied soil. This is possibly due to the anthropogenic contamination by the input of CCA-C in the soil study. Thus, we will discuss in detail the relationships between copper concentration in studied soil and physico-chemical soil parameters.

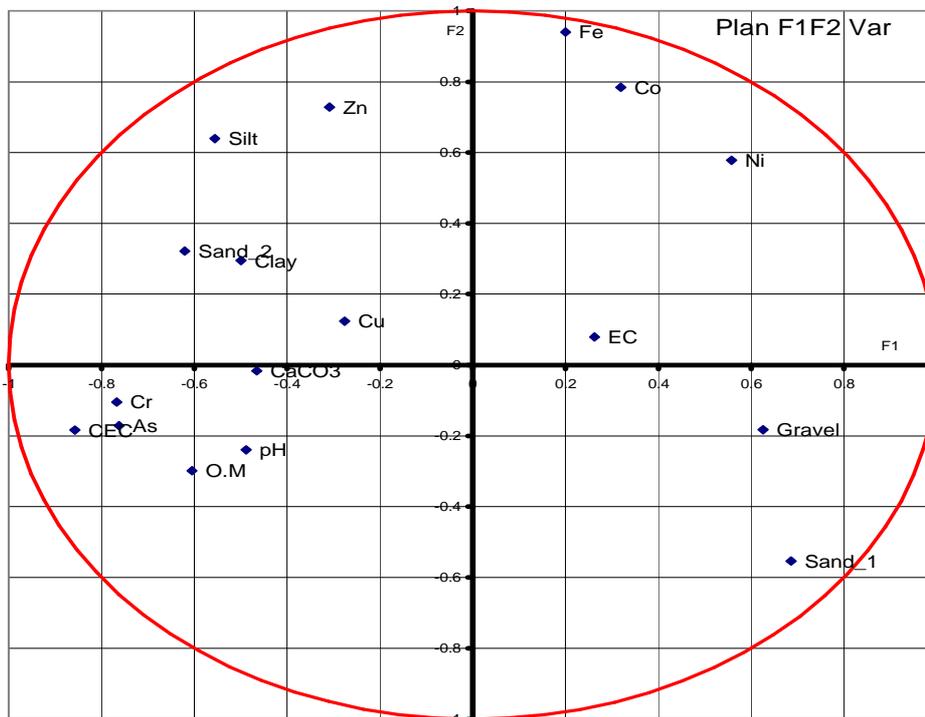


Figure 5.2: The principal plan component analysis performed for trace elements concentrations and physico-chemical soil properties of the soil samples

Table 5.4: Linear correlations coefficients between physico-chemical properties and trace elements contents in soil study

Parameters	Gravel %	Sand 1 (>100 μ)	Sand 2 (50-100 μ)	Silt %	Clay %	CaCO ₃ %	OM %	pH 1:1	EC dS/m	CEC (cmol (+)/kg)
Gravel %	1	0.60	-0.49	-0.55	-0.39	-0.29	-0.29	-0.09	-0.05	-0.26
Sand 1 (>100 μ)	0.60	1	-0.75	-0.87	-0.76	-0.24	-0.04	-0.18	0.04	-0.38
Sand 2 (50-100 μ)	-0.49	-0.75	1	0.55	0.38	-0.02	0.06	0.38	-0.28	0.48
Silt %	-0.55	-0.87	0.55	1	0.44	0.46	0.00	0.08	-0.11	0.32
Clay %	-0.39	-0.76	0.38	0.44	1	0.03	0.04	0.05	0.25	0.160
CaCO ₃ %	-0.29	-0.24	-0.02	0.46	0.03	1	0.48	-0.09	-0.17	0.36
O.M %	-0.29	-0.04	0.06	0.00	0.04	0.48	1	0.19	-0.11	0.56
pH 1:1	-0.09	-0.18	0.38	0.08	0.05	-0.09	0.19	1	-0.77	0.50
EC dS/m	-0.05	0.04	-0.28	-0.11	0.25	-0.17	-0.11	-0.77	1	-0.30
CEC (cmol (+)/kg)	-0.26	-0.38	0.48	0.32	0.16	0.36	0.56	0.50	-0.30	1
Cu mg/kg	-0.25	-0.17	-0.11	0.01	0.49	0.08	0.46	-0.01	0.25	-0.01
Co mg/kg	0.26	-0.06	-0.12	0.27	-0.11	-0.02	-0.33	-0.22	-0.14	-0.30
Cr mg/kg	-0.19	-0.25	0.35	0.19	0.11	0.35	0.62	0.35	-0.25	0.92
Ni mg/kg	0.51	0.24	-0.12	-0.03	-0.44	-0.26	-0.42	-0.20	-0.15	-0.35
Zn mg/kg	-0.26	-0.35	0.18	0.43	0.18	0.11	0.25	0.02	-0.05	0.18
As mg/kg	-0.20	-0.27	0.28	0.16	0.22	0.31	0.46	0.42	-0.22	0.88
Fe μ g/kg	0.01	-0.30	0.20	0.39	0.09	-0.18	-0.32	-0.35	0.17	-0.27

5.3.3. Relationship between copper concentration and physico-chemical soil parameters

The mobility of copper in soil is controlled by different physico-chemical soil properties such as, the soil particle size distribution, organic matter content, CEC, soil salinity, pH soil and iron and aluminum oxide content (Qian *et al.*, 1996; Brun *et al.*, 1998; Chaignon *et al.*, 2003; Hernandez *et al.*, 2003). In addition, copper is complexed with organic matter and adsorbed onto the surface of clay fractions that will strongly influence on the mobility and bioavailability of copper in the soil (Adamo *et al.*, 1996; Chaignon *et al.*, 2003; Sterckeman *et al.*, 2006).

5.3.3. 1. Relationship between copper concentration and particle size distribution soil

According to data obtained from the principal component analysis (PCA), the results indicate that there is no relationship between copper contents and gravel content and sand fractions in soil samples. A weak positive correlation can be observed between copper content and clay proportion for the soil samples but it is weak due to the low clay content in soil profiles ($r^2 = 0.24$) (Figure 5.3). Particle size distribution soil can be used to assess the distribution of copper in soil contaminated. In general, from the particle size fractions (sand, silt and clay) the metals tend to accumulate in fine particles especially on the clay fractions of the soil due to increased the surface area, higher clay content and organic matter content (Qian *et al.*, 1996; Acosta *et al.*, 2009). Besnard *et al.* (2001) found that copper contents in soil increased with a decreasing size fraction and the soil having highest amounts of clay fractions showed the highest values for metal adsorption (Singh and Oste, 2001). In fact, the soil clay mineralogy influences the chemical adsorption and co-precipitation, thereby affecting the solubility and mobility of trace elements contaminated soil (Hesterberg, 1998). Thus, it can be noticed that the high concentrations of copper related with increased clay size fraction in all soil profiles but not enough to explain the Cu distribution into the different soil profiles. The level of Cu on the surface is so high that remobilization of the Cu allow its precipitation under mineralogical phases (Cuprite, Malachite, Copper oxide). The period is too short to allow mineral precipitation of copper phases and only a biological process is able to generate such mineralization. This point should be discussed after another experimentation and analysis.

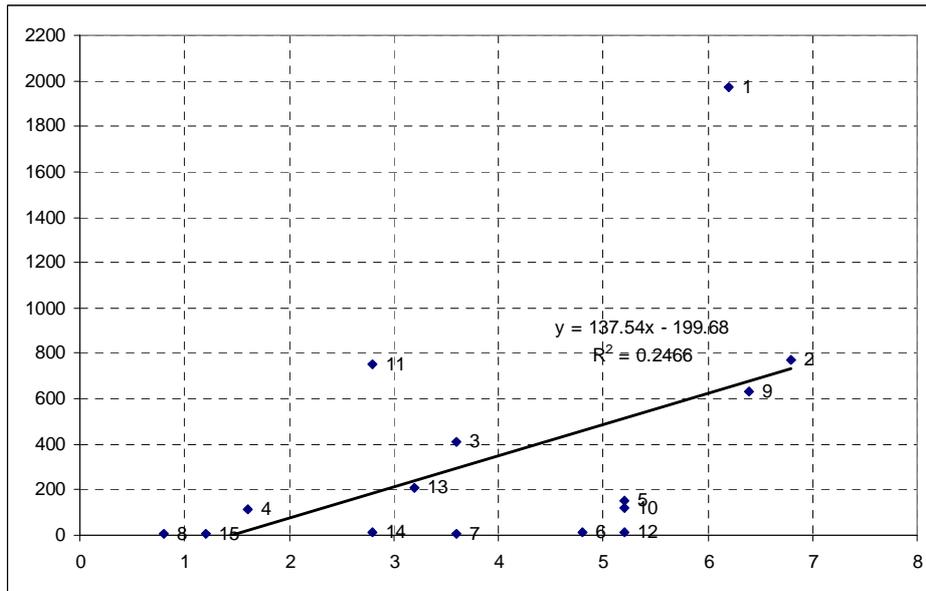


Figure 5.3: Relationship between copper and clay contents in soil samples

5.3.3. 2. Relationship between copper concentration and soil organic matter

The relationship between copper concentration and organic matter content in the soil profiles study is given in Figure 5.4. Organic matter has a direct effect on the retention copper in the soil. In fact, the high OM content can retain copper fraction by 96% of the total copper in the soil (Balasoiu et al., 2001). In our study, organic matter was much higher in the surface soil than in the subsurface and deepest layers of all soil profiles. The high concentrations of copper in the surface layer of some soil profiles were related with the increasing organic matter content. Copper content in the surface layer was high increased as the OM content increases (Besnard et al., 2001). The results indicate the correlation analysis shows that copper was low strongly associated with OM of soil samples ($r^2 = 0.22$). McBride et al. (1997) found that the absence of correlation between trace metals adsorption and soil organic matter is probably caused by the reactive fraction of the OM could be assessed in the relationship.

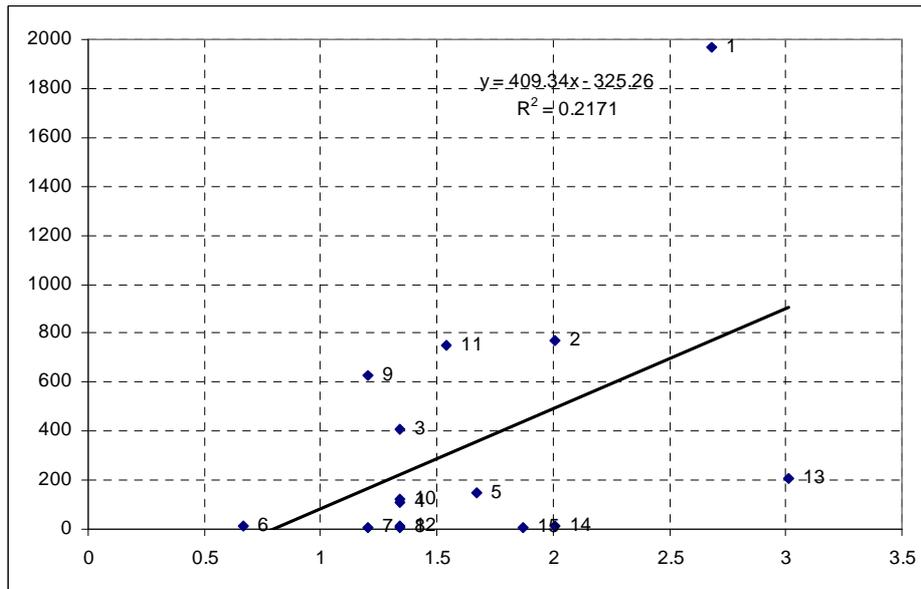


Figure 5.4: Relationship between copper and OM contents in soil samples

5.3.3. Relationship between copper concentration and pH soil

The relationship between copper concentration and soil pH in the soil samples study is presented in Figure 5.5. The results indicate that the correlation analysis shows that there is no relationship between copper content and pH soil which related to the anthropogenic contamination influence probably related to the input of CCA-C in the soil study. All surface soil has been mainly contaminated by Cu originated mainly from Cu sulphate and in a lesser extent from standard CCA type C (copper oxide 11.1 % w/w, chromium trioxide 30 % w/w, arsenic pentoxide 19.9 % w/w) used as wood impregnation from an industrial site (Bes and Mench, 2008; Mench and Bes, 2009). The pH of the soil system is a very important parameter, directly influencing the sorption /desorption, precipitation / dissolution, complex formation, and oxidation-reduction reactions (McLean and Bledsoe, 1992). In general, the stability of copper in the soil is strongly pH dependent and the mobility of copper increases with decreasing pH. The high concentrations of copper in the surface layer of soil profile P7, subsurface and deepest layers of profiles P1-3 and P7 was occur with an decreased soil pH indicated that copper concentration is a high mobility with pH decreased in the soil.

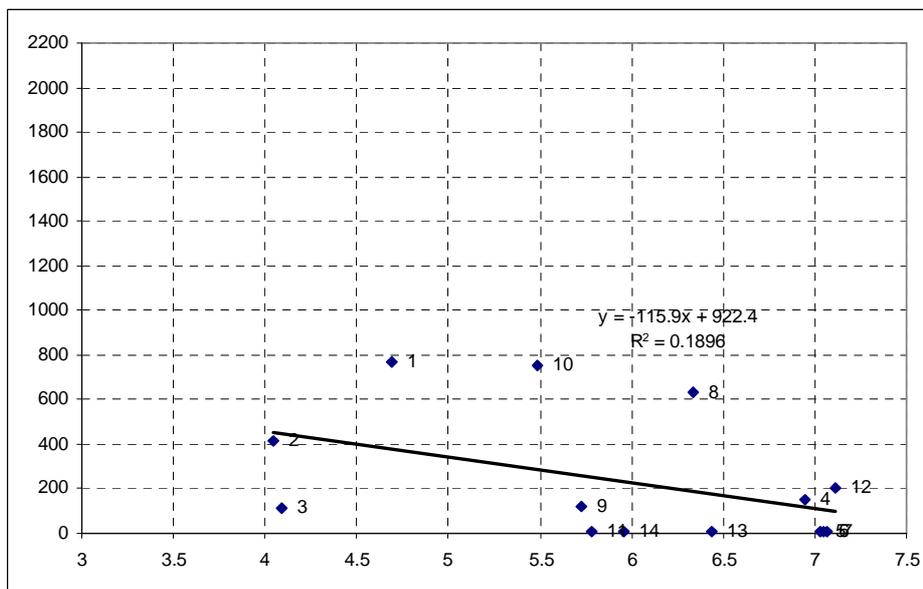


Figure 5.5: Relationship between copper contents and pH in soil samples

Copper is distinctly soluble under oxidised condition than under reduced in the pH rang 5.4-6.5 (Bhattacharya *et al.*, 2002). In addition, the cupric ion Cu^{2+} is the most common mobile in the surface environment below pH 6.9 (Alloway, 1995; Kabata-Pendias, 2001). In general the mobility of copper in the soil is usually lowest at slightly alkaline pH (Kumpiene *et al.*, 2008). In most cases, our study indicates that copper content in the surface layer of profiles, P1-3, P5 and P9 was increased as above pH 7. This is possibly causing by the accumulation of copper concentration from the use of CCA-C in treatments wood in the soil. Therefore, increasing pH soil causing Cu was strongly adsorbed at the colloidal surfaces by decreasing the exchangeable form. It has also been suggested that in the pH =7, copper tend to precipitate in the form carbonate and hydroxide (Alloway, 1995; Gagnon, 1998).

5.4. Conclusion

The soil studied was strongly Cu-contaminated originated mainly from Cu sulphate and in a lesser extent from standard CCA type C (copper oxide 11.1 % w/w, chromium trioxide 30 % w/w, arsenic pentoxide 19.9 % w/w). Physico-chemical soil

properties and distribution of trace metals in the contaminated soil were investigated. The relationships between copper concentration in the contaminated soil and soil properties were measured using PCA. Results indicate that the sandy texture dominates in most soil samples followed by loamy sand and all soil samples were very low contents in fine materials (silt + clay). Organic matter content in soil samples ranges between 0.67 to 3.01% and decreases with depth. Calcium carbonate distribution in soil samples showed that the range is between 1.34 and 2.3%. The pH soil varied from 4.04 to 7.11 and decreases with depth. The EC values of the soil study ranged from 0.02 to 0.44 dS/m. Cation exchange capacity (CEC) indicates that the soil study ranged between 1 and 10.6 cmol (+)/kg and decreased with depth. The distribution of trace metals indicates that Cu is the dominant followed by Cr, Zn, As, Ni then Co and they ranged from 4.2 to 1970, 10.9 to 114, 15.4 to 95.7, 1.93 to 51.1, 5.22 to 14 and 1.66 to 4.81 mg/kg for Cu, Cr, Zn, As, Ni and Co respectively. The distribution of Cu, Cr, As and Zn increases in the surface layer of soil profiles and then decreases with depth in all soil profiles. Co and Ni decreased in the surface layer of soil profiles and then increased with depth. In most cases, Cu concentration exceeded 100 mg/kg in all surface soil profiles and some subsurface and deepest layers of soil profiles indicating that all soil profiles were Cu contaminated. PCA indicates that there was a relationship between copper contents and clay proportion for the soil samples but it is weak due to the low clay content in soil profiles ($r^2= 0.24$). While copper was low strongly associated with OM of soil samples ($r^2= 0.22$). There was no relationship between copper content and pH soil. This is possibly resulted from the anthropogenic contamination influence probably related to the input of CCA-C in the soil.

CHAPTER 6: Slag Characterisation

6.1. Chemical composition of the slag samples

The elemental composition of both slag samples (BS and BSP) expressed as oxides in mass percentage are presented in Table 6.1. The results indicate that the major compound of BS is mainly consists of Ca (60.69 wt % CaO), Fe (14.61 wt % Fe₂O₃), Si (12.54 wt % SiO₂), Al (5.91 wt % Al₂O₃) and Mg (2.51 wt % MgO). Other compounds such as TiO₂, MnO, P₂O₅ and K₂O are low contents; they represent respectively 1.47, 1.06, 1.05 and 0.15 wt%. In general, steel slag is mainly consists of CaO, Fe₂O₃, SiO₂, MgO, Al₂O₃ and MnO (Shen and Forssberg, 2003; Tsakiridis *et al.*, 2008). In addition, the composition of steel slag is mainly composed of CaO, SiO₂, Fe₂O₃, Al₂O₃, MgO, MnO and P₂O₅ (Cha *et al.*, 2006; Tossavainen *et al.*, 2007). Other studies reported that the chemical composition of steel slag is mainly contains CaO (45-60 wt %), Fe₂O₃ (3-9 wt %), FeO (7-20 wt %), SiO₂ (10-15 wt %), MgO (3-13 wt %) and Al₂O₃ (1-5 wt %) (Shi and Qians, 2000).

The major compound of BSP is mainly composed of Ca (30.71 wt % CaO), Fe (21.4 wt % Fe₂O₃), Si (14.63 wt % SiO₂), P (14 wt % P₂O₅), Mg (9.55 wt % MgO), Al (5.56 wt % Al₂O₃) and Mn (2.53 wt % MnO₂). Other compounds such as, TiO₂ and K₂O are observed in few amounts; they represent respectively 1.09 and 0.53 wt %. Thomas basic slag is used as a phosphorus fertilizer in acidic soils and it is consists of 37.8% CaO, 2.8% Al₂O₃, 14.4% Fe₂O₃, 10.6%, SiO₂, 1.9%, MgO, 1.6 MnO₂ and 1.2% P₂O₅ (Sinaj *et al.*, 1994; Panfili *et al.*, 2005). Other studies showed that the main components of basic slag phosphate are composed of CaO, Fe₂O₃, SiO₂, P₂O₅, MnO and MgO (Forghani *et al.*, 2006; Ali and Shahram, 2007). The comparison between chemical composition of BS and BSP revealed that the levels of the elements in BSP are higher than in the BS contents with the excepted Ca, Al and Ti which increased in the BS composition. In addition it can be noticed that the amounts of phosphorus oxide in the BSP is very much higher than in the BS indicating that BSP is rich in phosphorus oxide.

Some steel slag contain higher amount of P_2O_5 than iron content (Shen and Forsberg, 2003). Both slag samples (BS and BSP) are basic resulting by index $M_b = (CaO + MgO / Al_2O_3 + SiO_2) > 1$ (Tossavainen *et al.*, 2007). The values of M_b in BS and BSP are > 1 and they represent respectively 3.42 and 2.

Table 6.1: Chemical composition of both slag samples

Oxide	BS wt %	BSP wt %
Al₂O₃	5.91	5.56
CaO	60.69	30.71
Fe₂O₃	14.61	21.4
K₂O	0.15	0.53
MgO	2.51	9.55
MnO	1.06	2.53
P₂O₅	1.05	14
SiO₂	12.54	14.63
TiO₂	1.47	1.09
$M_b = (CaO + MgO / Al_2O_3 + SiO_2)$	3.42	2

From this table BS can be described as a calco iron silicate while BSP is a calco phospho silicate.

6.2. Polarizing microscope

The examination of both slag (BS and BSP) by polarizing microscope were shown in Figures 6.1 and 6.2. The results indicate that both slag samples mainly consist of opaque minerals and they mostly composed of iron materials (illmenite, magnetite, hematite and limonite) and sulfied (pyrite). They show subangular to subrounded shapes and represent more than 80% of the total minerals. Zircons and epidotes are the predominant of non-opaque minerals in BSP and they represent 16% of the total minerals. Other minerals such as feldspars (plagioclases and orthoclases), quartz, garnet, calcite, rutile, and tourmaline were observed in low amounts in BS and BSP. The POM reveal that the two samples are amorphous with microlitic minerals randomly distributed into the aphanitic phase. The range size of the mineral is between 100 and 500 micrometers and porosity is also present in the two samples.

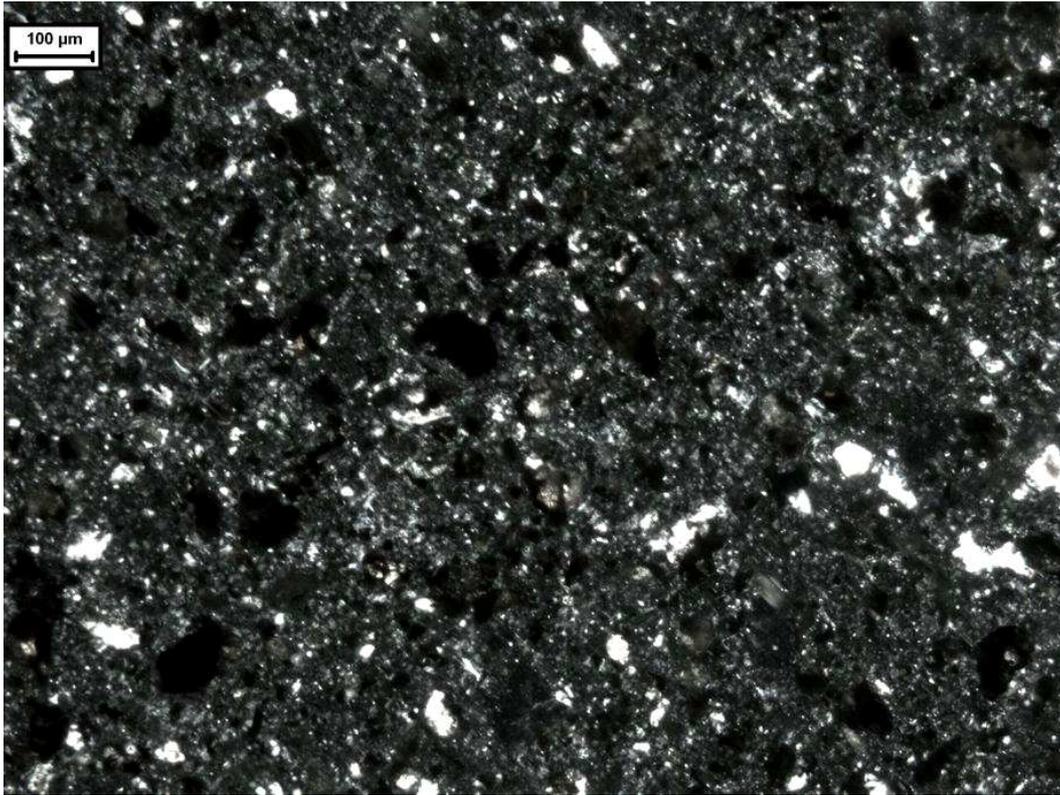


Figure 6.1: Thin section image of BS under polarised light

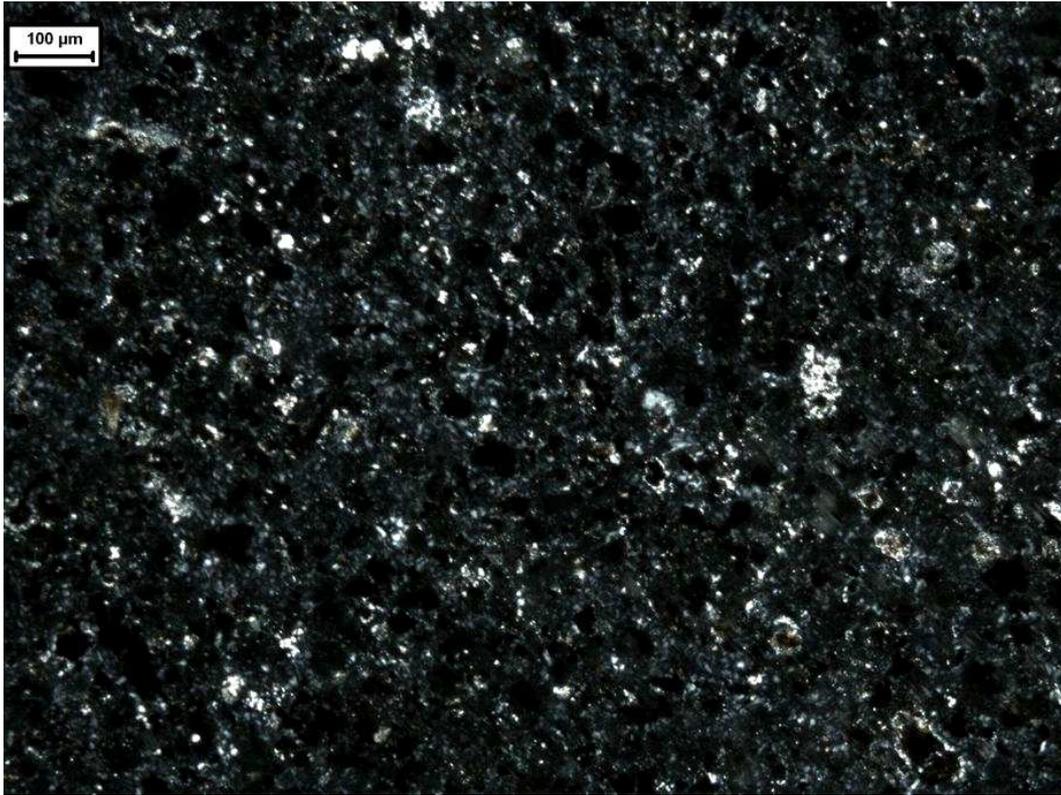


Figure 6.2: Thin section image of BSP under polarised light

6.3. X – ray diffraction analysis

According to XRD analysis, the diffraction patterns and the principal crystalline phases of both slag samples (BS and BSP) are given in Table 6.2 and Figure 6.3. The examination of XRD analysis gives a high several phases identified by the search-match program. Comparison between the results of XRD analysis for both slag samples revealed that many phases compounds such as larnite, wustite, brownmillerite, calcite and merwinite are generally similar in BS and BSP composition. In general, the main mineral composition of the slag may include major solid phases such as calcium-silicate (dicalciumsilicate, tricalciumsilicate and dicalciumferrite), calciowustite, magnesiowustite, calcium aluminate and free lime and magnesium (Dimitrova, 1996; Geiseler, 1996; Dimitrova and Mehanjiev, 1998; Motz and Geiseler, 2001).

Some phases were observed in BS such as mayenite, portlandite, melilite, grossular, imandrite and calcium silicate oxide. In addition, some crystallized compounds were detected in BSP than BS phases such as rodolicoite, calcium silicon, calcium aluminum iron oxide, calcium phosphate, titanium hydrogen phosphate, amonium hydrogen phosphate oxide and whitlockite. Thomas basic slag contains some phases such as larnite, calcium silico phosphate containing P_2O_5 , calcium ferrite ($Ca_2Fe_2O_3$), wustite (FeO), lime and magnetite (Panfili *et al.*, 2005). On the other hand, in acidic soils, the phosphorus availability of Thomas slag is similar to that of other water soluble phosphorus fertilizer (Sinaj *et al.*, 1994). Thomas slag was composed of silicato-calcium phosphates which were the prevailing form of P in the cells and a high Fe, Ca and Mn content in the walls (Sinaj *et al.*, 1994). Our results are in line with Setien *et al.* (2009) who observed that the major compounds of basic slag are calcium silicates such as (merwinite and larnite), portlandite, iron oxides and mayenite or tricalcium aluminate. Similar result obtained by XRD analysis for basic slag that compounds some phases such as tricalcium silicate ($3CaO.SiO_2$), dicalcium silicate ($2CaO.SiO_2$), merwinite, mayenite, wustite, larnite and portlandite (Shi, 2002; Tossavainan *et al.*, 2007; Taskiridis *et al.*, 2008).

Table 6.2: The principal crystalline phases of BS and BSP analysis

Mineral compound	Formula	BS	BSP
Larnite	Ca_2SiO_4	+	+
Wustite	$\text{Fe}_{0.942}\text{O}$	+	+
Brownmillerite	$\text{Ca}_2 (\text{Fe}_{1.44} \text{Al}_{0.559}) \text{O}_5$	+	+
Calcite	CaCO_3	+	+
Merwinite	$\text{Ca}_3\text{Mg} (\text{SiO}_4)_2$	+	+
Mayenite	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	+	-
Portlandite	Ca OH_2	+	-
Melilite	$\text{Ca}_8\text{Al}_2\text{Mg}_3\text{Si}_7\text{O}_{28}$	+	-
Grossular	$\text{Ca}_3\text{Al}_2 (\text{SiO}_4)_3$	+	-
Imandrite	$\text{Na}_{12}\text{Ca}_3\text{Fe}^{+3} 2\text{Si}_{12}\text{O}_{36}$	+	-
Calcium silicate oxide	$\text{Ca}_3 (\text{SiO}_4) \text{O}$	+	-
Rodolicoite	$\text{Fe}^{+3} \text{PO}_4$	-	+
Calcium silicon	CaSi_2	-	+
Calcium aluminum iron oxide	$\text{Ca}_2\text{Fe}_{1.40} \text{Al}_{0.60}\text{O}_5$	-	+
Calcium phosphate	Ca_3PO_4	-	+
Titanium hydrogen phosphate	$\text{Ti}(\text{PO}_4)(\text{H}_2\text{PO}_4)$	-	+
Amonium hydrogen phosphate oxide	$(\text{NH}_4)_2\text{H}_2\text{P}_2\text{O}_7$	-	+
Whitlockite	$\text{Ca}_{18}\text{Mg}_2\text{H}_2(\text{PO}_4)_{14}$	-	+

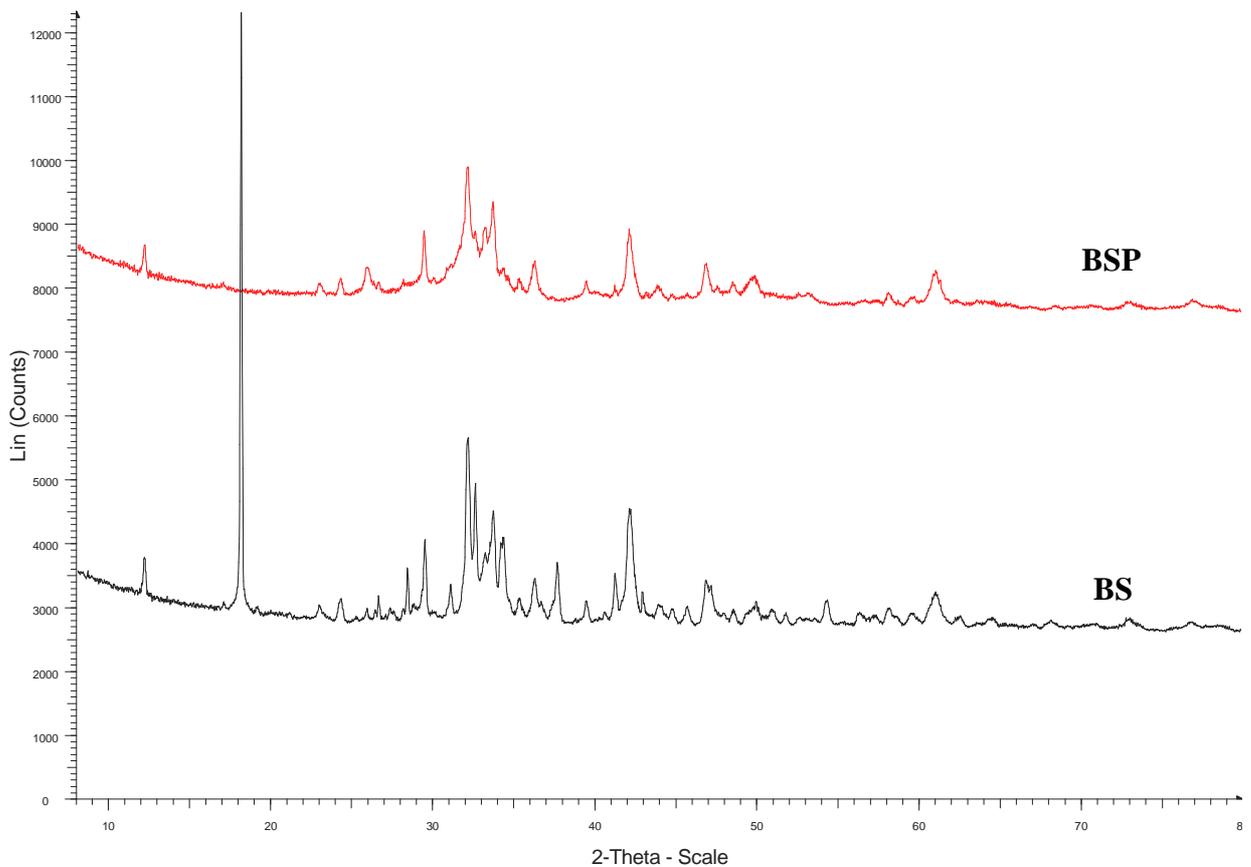


Figure 6.3: XRD spectrogram of BS and BSP analysis

From XRD analysis, it is possible to conclude that BS is depleted in phosphate phase while BSP is enriched in phosphate phases.

6.4. Scanning electron microscope (SEM/EDS)

According to the combination of SEM/X-EDS analysis to identify the elements in both slag samples, the chemical analysis is given in Table 6.3 and Figures 6.4, 6.5, 6.6, 6.7 and 6.8. From the EDS analysis the results indicate that the major elements of BS is mainly consists of Ca, Fe and Si. They are represented more than 90% of the total mass. Other elements such as Mn, P, Mg, K and Al are observed low amounts in BS. Setien *et al.* (2009) reported that the major compounds of basic slag are mainly silicates and aluminates of calcium and magnesium due to Ca, Si, Mg and Al oxides contains

more than 95% of the total mass. While Ca, P, Fe and Si are the major elements in BSP and they are represented more than 95% of the total mass. In addition, few amounts of the elements such as Mn, K, Mg and Al were also observed in the BSP. Tomas basic slag is used as phosphorus fertilizer and composed of silico-calcium phosphate (Sinaj *et al.*, 1994). A comparison SEM analysis between BS and BSP revealed that the amounts of Ca, Fe and Si are higher in both slag. In addition the level of P in BS is very low compared with the P content in BSP indicating that the BSP is rich in this element.

Table 6.3: SEM analysis of both slag (BS and BSP)

Element	BS (wt. %)	BSP (wt. %)
Al	0.65	0.62
Ca	69.06	68.16
Fe	17.71	10.0
K	0.93	1.26
Mg	1.20	0.69
Mn	2.64	1.43
P	1.46	10.60
Si	5.81	7.23

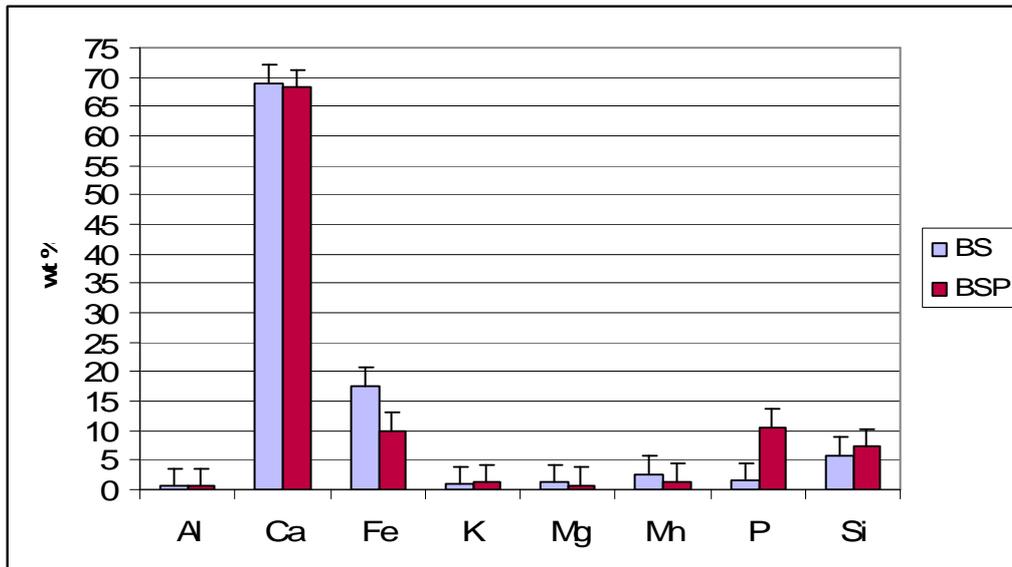


Figure 6.4: Comparison SEM analysis between BS and BSP

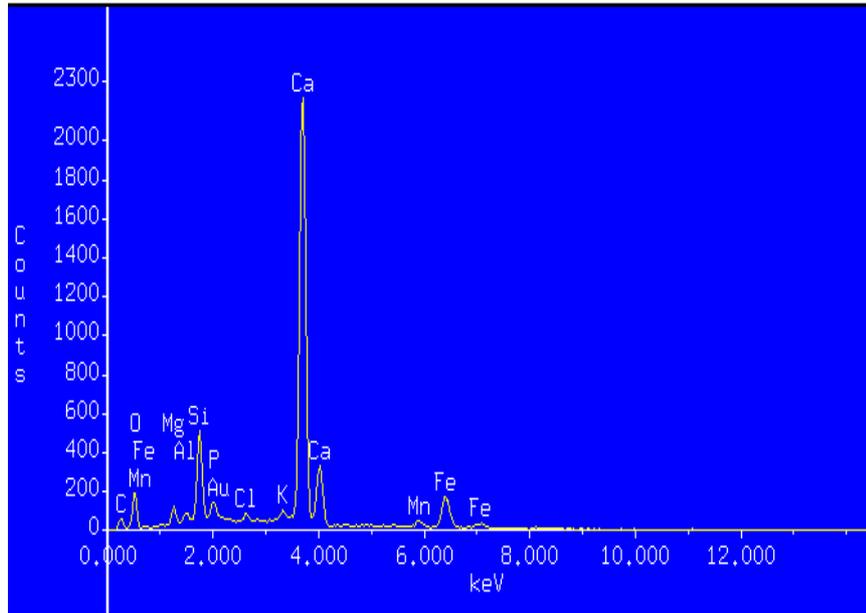


Figure 6.5: X-EDS of BS

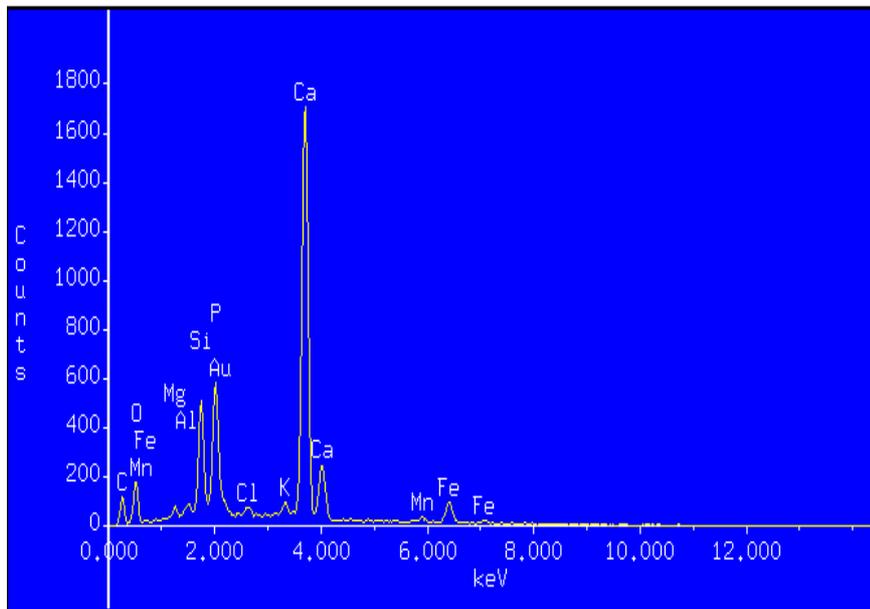


Figure 6.6: X-EDS of BSP

From X-EDS data, it is clear that the enrichment of BSP by P compared to BS is evident. In addition X-EDS is performed on local region of few micrometer (here about $10 \times 10 \mu\text{m}$) and confirmed that P is not distributed randomly but in phases identified previously by the XRD.

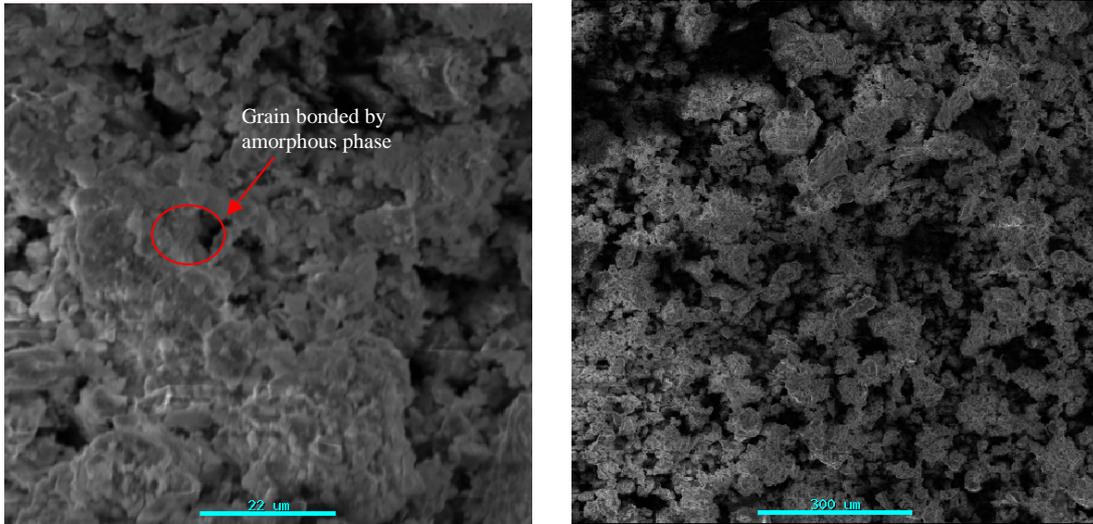


Figure 6.7: SEM images of BS

The texture of BS is a random distribution of the microlit of several micrometers. The microlit exhibit a granular microtexture bonded by an amorphous phase. Large open porosity is managed by this texture

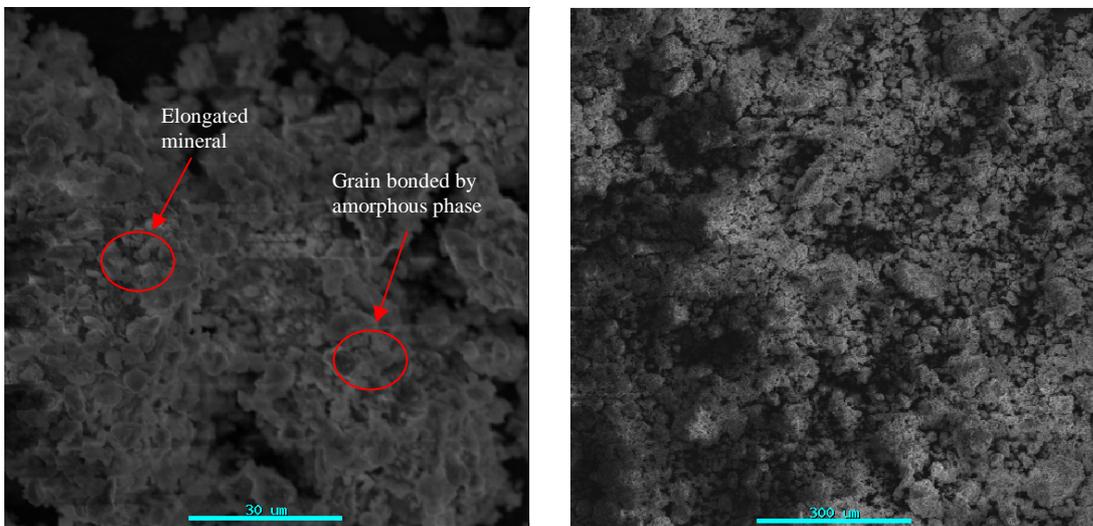


Figure 6.8: SEM images of BSP

The texture of BSP is quite similar to BS one with granular texture and large open porosity. But in detail (Fig.6.8) it is possible to distinguish different shape of the microlit with spheric one and tabular or rectangular ones. Phosphate mineral are knownd to exhibit different forms and especially elongated ones.

6.5. Electron microprobe analysis (EPMA)

The results of both slags analysis by electron microprobe analysis (EPMA) are presented in Figure 6.9 and Appendixes 1 and 2. The EPMA reveal that the major compounds of BS are Ca, Fe, Si and Mg; they are represented more than 90% of the total mass. Mn, Al, P, Ti and Cr are observed in few amounts. On the other hand, the major compounds of BSP are Ca, Fe, Si and P; they contain more than 95% of the total mass. Lesser amounts of the elements Al, Ti, Mn, and Cr were also observed.

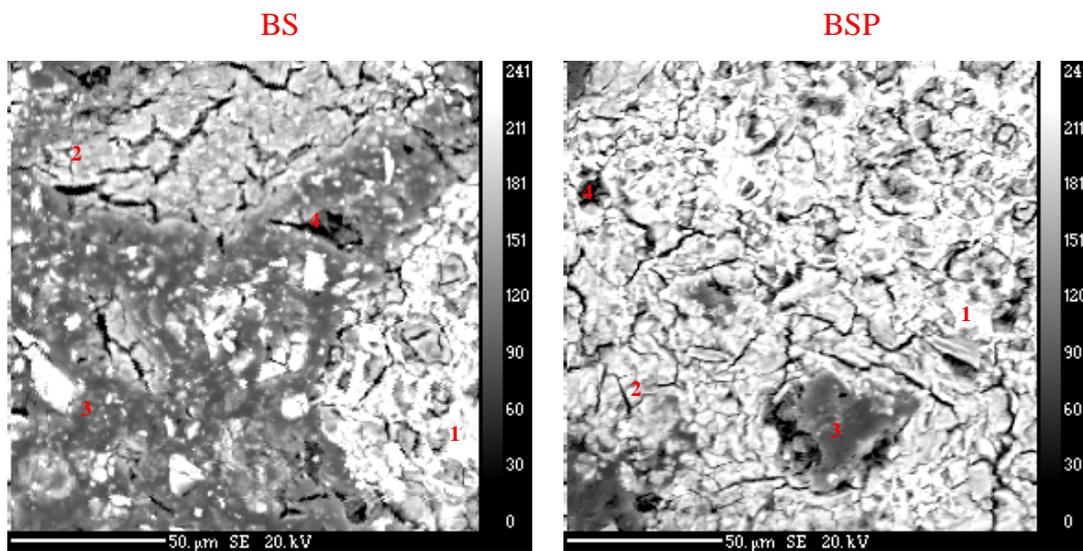


Figure 6.9: EPMA image of BS and BSP

According to data obtained from EPMA (Appendices 1 and 2), it can be seen that higher levels of Ca, Fe and Si are observed in both slag. While higher concentration of P is found in BSP compared with P content in BS indicated that the BSP is rich in phosphorus. Similar results were obtained by chemical composition analysis and scanning electron microscope.

CHAPTER 7: Effect of Basic Slag Addition on Soil Properties, Growth and Leaf Mineral Composition of Beans in a Cu-Contaminated Soil

7.1. Introduction

In contaminated soils, stabilization techniques aim at decreasing the labile pool of metals and metalloids such as As, Cr, Cu, Pb, Cd and Zn by the incorporation of amendments. These techniques are able to enhance one or several processes such as the metal adsorption through increased surface charge, the formation of organic and inorganic metal complexes, sorption on Fe, Mn, and Al oxides, and precipitation. It can be used in *in situ* and *ex situ* applications to reclaim and re-vegetate industrially devastated areas and mine-spoils, restore the physical, chemical, and biological soil properties, and reduce the contaminant mobility and bioavailability with various chemical and mineralogical agents such as industrial by-products (Bolan and Duraisamy, 2003; Pérez de Mora *et al.*, 2005; Raicevic *et al.*, 2005; Kumpiene *et al.*, 2008). Elements such as As, Cu, Cr, and Zn can be found in excess in contaminated soils at wood treatment facilities, especially when Cu sulphates and chromated copper arsenate (CCA) were used as a preservative against insects and fungi, which may result in soil phytotoxicity (Kumpiene *et al.*, 2008). The As stabilization can occur through sorption on Fe oxides by replacing the surface hydroxyl groups with the As ions and also by the formation of amorphous Fe (III) arsenates and/or insoluble secondary oxidation minerals. The Cr immobilisation mostly deals with Cr reduction from toxic and mobile hexavalent form Cr (VI) to stable Cr (III) in natural environments. Copper immobilisation by clays, organic matter, carbonates, phosphates, and Fe oxides amendments was reported with precipitation of Cu carbonates and oxy-hydroxides, ion exchange and the formation of ternary cation–anion complexes on the surface of Fe and Al oxy-hydroxides (Kumpiene *et al.*, 2008). Phosphorus amendments, clays, birnessite and coal fly ash such as beringite can successfully immobilise Zn in soil (Mench *et al.*,

2000; Bolan *et al.*, 2003; Kumpiene *et al.*, 2008). Several amendments such as coal or bio-fuel fly ashes have been used for the *in situ* immobilisation of metals in contaminated soils (Clark *et al.*, 2001; Dermatas and Meng, 2003; Kumpiene *et al.*, 2007). Copper and Pb mobility and bioavailability in contaminated soil can be effectively reduced using a combination of coal fly ash and peat by 96 % and 97 % in the field respectively (Kumpiene *et al.*, 2007) but also by sewage and paper mill sludge (Merrington *et al.*, 2003; Sajwan *et al.*, 2003; Battaglia *et al.*, 2006). Soil amended with composted sewage sludge (Herwijen *et al.*, 2006), organic matter (Brown *et al.*, 2003; Brown *et al.*, 2004; Farfel *et al.*, 2005; Stuczynski *et al.*, 2007), lime (Hooda and Alloway 1996; Dutré *et al.*, 1998; McKinley *et al.*, 2001; Moon *et al.*, 2004 ; Chen and Wong, 2006), gypsum and lime-rich industrial by-products (Illera *et al.*, 2004; Garrido *et al.*, 2005), hydroxyapatite (Boisson *et al.*, 1999a), zeolites (Lin *et al.*, 1998; Edwards *et al.*, 1999; Oste *et al.*, 2002; Friesl *et al.*, 2003 ; Mahabadi *et al.*, 2007), birnessite (Mench *et al.*, 2000), iron grit (Mench *et al.*, 1994b) and beringite (Vangronsveld *et al.*, 1996; Boisson *et al.*, 1999b; Lombi *et al.*, 2002 ; Mench *et al.*, 2006) were used for the *in situ* stabilization of metals in contaminated soils. The application of both lime and red mud at 3 or 5% increased the soil pH and decreased the metal availability; thus it can be used to remediate a heavily contaminated acid soil to allow re-vegetation (Gray *et al.*, 2006). Out of amendments including various alkaline materials, organic matter, phosphates, alumino-silicates and iron grit, basic slag (3.9%) and compost of sewage sludge (5%) combined with iron grit were the most efficient to promote shoot production and limit the foliar Cu accumulation in dwarf beans cultivated in a highly Cu-contaminated soil (Bes and Mench, 2008).

Several alkaline slags have been used for amending acid soils. Phosphogypsum can improve soil properties such as pH, soil EC, CEC, exchangeable Ca, Mg, and metal availability to plant, and also increase the crop yield (Alva and Sumner, 1990). Slag treatments increased more soil pH than converter sludge treatments (Forghani *et al.*, 2006). Combination of slag and converter sludge treatments enhanced the plant Ca and Mg concentrations. The application of calcium silicate slag reduced the soil acidity and increased the available P, Si and exchangeable Ca in soil (Barbosa Filho *et al.*, 2004). Blast furnace slag are used to correct soil acidity and can promote root growth and

distribution in the soil profile, which results in higher shoot dry matter and grain yield of upland rice under sprinkler irrigation (Carvalho-Pupatto et al., 2004). A combination of converter slag and fungicide did not decrease the density of dormant spores of *Plasmodiophora brassicae* in the soil but suppressed the clubroot disease (Murakami and Goto, 2004). The application of Linz-Donawitz (LD) slag in acid soils managed under pastures increased the soil pH with and without NPK fertilization (Pinto et al., 1995), increased exchangeable soil Ca and Mg whereas exchangeable soil Al, Mn, Cu and Zn decreased (Besga et al., 1996), and its combination with NPK fertilizers resulted in highest crop yields and nutrient concentrations in plants (Lopez et al., 1995). Both calcitic limestone and BS applied in Brazil sugarcane fields generated a beneficial residual effect in the correction of soil acidity, the increase of base saturation and the yield of sugar cane ratoon (Prado et al., 2003). For Ali and Shahram (2007), the increasing rate of soil pH was proportional to the slag amount used. The slag decreased the Fe availability at a pH range of 7.4 - 8.5 but increased at higher pH, while the use of slag also proportionately increased the P and Mn availability. In greenhouse studies the application of respectively 1 % and 2 % (w/w) of slag in tea garden soil and 0.5, 1 and 2 % slag in rice field soil increased the plant shoot dry yield and P and Mn uptake. Fe and K uptake increased in rice field, K uptake decreased in tea garden soil and Fe uptake was not changed. The addition of Thomas basic slag (TBS), hydrous manganese oxide (HMO), iron grit (ST) and beringite to a contaminated soil did not increase the plant biomass production but decreased the mobility and bioavailability of Cd, Zn and Pb (Mench et al., 1994a,b). These agents effectively mitigated the Cd uptake by plants. In ryegrass, HMO and ST decreased either shoot Pb or Zn concentrations, and TBS reduced shoot Pb concentrations.

The Ca and P contents in BS make it a potential liming agent to increase the precipitation and sorption of metals such as Cu and a potential fertiliser promoting plant growth and improving the physico-chemical properties of the soil. Therefore this study aimed at investigating a BS addition into a soil mainly Cu-contaminated from a wood treatment facility to improve soil characteristics such as pH and EC and reduce the labile pool of trace elements in soil for root-to-shoot transfer in beans. Hypotheses were that BS compounds may influence the composition of soil solution through acid-base,

precipitation and sorption reactions, and foliar concentrations through changes in soil solution, competitions for root uptake and root-to-shoot transfer. Beans plants were cultivated in potted soils with increasing BS addition rates, from 0% to 4%, placed in controlled conditions. Changes in soil EC and pH, plant growth, biomass production and the foliar elemental concentrations of primary leaves were determined.

7.2. Material and Methods

7.2.1. Basic slag characterisation

BS is a by-product of the steel industry, containing mainly calcium oxide, silicon oxide, iron oxide, and other metal oxides. They were determined by using an atomic absorption spectrophotometer. Arsenic (As) was analysed by GF-AAS according to norm NF EN ISO 15586 (T90-119) after digestion with regal water (NF EN 13346), other trace elements were analysis by ICP-AES according to norm NF EN ISO 11885 after mineralisation (total digestion NFX31-147). The pH and electrical conductivity (EC) for BS were measured in 1:1 BS: water suspension by using pH meter and glass electrode EC respectively. The characterisation of BS is shown in Table 7.1.

Table 7.1: Characterisation of the BS

pH 1:1	12.72
EC mS/cm	12.2
Al₂O₃ %	5.91
CaO %	60.69
Fe₂O₃ %	14.61
K₂O %	0.15
MgO %	2.51
MnO %	1.06
P₂O₅ %	1.05
SiO₂ %	12.54
TiO₂ %	1.47
As mg/kg	<5
Cr mg/kg	615
Co mg/kg	<5
Ni mg/kg	<10
Cu mg/kg	5
Zn mg/kg	42
Pb mg/kg	<20
Mn %	0.01

7.2.2. Pot experiment

The topsoil of P7 (0-0.25 m) of a soil mainly contaminated by Cu was sampled from a soil French wood treatment facility (Mench and Bes, 2009). Pot experiments were carried out on a 2-week period with *Phaseolus vulgaris* L. An uncontaminated, sandy soil was used as a control (CTRL). BS was added into the soil (1 kg soil/pot) to constitute four treatments in triplicates: 0 % (T1), 1 % (T2), 2 % (T3) and 4 % (T4) BS/kg air-dried soil. Four dwarf beans (*Phaseolus vulgaris* L. cv vroege Limburgs) were sown in all pots and cultivated (15 days) in controlled conditions: illumination 12 h light/12 h darkness regime, intensity $150 \mu\text{mol m}^{-2} \text{s}^{-1}$, temperature $25^{\circ}\text{C}/22^{\circ}\text{C}$, and 50% relative humidity. Pots were arranged in a fully randomised block design on a bench and watered daily with deionised water (at 50% WHC) without loss from drainage. The plant growth was monitored on a daily basis using an index based on plant development steps for two weeks and then plants were harvested. Biometrical parameters, i.e. fresh weight (FW) of roots, shoots, and primary leaves were measured. Plant materials were washed with deionised water (2 times) and distilled water, oven dried at 70°C , and weighted to determine the DW biomass production. Plant samples (0.5 g) were wet digested in 5 mL 14M HNO_3 , 2 mL H_2O_2 and 1 mL distilled water at 180°C in PFA (perfluoroalkoxy copolymer resin) tubes under microwaves (MarXpress, CEM). The mineral composition in the plant digests were measured by ICP-AES (Ultima, Jobin Yvon Horiba, Longjumeau, France). The soil samples were taken from all pots experiment to measure the soil pH and the EC in suspension soil: water in the ratio 1:1 using a glass electrode pH meter and electrical conductivity respectively (Jackson, 1967).

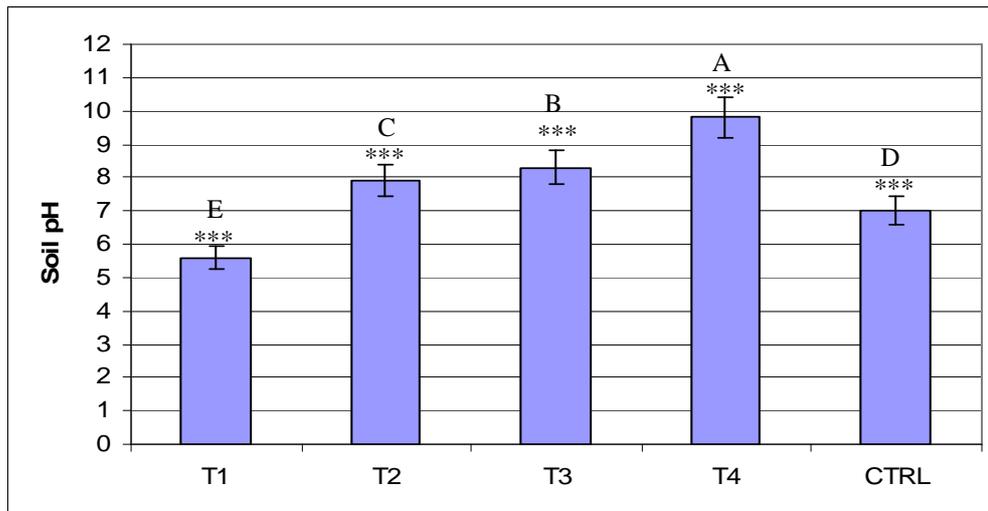
7.2.3. Statistics

The soil properties and plant yield, element concentrations and total element amount in primary leaves [$\mu\text{g plant}^{-1}$, so-called here element accumulation and calculated based on foliar element concentration ($\mu\text{g kg}^{-1}$ DW) and leaf biomass production ($\mu\text{g DW plant}^{-1}$)] of plants from the pot experiment were tested by statistical analysis (ANOVA, Kruskal-Wallis and Tukey test) with SAS software version 9.1.

7.3. Results and Discussion

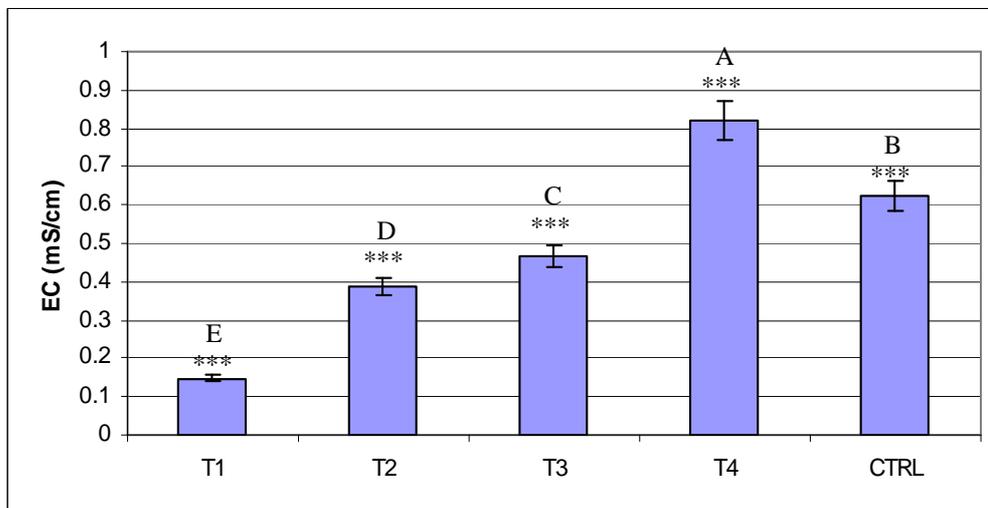
7.3.1. Soil parameters

The BS incorporation in soil P7 increased the soil pH in relation with the addition rate, from 5.6 for the T1 treatment to 7.9, 8.3 and 9.8 for the T2, T3, and T4 treatments respectively. This resulted in soil pH values higher in the T2, T3, and T4 treatments than in the control soil (7.0) (Figure 7.1). Increase in soil pH was predicted by a polynomial equation ($y = -0.223x^2 + 1.883x + 5.774$, $R^2 = 0.96$). Ali and Shahram (2007) found that the increasing rate of soil pH was proportional to the slag amount used in the soils. Basic slag affected also the soil EC which increased from (in mS cm^{-1}) 0.14 (T1) to 0.39, 0.46 and 0.82 for the T2, T3, and T4 treatments respectively. Consequently, the soil EC was lower in the T1, T2 and T3 treatments and higher in T4 than in the control soil (0.62 mS cm^{-1}) (Figure 7.2). A linear equation predicted the increase in soil EC in relation with the BS addition rate ($y = 0.161x + 0.176$, $R^2 = 0.97$). The enhanced soil pH and EC in amended soils were likely due to the alkaline property and composition of BS. Su and Evans (1996) reported that EC increased in soil treated with lime. Amelioration of acid soils with amendments such as alkaline by-products can improve soil properties such as pH and EC (Alva and Sumner, 1990). Our results are in line with Pinto *et al.* (1995) who reported that BS application in acid soils increased the soil pH with and without NPK fertilization. In addition, the incorporation of Thomas basic slag into an excessively Cu contaminated topsoil from a wood treatment facility increased the soil pH (Bes and Mench, 2008). Our results confirmed BS as a potential liming agent able to improve the soil acidity. A 1% addition rate would correspond to 25000-30000 kg BS/ha depending of the soil depth considered, *i.e.* 0.25 or 0.3 m. Rodriguez *et al.* (1994) suggested that Linz-Donawitz (LD) slag application increased the soil pH linearly, especially where fertiliser was not applied. In fact the addition of 7500 kg, without NPK fertilisation, increased the soil pH from 5.3 to 6.5. When 3000 kg ha^{-1} of slag was added, the increase in soil pH was accompanied by a decrease of Al saturation percentage in the cation exchange complex to <10%.



Values are mean ± standard errors (n=3). Bar graphs with different letters were significantly difference; P (0.001<***<0.0001).

Figure7.1: Effects of BS addition on the soil pH



Values are mean ± standard errors (n=3). Different letters on bar graphs indicate a significant difference; P (0.001<***<0.0001).

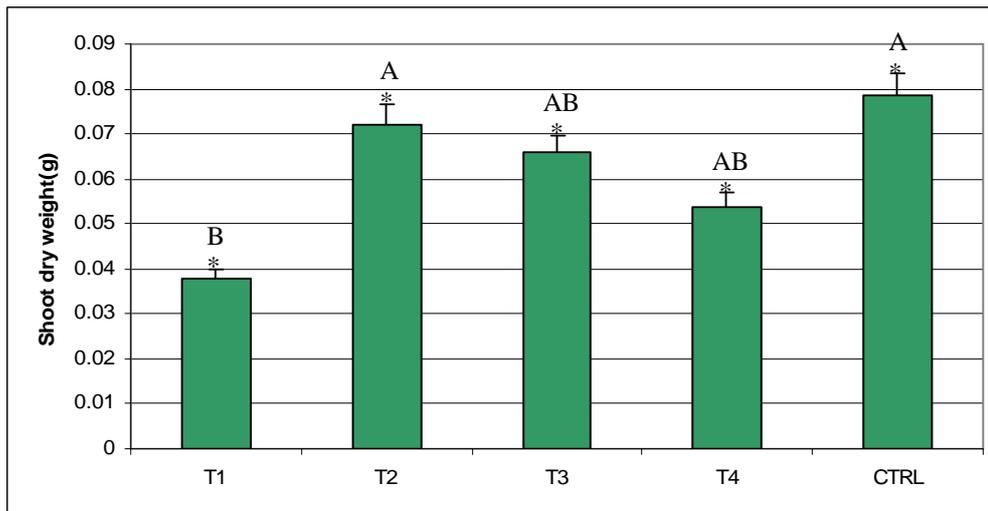
Figure7.2: Effects of BS addition on the soil EC

7.3.2. Plant analysis

7.3.2.1. Plant yield

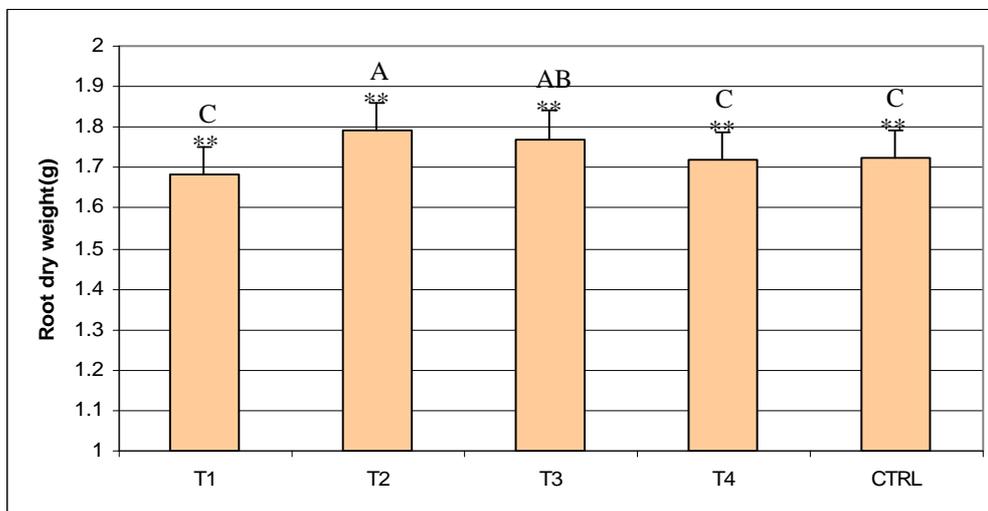
Some basic slags previously used in acid soils have ameliorated plant growth and their biomass production (Lopez et al., 1995). Shoot yield DW are presented in Figure 7.3. The biomass of beans primary leaves is affected by the BS incorporation into soil P7 and its effect varied across the treatments. The shoot yield was the highest for the control soil and the lowest for the T1 treatment. This confirmed that soil P7 negatively impacted beans (Bes and Mench, 2008). Shoot yield numerically increased for all amended soils. Compared to the untreated soil P7 (T1), T2 and T3 treatments delivered the highest increases for the shoot yield, i.e. 1.89 and 1.75 times for T2 and T3, while the T4 treatments gave an intermediate value. These values for shoot yields in the T2 and T3 treatment corresponded to 89 % and 83 % based on the control soil value. Only the difference between T1 and T2 treatments however was statistically significant. The application of respectively 1 % and 2 % (w/w) of the slag in tea garden soil and 0.5, 1 and 2 % slag in rice field soil increased the plant shoot dry yield (Ali and Shahram, 2007). In addition, the application of Linz-Donawitz (LD) slag in acid soils combination with NPK fertilizers resulted in highest crop yields (Lopez *et al.*, 1995). The decrease in shoot yield for the T4 treatment compared to the T2 and T3 treatments likely indicated an excessive BS addition rate. The ideal soil pH for beans is in the 6.0-7.5 range (Gardener's Network, 2009) and soil pH for the T4 treatment largely exceeded these values. In addition the soil conductivity in the 0-0.45 mS cm⁻¹ range is suitable for most plants if recommended fertilisers are used, but a high conductivity (0.46-0.7 mS cm⁻¹) may reduce the emergence and cause a slight to severe damage to salt sensitive plants (Omafra, 2008). Indeed the soil EC in the T4 treatment which reached 0.8 mS cm⁻¹ would be excessive and may contribute to limit beans shoot yields.

The BS effect on the root DW yield varied with the BS addition rate in soil. Results are given in Figure 7.4. The highest value of the root DW yield occurred in the T2 treatment and the lowest value in the T1 treatment. Root yield was significantly higher in T2 and T3 BS-amended soils than in the untreated soil (T1) and control soil (CTRL). The differences however remained relatively low.



Values are mean \pm standard errors (n=3). Different letters on bar graphs indicate a significant difference; P (0.05 < * < 0.01).

Figure 7.3: Effect of BS on the shoot yield of beans (g DW plant⁻¹) for each treatment



Values are mean \pm standard errors (n=3). Different letters on bar graphs indicate a significant difference; P (0.01 < ** < 0.001).

Figure 7.4: Effect of BS on the root yield of beans (g DW plant⁻¹) for each treatment

For the T2 and T3 treatments, the root yield increased 1.06 and 1.05 times respectively compared to the untreated soil (T1). Higher increases in root biomass were previously obtained with the addition of Thomas basic slag (TBS) in a Cu-contaminated soil from a wood treatment facility (Bes and Mench, 2008) and of blast furnace slag to upland rice (Carvalho-Pupatto et al., 2004). At 4% addition rate, the beneficial BS effect on root yield disappeared again likely due to excessive increases in soil pH and EC.

7.3.2.2. Foliar elemental concentrations and accumulations

The effect of BS addition in soil on the foliar element concentrations and foliar element accumulations are presented in Tables 7.2 and 7.3 respectively.

7.3.2.2.1. Foliar nutrients concentrations and accumulations

Foliar Al concentrations significantly decreased in plants from all BS-amended soils, especially for the T3 plants, and were similar compared to the control level. The decrease in foliar Al concentration is likely due to the liming effect, *i.e.* the increase in the soil pH and competition with Ca for root uptake, and increase in primary leaf biomass. The foliar Al accumulation varied in the 1.2-3.3 $\mu\text{g plant}^{-1}$ range with lowest and highest values for T3 and T2 plants but differences were not significant. Foliar Mg concentration was higher in T1 plants than in control plants likely due to a lower leaf biomass. The increase in the leaf biomass for the T2 and T3 beans reduced foliar Mg concentration. In addition the increase in foliar Ca concentration may have also decreased foliar Mg concentration in plant. Changes in foliar Mg accumulation were not significant. The calcium concentration was 3 times lower in the primary leaves of beans grown in soil compared to that in control beans. It was also below frequent values for primary leaf Ca concentrations in dwarf beans. In the literature, 1% slag and 1% converter sludge treatments increased Ca and Mg concentration in the plant (Forghani *et al.*, 2006). Bes and Mench (2008) suggested that the low foliar Ca concentration vs. foliar Cu concentration can limit beans growth. The foliar Ca concentration was increased 8.9 times for both T2 and T3 plants compared to T1 plants and 2.7 times compared to the control plants. This reflected the Ca inputs in soil P7 due to the BS incorporation. It decreased in T4 plants probably because roots were negatively

impacted by the high soil EC value. The foliar Ca accumulation classed as: T1 < CTRL, T4 < T2, T3. The foliar P concentrations ranked in the following order: T2, T3 < T4 < CTRL, T1. The control soil contained a high organic matter content which could supply organic P and was regularly fertilised. Both low leaf yield for the T1 plant and acid soil pH in T1 treatment could likely enhance the foliar P concentration. Despite P inputs in soil due to the BS incorporation, the foliar P concentration was not increased in beans from BS-amended soils. We assumed that several soil and plant factors can explain this result. Firstly, the BS contained a high Ca content and relatively high Fe and Al contents. Therefore phosphates could be sorbed with these 3 cations and not easily available in the soil solution for root uptake. Increase in the leaf yield could contribute to reduce foliar P concentration in T2 and T3 beans. Regarding foliar P accumulation, plants from untreated and BS-treated P7 soils have a lower value than the CTRL soil.

Table 7.2: Elemental concentrations in the primary leaves of beans

Treatments	T1	T2	T3	T4	CTRL	Frequent values (#)
Al mg/kg	0.07 a ± 0.01*	0.04 ab ± 0.02*	0.02 b ± 0.01*	0.04 ab ± 0.01*	0.03 b ± 0.01*	
Mg g/kg	3.14 a ± 0.10***	1.93 c ± 0.20***	1.93 c ± 0.15***	2.18 c ± 0.03***	2.51 b ± 0.21***	1.9 - 3.7
Ca g/kg	3.37 d ± 1.03***	29.41 a ± 3.21***	29.45 a ± 1.37***	21.54 b ± 1.77***	10.97 c ± 1.95***	6.4 - 29
P g/kg	5.24 a ± 0.52**	3.16 b ± 0.55**	3.30 b ± 0.41**	4.23 ab ± 0.42**	4.82 a ± 0.14**	1 - 6
K g/kg	16.01 b ± 1.23**	18.62 b ± 2.78**	21.17 b ± 2.16**	29.77 a ± 3.95**	19.31 b ± 0.13**	13 - 22
Cd mg/kg	0.11 a ± 0.10 NS	<dl	<dl	<dl	<dl	0.03 - 0.07
Cr mg/kg	0.41 a ± 0.09 NS	0.33 a ± 0.11 NS	0.61 a ± 0.27 NS	0.65 a ± 0.07 NS	1.70 a ± 1.02 NS	0.13 - 1.7
Cu mg/kg	53.13 a ± 14.04**	22.59 b ± 1.59**	27.54 b ± 1.51**	27.64 b ± 0.71**	5.65 c ± 0.67**	4.9 - 7.9
Zn mg/kg	25 a ± 14 NS	31.5 a ± 20.5 NS	16.5 a ± 3.5 NS	24 a ± 12 NS	12 a ± 2.5 NS	13 - 20

- In a column mean values (± standard deviations) followed by the same letter do not differ significantly P (0.05 < * < 0.01), P (0.01 < ** < 0.001), P (0.001 < *** < 0.0001) and non significant NS (p > 0.05).
- (#) ranges of frequent values for element concentrations in the primary leaves of dwarf beans grown on uncontaminated control soils (Mench *et al.*, 1996).
- dl: (detection limit).

Table 7. 3: Elemental accumulation in the primary leaves of beans ($\mu\text{g plant}^{-1}$)

Treatments	T1	T2	T3	T4	CTRL
Al	2.87 a ± 1.28 NS	3.31 a ± 2.26 NS	1.18 a ± 0.25 NS	2.16 a ± 0.97 NS	2.28 a ± 0.40 NS
Mg	119 a ± 34 NS	138 a ± 16 NS	128 a ± 30 NS	117 a ± 25 NS	195 a ± 34 NS
Ca	127 c ± 49 ***	2140 a ± 531 ***	1950 a ± 430 ***	1170 b ± 337 ***	843 b ± 71 ***
P	198 b ± 57 *	225 b ± 27 *	214 b ± 22 *	224 b ± 29 *	377 a ± 87 *
K	602 b ± 151 *	1354 a ± 343 *	1405 a ± 361 *	1583 a ± 260 *	1521 a ± 406 *
Cd	0.01 a ± 0.01 NS	<dl	<dl	<dl	<dl
Cr	0.02 a ± 0.01 NS	0.02 a ± 0.01 NS	0.04 a ± 0.02 NS	0.03 a ± 0.00 NS	0.15 a ± 0.10 NS
Cu	2.04 a ± 0.80 NS	1.63 a ± 0.32 NS	1.81 a ± 0.34 NS	1.48 a ± 0.27 NS	0.43 b ± 0.06 NS
Zn	0.92 a ± 0.04 NS	2.26 a ± 1.08 NS	1,07 a ± 0.06 NS	1.27 a ± 0.8 NS	0.94 a ± 0.03 NS

- In a column (mean values \pm standard deviations) followed by the same letter do not differ significantly P (0.05 < * < 0.01), P (0.001 < *** < 0.0001) and non significant NS (P > 0.05).

- dl: (detection limit).

The foliar K concentration increased in relation with the BS addition rate but differences were only significant between T4 plants and the other plants. The foliar K concentration was 1.8 times and 1.5 times higher in T4 plants than in T1 plants and control plants, respectively. This slightly exceeded frequent values for foliar K concentration in beans primary leaves. However in plants the critical K concentration is in the range of 20-50 g kg⁻¹ DW (Marschner, 1995). The foliar K accumulation was similar in T2, T3, T4 and CTRL. Only the T1 plants showed a decrease in foliar K accumulation compared to all other plants.

7.3.2.2.2. Foliar trace element concentrations and accumulations

The foliar Cu concentration varied from 5.6 mg kg⁻¹ to 53.1 mg kg⁻¹ in the following order: CTRL < T2, T3, T4 < T1. The foliar Cu concentration in T1 plants exceeded its frequent values and the critical Cu concentration for beans leaves *i.e.* 15-30 mg Cukg⁻¹ DW (MacNicol and Beckett, 1985). We assumed that this mainly caused the

phytotoxic effect in plants grown in the untreated, Cu-contaminated soil 630 mg Cu/ kg. The highest decrease in the foliar Cu concentration, *i.e.* 2.3 times compared to the T1 plants, was obtained for the T2 plants. This suggested that the Cu labile pool for root uptake in the soil is low at the T2 soil pH and that further increase in the soil pH for the T3 and T4 treatments could enhance Cu complexation with dissolved organic matter in the soil solution (Sauvé *et al.*, 1997). The mobility of copper in soil depended on several factors, including the Cu-complexing ability of the solid phase, the Cu-complexing ability of the DOM, and the molecular weight of the DOM fractions (Han and Thompson, 2003). Cu–DOM complexation increases approximately 10-fold per pH unit (Lu and Allen, 2000). However the availability of such Cu-DOM complexes for root uptake in T3 and T4 soils is questionable. The BS addition at 1% into studied soil promoted beans growth with the lowest foliar Cu concentration and highest Ca concentrations. Foliar Cu accumulation varied from 0.4 mg to 2.0 mg plant⁻¹ in the following order: CTRL < T4, T2, T3, T1. Indeed the Cu amount accumulated in primary leaves was not significantly changed in plants from BS-treated soils, but their improved shoot yield resulted in reducing foliar Cu concentrations through a biomass dilution effect. The rise in foliar Ca accumulation in BS-treated plants may contribute to a better pectin methylesterase functioning (Micheli, 2001), resulting in the restoration of cell elongation and a higher Cu sorption on the cell walls. Restoration of Ca homeostasis may also promote plant metabolism and the Cu sorption by various ligands (Pilon *et al.*, 2006). Changes in foliar Zn concentration were not significant across the treatments. Foliar Zn concentration exceeded its frequent values in some dwarf beans from BS-treated soils but remained below the critical leaf concentration for dwarf beans *i.e.* 100 mg kg⁻¹ DW (Mench *et al.*, 2000). Usually an increase in soil pH reduces Zn availability in the soil solution and changes in the leaf yield affect the foliar Zn concentration causing a decrease in foliar Zn concentration (Mench *et al.*, 2000). For instance the addition of Thomas BS decreased the mobility and bioavailability of Cd, Zn and Pb in a highly contaminated soil, near smelters at Evin (Pas de Calais, France) (Mench *et al.*, 1994a). But here our results did not confirm such previous studies. The foliar Cr concentration was not significantly changed in BS-treated soils compared with the control soil, and all values fell in the range of Cr frequent values. The foliar Cr accumulations were also similar for all treatments. Foliar Cd concentration and

accumulation decreased below the analytical detection limits with the BS application compared with untreated soil.

7.4. Conclusion

A BS was incorporated at increasing addition rates (1, 2 and 4%) in an acid sandy Cu-contaminated soil. The soil pH was increased from 5.6 in the untreated soil up to 9.8 for the 4 % BS-amended soil. The soil conductivity rose from 0.14 mS cm⁻¹ in the untreated soil to 0.38 mS cm⁻¹, 0.46 mS cm⁻¹, and 0.82 mS cm⁻¹ in the 1%, 2%, and 4% BS-amended soils respectively. These increases in soil pH and EC in all BS-amended soils likely resulted from the BS composition and in particular its high Ca content. The pot experiment carried out with dwarf beans demonstrated that (i) the foliar Cu concentration likely caused a phytotoxic effect in plants grown in the untreated, Cu-contaminated soil, (ii) the BS incorporation at 1% addition rate into the contaminated soil promoted beans growth with the lowest foliar Cu concentration and highest Ca concentrations, and (iii) foliar P concentration however was not enhanced by the BS incorporation into the Cu-contaminated soil. Instead, foliar K accumulation in primary leaves was restored up to the control level. Therefore this by-product was effective at 1% addition rate as a liming material but not as a P fertilizer in this short-term experiment. The BS incorporation in the contaminated soil did not increase the foliar concentrations and accumulations for Cd, Cr, and Zn.

CHAPTER 8: In Situ Remediation of Trace Elements in Chromated Copper Arsenate (CCA)-Contaminated Soil Using Basic Slag Phosphate (BSP)

8.1. Introduction

Soil contamination by trace elements is a widespread problem in many parts of the world. The accumulation of toxic metals in soil is mainly inherited from parent materials or inputs through human activities (He *et al.*, 2005). One of the sources of soil contaminations is very important resulting from chemical widely used wood preservative industries in aquatic environments and storing the wood after treatment by chromated copper arsenate (CCA). Elements such as As, Cu, Cr, and Zn can be found in excess in contaminated soils at wood treatment facilities, especially when Cu sulphates and chromated copper arsenate (CCA) were used as a preservative against insects and fungi, which may result in soil phytotoxicity (Kumpiene *et al.*, 2008). After impregnation of the wood with a CCA solution the metal compounds are fixed to the cell walls of the wood matrix (Helsen *et al.*, 1998). The rain is playing a key-role in leaching these metals from the recently treated timber and lumber stored at the treatment facility. Under conditions storage the soils contain high concentrations of CCA (Buchireddy *et al.*, 2008). Therefore it is very important to reduce or immobilise these metals in contaminated soil. Currently there are several technologies can be used to clean up or remove the soils and the mining wastes contaminated by toxic metals, such as thermal treatments, biological and physical/chemical procedures. These removal technologies are generally costly to practice and destructive to the application sites, and only partially effective for the total removal (efficient clean up) of toxic metals, or for the sufficient reduction of their mobility and bioavailability (Raicevic *et al.*, 2005). In the past few decades, the stabilization technique or *in situ* immobilisation of trace elements in contaminated soil by adding amendments is one of the common practices reducing negative effects of contaminants such as As, Cr, Cu, Pb, Cd and Zn to improve the quality of contaminated soil. It is considered as a simple and cost-effective approach for the treatment of metals in contaminated soils, particularly when these soils are

difficult or costly to be removed or treated *ex situ*. *In situ* immobilisation aims at enhancing natural attenuation mechanisms such as (ad)sorption through increased surface charge, precipitation, complexation and redox reactions that occur naturally in the soils to reclaim and re-vegetate industrially devastated areas and mine-spoils, restore the physical, chemical, and biological soil properties, and reduce the contaminant mobility and bioavailability with various chemical and mineralogical agents (Mench *et al.*, 2000; Oste *et al.*, 2002; Bolan and Duraisamy, 2003; Adriano *et al.*, 2004; Pérez de Mora *et al.*, 2005; Raicevic *et al.*, 2005; Kumpiene *et al.*, 2006; Kumpiene *et al.*, 2008).

Several application studies have demonstrated that *in situ* immobilisation of contaminated soils and groundwaters by using inexpensive soil amendments. The amendments can significantly reduce the mobility of metals in soils, metal uptake by plants and metal phytotoxicity. Neutralizing agents in form of alkaline materials are usually added to acidic soils to ameliorate soil chemical and physical properties and reduce the bioavailability of contaminant to plants. (Brallier *et al.*, 1996; Brown *et al.*, 1997; Bolan and Duraisamy, 2003; Gray *et al.*, 2006; Tlustos *et al.*, 2006). A range of liming materials available, such as calcite (CaCO_3), burnt lime (CaO), slaked lime (Ca(OH)_2), dolomite ($\text{CaMg(CO}_3)_2$), and slag (CaSiO_3), varying in their ability to neutralise the acidity (Bolan and Duraisamy, 2003). According to changes in the soil pH, alkaline materials may be effective treatment chemicals to induce metal hydrolysis reactions and/or co-precipitation with carbonates, acting as a precipitating agent for metals in the soil solution acid (Tylar and McBride, 1982; Mench *et al.*, 1998; Singh and Oste, 2001; Bes and Mench, 2008). The application of lime in acid soil decreased the soluble fraction and plant uptake of Ni, Cd, Zn and Cu to crops as well as increasing crop yield (Brallier *et al.*, 1996; Krebs *et al.*, 1998; Singh and Oste, 2001). The addition of alkaline materials in a highly Cu-contaminated soil can improved the plant growth and decreased the Cu concentration in both soil and plants (Fessenden and Sutherland, 1979; Bes and Mench, 2008). The combination of $\text{Ca (H}_2\text{PO}_4)_2$ and CaCO_3 in a multi-metal contaminated site reduced the toxicity and leaching extractable concentrations of Cd, Cu, Pb, Ni and Zn by more than 96% for Cd, Cu, Pb, Zn and Ni (Wang *et al.*, 2001). Phosphogypsum can improve soil properties such as pH, EC, CEC, exchangeable

Ca, Mg, and metal availability to plant, and increase the crop yield (Alva and Sumner, 1990).

Phosphate compounds and associated materials such as phosphoric acid, phosphate rocks, synthesized apatites have been successfully applied to stabilise the mobility of Pb, Cd, Zn and Cu in contaminated soils, sediments and solid wastes, reducing their bioavailability for plant uptake and thus their transport in soils and subsequent groundwater contamination (Bolan *et al.*, 2003; Liu and Zhao, 2007). Phosphate minerals have the potential to sorb and /or coprecipitate trace metals (Barrow, 1987; Ma *et al.*, 1993; Pierzynski and Schwab, 1993; Xu *et al.*, 1994; Ma, 1996; Mench *et al.*, 1998). The use of hydroxyapatite (HA) as a soil additive for the *in situ* remediation of metals (Zn, Pb, Cu, and Cd) in contaminated soils resulted in a decreased of the exchangeable metal contents in soil, increased plant growth and decreased the concentrations of toxic metals in the plant leaves (Boisson *et al.*, 1999a,b). When iron phosphate (vivianite) was used as *in situ* immobilisation of copper contaminated soils to reduce the Cu availability in soils, precipitation and adsorption processes were probably responsible for the decrease of Cu availability in soils (Liu and Zhao 2007).

Slag, which consists of calcium oxide, aluminium oxide, and other metal oxides, is an alkaline by-product of metallurgical processes or a residue of incineration processes. It has been used as a soil additive to remove various metals contaminated soil by precipitation and adsorption on the surface of metal oxide. The mechanism of copper removal using slag is precipitation with hydroxide dissolved from slag rather than adsorption on slag surface (Kim *et al.*, 2008). Blast-furnace slag is an effective sorbent for Cu, Zn Ni and Pb ions in a wide range of ion concentrations and pH values (Dimitrova, 1996; Dimitrova and Mehandjiev, 1998). The application of blast furnace slag to correct soil acidity promotes maximum root growth in depth, higher shoot dry matter and grain yield (Carvalho-Pupatto *et al.*, 2004). Calcium silicate slag can reduce the soil acidity and increased the available Ca, Mg, Si and P content (Besga *et al.*, 1996; Barbosa Filho *et al.*, 2004), whereas exchangeable Al, Mn, Cu and Zn decreased (Besga *et al.*, 1996). The application of slag addition rate in tea garden and rice field soils

increased soil pH, plant shoot dry yield and P and Mn uptake, while the Fe and K uptake increased in the rice field and K uptake decreased in the tea garden soil whereas Fe uptake was not changed (Ali and Shahram, 2007). Thomas phosphate basic slag (TBS) was used as an amendment in several contaminated soils and did not increase the plant biomass production but decreased the mobility and bioavailability of Cd, Zn and Pb (Mench *et al.*, 1994a,b). While the combination of BS and steel shots were more effective in reducing Zn and Cd mobility than when used separately in contaminated soils (Mench *et al.*, 1998). The incorporation of Thomas basic slag into an excessively Cu contaminated topsoil from a wood treatment facility increased the soil pH, shoot and root biomass, and foliar Ca concentration whereas foliar Cu concentration in plant decreased (Bes and Mench, 2008). The application of steel abrasive (SA) or oxygen scarfing granulate (OSG) to stabilise metals from CCA-contaminated soil can decrease the concentrations of As, Cr, Cu, and Zn in leachates and soil pore water (Lidelöw *et al.*, 2007).

In this study, BSP was used as a soil remediation technique to improve physical and chemical soil properties and also for the *in situ* immobilisation of copper and other trace elements in chromated copper arsenate (CCA) contaminated soil by increased the precipitation and adsorption on the surface metal oxide thus changing the availability and mobility of metals. The objectives of this study were :(1) to determine the influence of BSP addition into a strongly Cu-contaminated soil 630 mg/kg from a wood treatment facility by solutions of Cu sulphates and chromated copper arsenate to improve soil properties such as soil pH and EC, (2) to evaluate the effect of different BSP addition rates on the plant yield production and the foliar elemental concentrations of primary leaves, (3) to determine the potential of BSP to reduce copper and trace metals in CCA contaminated soil as well as to reduce the metal toxicity uptake by beans plants. Pot experiments were carried out on a 2-weeks period with dwarf beans (*Phaseolus vulgaris* L.). BSP was added into the pots (1 kg soil) with four different treatments in triplicates: 0 % (T1), 1 % (T2), 2 % (T3) and 4 % (T4) BSP/kg air-dried soil. An uncontaminated, sandy soil was used as a control (CTRL). After the two weeks period, soil and plant samples were collected to determine soil pH, EC soil, yield production and mineral analysis of plants. The mineralogy of the clay and silt fractions of soil treated with BSP

addition rate were determined by X – ray powder diffraction analysis (XRD) to identify the copper crystalline phases.

8.2. Material and Methods

8.2.1. Characteristics of the soil amendment

BSP has been used as a soil amendment to improve the physical and chemical soil properties and for *in situ* immobilisation of copper and trace elements in chromated copper arsenate (CCA) contaminated soil. In this study BSP containing mainly of calcium oxide, phosphorus oxide, silicon oxide, iron oxide, and other metal oxides. They were determined by using an atomic absorption spectrophotometer. Arsenic (As) was analysed by GF-AAS according to norm NF EN ISO 15586 (T90-119) after digestion with regal water (NF EN 13346), other trace elements were analysis by ICP-AES according to norm NF EN ISO 11885 after mineralisation (total digestion NFX31-147). The pH and electrical conductivity (EC) for BSP were measured in 1:1 BSP: water suspension by using pH meter and glass electrode EC respectively. The chemical characteristics of BSP are shown in Table 8.1.

Table 8. 1: Chemical characteristics of BSP

pH 1:1	11.65
EC mS/cm	2.15
Al₂O₃ %	5.56
CaO %	30.71
Fe₂O₃ %	21.4
K₂O %	0.53
MgO %	9.55
MnO %	2.53
P₂O₅ %	14
SiO₂ %	14.63
TiO₂ %	1.09
As mg/kg	<5
Cr mg/kg	511
Co mg/kg	<5
Ni mg/kg	<10
Cu mg/kg	<5
Zn mg/kg	24
Pb mg/kg	<20
Mn %	1.13

8.2.2. Pot experiment

The top layer of P7 (0-25 cm) of a Cu contaminated soil (630 mg/kg) originating mainly from Cu sulphate and in a lesser extent from standard CCA type C was sampled. BSP treatments were applied to improve soil properties and stabilize copper and trace elements in the contaminated soil. Four soil treatments (1 kg air-dried weight) were prepared and mixing with 0 %, 1 %, 2 % and 4 % of BSP addition rate (Table 8.2). Three replicates of each treatment were homogenised by rotation in 2-L plastic flasks, transferred into 1.3-L plastic pots. The control soil (CTRL) was treated in the same way. After incorporation of the BSP into the soil, the moisture content was raised to 70 % of water holding capacity (WHC, 10% of soil air-dried weight) by manual irrigation with distilled water and the soil was allowed to react for four weeks at 20°C before seeds were sown. Four dwarf beans (*Phaseolus vulgaris* L. cv vroege Limburgs) were sown in all pots just below the soil surface. Plants were cultivated in the laboratory under controlled environmental conditions: illumination 12 h light/12 h darkness regime, intensity $150 \mu\text{mol m}^{-2} \text{s}^{-1}$, temperature 25°C/22°C, and 50% relative humidity. Pots were arranged in a fully randomised block design on a bench and watered daily with deionised water (at 50% WHC) without loss from drainage. The plant growth was monitored on a daily basis using an index based on plant development steps for two weeks and then plants were harvested.

Several biometrical parameters, *i.e.* fresh weight (FW) of roots, shoots, and primary leaves were measured. Plant parts were washed with deionised water (2 times) and distilled water, oven dried at 70 °C, and weighted to determine the DW biomass production. Plant samples (0.5 g) were wet digested in 5 mL 14M HNO₃, 2 mL H₂O₂ and 1 mL distilled water at 180°C in PFA (perfluoroalkoxy copolymer resin) tubes under microwaves (MarXpress, CEM). The acid digested plants; then the solution was filtered through ash free paper. Mineral composition in digests plants was determined by ICP-AES (Ultima, Jobin Yvon Horiba, Longjumeau, France). The soil samples were taken from all pots experiment to measure the soil pH and the EC in suspension soil: water in the ratio 1:1 using a glass electrode pH meter and electrical conductivity respectively (Jackson, 1967). Clay and silt fractions of soil mixed with BSP were

separated by pipette methods (Richards, 1954; Jackson, 1969). They were determined by X – ray powder diffraction analysis (XRD), performed on a PANalytical Xpert MPD diffractometer using Cu K α radiation of 40Kv and 40 mA with the range 2 θ secondary monochromator and counting time of one hour.

Table 8. 2: Basic slag phosphate (BSP) added to the soil treatments

Treatments	Addition
T1 (0%)	Untreated soil
T2 (1%)	10 g BSP kg ⁻¹ soil
T3 (2%)	20 g BSP kg ⁻¹ soil
T4 (4%)	40 g BSP kg ⁻¹ soil
CTRL	Control soil

8.2.3 Statistical analysis

The soil and plant samples data collected from the pots experiment were tested by statistical analysis (ANOVA, Kruskal-Wallis and Tukey test) with SAS software version 9.1 to evaluate soil properties (soil pH and EC soil), plant yield (root and shoot yield), elemental concentrations in primary leaves and the total element amount in primary leaves [$\mu\text{g plant}^{-1}$], so-called here elemental accumulation which calculated based on the foliar element concentration ($\mu\text{g kg}^{-1}$ DW) and leaf biomass production ($\mu\text{g DW plant}^{-1}$) of plants. All analytical determinations were performed in triplicate.

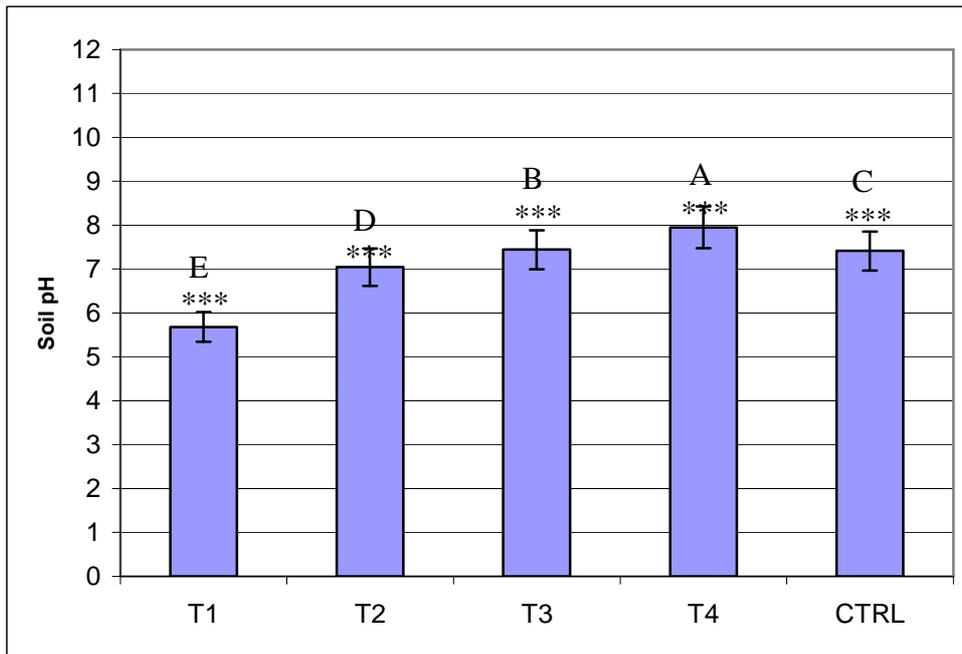
8.3. Results and Discussion

8.3.1. Effect of BSP on soil properties

The applications of the addition rate of BSP in copper and trace elements contaminated soil from CCA significantly increased the soil pH and EC soil. In fact the soil pH increased from 5.68 in the untreated contaminated soil (T1) to 7.04, 7.44 and 7.95 in the T2 (1%), T3 (2%), and T4 (4%) treated soils respectively. This results indicated that an increase in the soil pH in all treatments of BSP and the highest values of soil pH occurs for the T3, and T4 treatments compared with the control soil (7.41) (Figure 8.1). BSP also influences the EC soil which increased from 0.15 mS cm⁻¹ (T1)

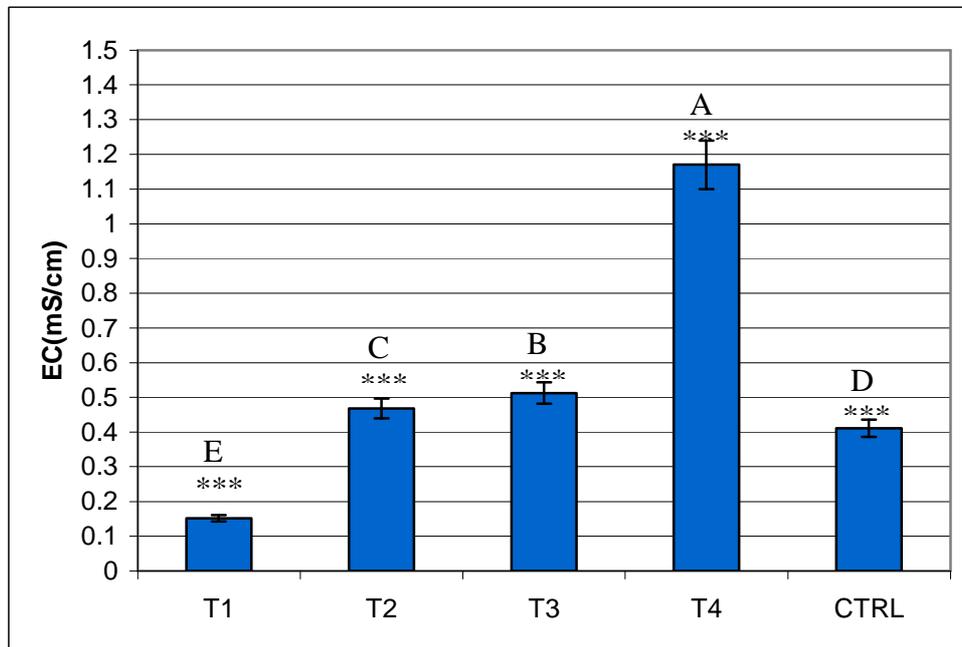
to 0.47 mS cm^{-1} , 0.51 mS cm^{-1} and 1.17 mS cm^{-1} for the T2, T3, and T4 treatments respectively. Consequently, EC soil was increased in the T2, T3 and T4 treatments compared to the control soil (0.41 mS cm^{-1}) (Figure 8.2).

These increases in soil pH and EC soil in all amended soils were caused by the application of BSP. This is possibly due to the compounds of BSP and in particular the Ca content in this alkaline product. Other studies showed that the addition of lime to acid soil increased the soil pH and EC soil. Su and Evans (1996) reported that the EC soil increased when the mixing of acid soil with lime. The application of lime in heavy metals contaminated soil increased the soil pH with a corresponding increase in the net negative charge of variably charged soil colloids such as clays and organic matter (Gray *et al.*, 2006). Moreover the amelioration of acid soils with the application of soil amendments such as alkaline by-products can improve the soil pH and EC (Alva and Sumner, 1990). The application of basic slag in acid soils increased the soil pH with and without NPK fertilization (Pinto *et al.*, 1995; Besga *et al.*, 1996; Forghani *et al.*, 2006). The incorporation of Thomas basic slag into acid soil contaminated by copper from a wood treatment facility can increase the soil pH (Bes and Mench, 2008). Our results confirmed that the application of BSP addition rates in acid soil is able to ameliorate the soil properties.



Values are mean \pm standard errors (n=3). Different letters on bar graphs indicate a significant difference; p ($0.001 < *** < 0.0001$).

Figure 8.1: Effects of BSP on the soil pH



Values are mean \pm standard errors (n=3). Different letters on bar graphs indicate a significant difference; p ($0.001 < *** < 0.0001$).

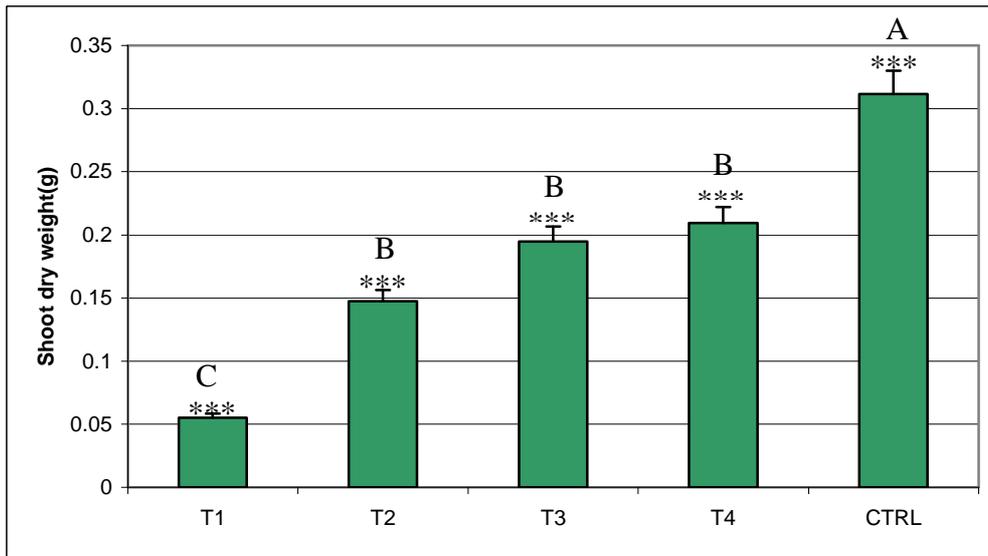
Figure 8.2: Effects of BSP on the soil EC

8.3.2. Plant analysis

8.3.2.1. Effect of BSP on shoot biomass

Data of shoot yields DW are given in Figure 8.3. All addition rates of BSP to copper contaminated soil resulted in increasing the shoot yield of beans primary leaves. The highest value of the shoot yield occurs in the control soil (CTRL) and the lowest value of the shoot yield has in the untreated contaminated soil (T1). The results of variance plant analysis indicated that the beans plants were not able to grow on the excessive copper contaminated soil 630 Cu mg/Kg. This confirmed that this soil negatively impacted beans plants (Bes and Mench, 2008). Shoot yield numerically positive for all amended soils. The best growth responses were obtained after the application of BSP at 2% and 4% addition rates. Therefore treatments T3 and T4 gave the highest shoot yields, *i.e.* 3.4 and 4.2 times respectively compared with the untreated contaminated soil (T1), while the T2 treatment gave an intermediary value. These values for the T3 and T4 treatment corresponded to 61 % and 67 % compared with CTRL treatment. The increases in shoot yields in T3 and T4 treatments compared with the T2 treatment were related to the increase of the BSP addition rate. This possible is caused by the application of BSP addition rate which had a positive effect on the chemical soil properties such as soil pH and EC.

These results agree well with those obtained by (Alva and Sumner, 1990; Barbosa Filho *et al.*, 2004; Carvalho-Pupatto *et al.*, 2004; Bes and Mench, 2008). They found that the addition of slag to correct soil acidity promotes higher shoot dry matter and grain yield. The best soil pH for growth beans plants ranges from 6.0 to 7.5 (Gardener's Network, 2009). Omafra, (2008) reported that most plants are suitable growth when the soil conductivity ranges from 0 to 0.45 mS cm⁻¹ ; however when the soil conductivity ranges from 0.46 to 0.7 mS cm⁻¹ , the plant growth may decrease and cause a slight to severe damage to salt sensitive plants. Our results indicate that when the soil pH was 7.95 and EC soil was 1.17 mS cm⁻¹ , the addition of 4% BSP increased more the shoot yield than a 2% BSP addition rate.



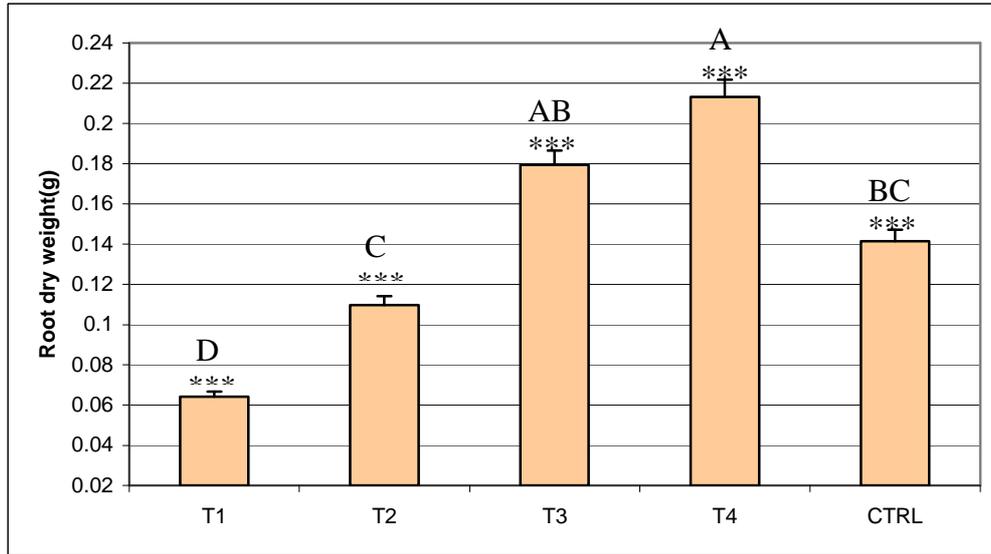
Values are mean \pm standard errors (n=3). Different letters on bar graphs indicate a significant difference, p ($0.001 < *** < 0.0001$).

Figure 8.3: Effect of BSP on the shoot yield of beans (g DW plant⁻¹) for each treatment

8.3.2.2. Effect of BSP on root biomass

For the root yield DW, the results indicate that the application of BSP increased the root yield DW in all amended soils compared with the untreated contaminated soil (T1) and CTRL soils. Results of the root yields DW are given in Figure 8.4. The treatment T4 has the highest value of the root yield DW whereas the lowest value of the root yield DW occurs in the T1 treatment. The T2 treatment gave an intermediary value. Root yield was significantly higher for the T3 and T4 treatments than for the untreated (T1) and control soils (CTRL). The root yield increased 3 and 3.5 times in the T3 and T4 treatments respectively compared with the untreated soil (T1), and they increased 1.3 and 1.5 times respectively compared with the CTRL treatment. These results are in good agreement with (Carvalho-Pupatto *et al.*, 2004; Bes and Mench, 2008). They reported that the application of slag to correct soil acidity increased the root biomass. In contrast, Thomas phosphate basic slag (TBS) was used as an amendment in several

contaminated soils and did not increase the plant biomass production but decreased the mobility and bioavailability of Cd, Zn and Pb (Mench *et al.*, 1994a,b).



Values are mean \pm standard errors (n=3). Different letters on bar graphs indicate a significant difference, p ($0.001 < *** < 0.0001$).

Figure 8.4: Effect of BSP on the root yield of beans (g DW plant⁻¹) for each treatment

8.3.2.3. Effect of BSP on concentrations and accumulations of elements in plants

The effects of BSP addition rate in the CCA contaminated soil on the foliar element concentrations and foliar element accumulations of beans plant are shown in Tables 8.3 and 8.4 respectively.

Aluminium

The application of BSP significantly decreased the foliar Al concentration in all treatments compared with the untreated contaminated soil (T1). Foliar Al concentration

Table 8. 3: Elemental concentrations in the primary leaves of beans

Treatments	T1	T2	T3	T4	CTRL
Al mg/kg	0.05 a ± 0.01**	0.03 b ± 0.01**	0.03 b ± 0.01**	0.02 b ± 0.00**	0.02 b ± 0.00**
Mg g/kg	3.02 a ± 0.20***	1.77 c ± 0.02***	1.72 c ± 0.11***	1.49 c ± 0.10***	2.47 b ± 0.39***
Ca g/kg	2.54 b ± 1.15***	16.31 a ± 0.92***	20.12 a ± 1.58***	19.25 a ± 3.23***	21.27 a ± 3.33***
P g/kg	5.21 a ± 0.19***	3.55 b ± 0.04***	2.71 c ± 0.59***	2.33 c ± 0.50***	5.23 a ± 0.12***
K g/kg	21.91 a ± 1.27***	13.03 d ± 1.05***	15.63 cd ± 1.5***	17.36 b ± 1.59***	19.02 b ± 1.74***
Cr mg/kg	6.02 a ± 2.01***	0.72 b ± 0.41***	0.79 b ± 0.19***	0.86 b ± 0.71***	0.42 b ± 0.18***
Cu mg/kg	35.73 a ± 1.31***	19.47 b ± 1.15***	17.41 c ± 1.01***	13.96 d ± 0.74***	6.23 e ± 0.67***
Zn mg/kg	10.18 a ± 6.77*	6.84 ab ± 0.31*	4.71 ab ± 1.31*	2.9 b ± 1.47*	10.91 a ± 0.65*

In a column mean values (± standard deviations) followed by the same letter do not differ significantly P (0.05<*<0.01), (0.01<***<0.001), P(0.001<****<0.0001) and non significant NS (p>0.05).

Table 8. 4: Elemental accumulation in the primary leaves of beans (µg plant⁻¹)

Treatments	T1	T2	T3	T4	CTRL
Al	2.61 a ±0.10 NS	3.79 a ±1.27 NS	5.26 a ±2.70 NS	4.09 a ±0.71 NS	5.94 a ±0.40 NS
Mg	166 b ±34***	262 b ±16***	336 b ±30***	311 b ±25***	774 a ±34 ***
Ca	150 c ±103***	2403 b ±142***	3934 b ±622***	4065 b ±1060***	6662 a ±1615***
P	289 b ±77***	524 b ±44***	529 b ±48***	480 b ±62***	1632 a ±281***
K	1219 c ±351***	1925 c ±245***	3055 b ±474***	3629 b ±509.83***	5874 a ±703.66***
Cr	0.32 a ±0.07 NS	0.11 a ±0.05 NS	0.15 a ±0.04 NS	0.19 a ±0.17 NS	0.13 a ±0.05 NS
Cu	1.96 b ±0.38***	2.86 a ±0.07***	3.41 a ±0.44***	2.91 a ±0.34***	1.92 b ±0.22***
Zn	0.65 b ±0.55***	1.01 b ±0.11***	0.91 b ±0.18***	0.58 b ±0.25***	3.39 a ±0.54***

In a column (mean values ± standard deviations) followed by the same letter do not differ significantly P (0.001<***<0.0001) and non significant NS (p>0.05).

significantly decreased in plants from all BSP-amended soils, especially in level BSP 4% which was similar compared with the control (CTRL). It can be noticed that the decrease in foliar Al concentration is possibly due to the influence of the liming agent in BSP, increasing pH and EC soil and competing with Ca for root uptake, and increase in primary leaf biomass. Other studies showed that the addition of lime on the soil surface significantly increased the soil pH and decreased Al toxicity (Brown *et al.*, 2008). In most cases the addition of phosphorus to acid soils results in the precipitation of Al (Wright, 1937). Calcium silicate slag can be reduced the soil acidity and decreased exchangeable soil Al (Besga *et al.*, 1996). The foliar Al accumulation ranges from 2.61 to 5.94 $\mu\text{g plant}^{-1}$. The lowest value occurs for the T1 treatment and the highest value has in CTRL plants. BSP addition rates significantly increased the foliar Al accumulation in all amended soil compared to the untreated contaminated soil (T1).

Magnesium

The foliar Mg concentration decreased in all amended soil compared with the untreated contaminated soil (T1) and control soil (CTRL). The foliar Mg concentration varied between 1.49 to 3.02 g/kg DW. The lowest value was for the T4 treatment and the highest value occurred for the CTRL plants. In general, Mg concentrations in plants range between 1.5 and 3.5 g kg⁻¹ DW (Marschner, 1995). It can be noticed the increases in the leaf biomass for the T3 and T4 treatments reduced the foliar Mg concentration. This is possibly due to the increases in foliar Ca concentrations. The foliar Mg accumulation was higher in the CTRL plant than in the untreated contaminated soil (T1) and all treatments BSP-amended soil. In addition, all BSP addition rates significantly increased the foliar Mg accumulation compared with the untreated contaminated soil (T1).

Calcium

The foliar Ca concentration significantly increased in all amended soil compared with the untreated contaminated soil (T1). The low foliar Ca concentration vs. foliar Cu concentration can limit beans growth. Similarly the incorporation of a Thomas basic slag into an excessively Cu-contaminated topsoil from a wood treatment facility can increase the foliar Ca concentration and decrease the foliar Cu concentration in plant

(Bes and Mench, 2008). The foliar Ca concentration ranges between 2.54 to 21.27 g/kg DW with the lowest and highest values for T1 and CTRL plants respectively. Generally the Ca concentration in plants normally ranges between 1 to 50 g/kg DW (Marschner, 1995) and the Ca concentration in the primary leaves of dwarf beans grown on uncontaminated soils varies between 6.4 to 29 g/kg DW (Mench *et al.*, 1996). The highest concentrations of Ca in the primary leaves of beans plants occurs for the addition of BSP 2 % (T3) and 4% (T4) with an increase of 7.92 and 7.57 times respectively compared with the untreated contaminated soil (T1), while the addition of BSP 1% (T2) gave an intermediary value. A slightly decrease occurs for the T4 treatment compared with the T3 treatment, probably due to the fact that the roots plants were negatively impacted by the high value of EC soil. The foliar Ca accumulation also significantly increased in all amended soil compared with the untreated contaminated soil (T1). The highest Ca accumulation in the primary leaves of beans plants has in the CTRL plant and the lowest Ca accumulation occurs in T1 treatment. Generally, the foliar Ca accumulation was classed as: T1 < T2 < T3, T4 < CTRL.

Phosphorus

In acidic soils the phosphorus availability of Thomas slag is similar to that of other water soluble phosphorus fertilizer (Sinaj *et al.*, 1994). Thomas slag was composed of a P, Si and Ca ; silicato-calcium phosphate was the prevailing form of P in the cells and a high Fe, Ca and Mn content in the walls (Sinaj *et al.*, 1994). The foliar P concentration decreased with the application of BSP in all treated soils compared to the untreated contaminated soil (T1) and control soil (CTRL). The foliar P concentration varies from 2.33 to 5.33 g/kg DW. The lowest value was for the T4 treatment and the highest values occur for the CTRL plants. The foliar P concentrations ranked in the following order: CTRL, T1 < T2 < T3, T4. It can be noticed that the reduced in P concentrations after applied the BSP in all treatments soil are probably directly related to increasing soil pH and foliar Ca concentrations. The P concentration in the primary leaves of dwarf beans grown on uncontaminated soils ranged between 1 to 6 g/kg DW (Mench *et al.*, 1996). The highest P concentration in CTRL plants was probably due to the increased decomposition of organic matter in soil control. On the other hand, the increased P concentration in the untreated contaminated soil (T1) may be related to the

low soil pH and low biomass production. It can be assumed because the BSP composition, particularly its high liming agent, the phosphates are not available in the soil solution for the root uptake due to the adsorption or precipitation with cations such as Ca, Fe and Al. Pinto *et al.* (1995) reported that the addition of slag in acid soil increases exchangeable soil Ca and Ca concentration in soil solution, therefore, available soil phosphate contents exhibit a general decrease due to the adsorption and displacement of phosphate by hydroxyl ions. The foliar P accumulation was higher in the CTRL than in T1 and all treatments BSP addition rate. In general, all BSP addition rates significantly increase the foliar P accumulation compared to the untreated contaminated soil (T1).

Potassium

The foliar K concentration decreased with the application of BSP in all amended soils compared to the untreated contaminated (T1) and control soils (CTRL). The foliar K concentration varies between 13.03 to 21.91 g/kg DW with lowest and highest concentration for T2 and untreated contaminated soil (T1) treatments respectively. The foliar K concentrations ranked in the following order: T1, CTRL < T4 < T3 < T2. It can be noticed that the foliar K concentrations were 1.3 and 1.1 times lower in T4 plants than in T1 and CTRL plants, respectively. However, the foliar K accumulation increased with the application of BSP in all treated soils compared with the untreated contaminated soil (T1), but a decrease in foliar K accumulation occurs after the application of BSP in all treated soils compared with the control plants (CTRL). Pinto *et al.* (1995) suggested that the application of slag in acid soil decreased soil K content as a result of the lime-induced increase in CEC resulting in the decrease in K content related to yield increase when slag was applied. K uptake decreased in a tea garden soil when the application slag addition rate (Ali and Shahram, 2007). Generally, the critical K concentration in some plants ranges between 20 to 50 g kg⁻¹ DW (Marschner, 1995), while in the primary leaves of dwarf beans grown on uncontaminated soils, the K concentration ranges between 13 to 22 g/kg DW (Mench *et al.*, 1996).

Copper

The foliar Cu concentration decreased with the application of BSP for all treated soils compared with the untreated contaminated soil (T1). The foliar Cu concentration varied from 6.23 to 35.73 mg kg⁻¹ DW with lowest and highest values for CTRL and T1 treatments respectively. Generally, the foliar Cu concentrations ranked in the following order: T1 < T2 < T3 < T4 < CTRL. The lowest concentrations of Cu in the primary leaves of beans plants occurred in the (T3) and (T4) treatments with a decrease of 2 and 2.5 times respectively compared with the untreated contaminated soil (T1). The critical Cu concentration for beans leaves *i.e.* 15-30 mg Cu kg⁻¹ DW (MacNicol and Beckett, 1985). This indicated that the beans plants were not able to grow on the excessive copper contaminated soil (630 Cu mg/Kg) caused by the phytotoxic effect in this soil. Kim *et al.* (2008) suggested that the mechanism of copper removal using slag is precipitation with hydroxide dissolved from slag rather than adsorption on slag surface. However Liu and Zhao, (2007) reported that the application of iron phosphate decreased the Cu availability in copper contaminated soils by precipitation and adsorption processes. It can be noticed that the levels 2% and 4% BSP incorporation into copper contaminated soil promoted best beans growth with the highest Ca concentrations and lowest foliar Cu concentration. The foliar Cu accumulation increased with the application of BSP in all treated soils compared to the untreated contaminated soil (T1) and the control plants (CTRL). The foliar Cu accumulation varied from 1.92 to 3.41 µg plant⁻¹ with lowest and highest values for CTRL and T3 treatments respectively. The increase in foliar Ca accumulation in all treatments BSP addition rate may contribute to a better pectin methylesterase functioning (Micheli, 2001), and also promote the Cu sorption by various ligands (Pilon *et al.*, 2006). These results agree well with those obtained by (Brallier *et al.*, 1996; Krebs *et al.*, 1998; Singh and Oste, 2001; Bes and Mench 2008). They found that the addition of alkaline materials in acid soil can decrease Cu concentration in soil and plant and increased crop yield.

Chromium

The foliar Cr concentration decreased with the application of BSP in all treated soils compared to the untreated contaminated soil (T1). The foliar Cr concentration varied from 0.42 to 6.02 mg kg⁻¹ DW with the lowest and highest values for CTRL and

T1 treatments respectively. Generally, the foliar Cr concentrations ranked in the following order: T1 < T4 < T3 < T2 < CTRL. The Cr concentration in the primary leaves of dwarf beans grown on uncontaminated soils was reported to range between 0.13 - 1.7 mg/kg DW (Mench *et al.*, 1996). The reduction of Cr in soils is accelerated by the presence of organic matter and divalent iron (Kumpiene *et al.*, 2008). The lowest value of Cr concentration in CTRL plants may be due to the presence of organic matter in the control soil. Kumpiene *et al.* (2006) reported that the application of zerovalent iron in a chromated copper arsenate (CCA) contaminated soil reduced Cr concentration in plant shoots by 95%. The decreased of Cr contaminated soil may be causing by presence iron oxide which reduced Cr (VI) to Cr,Fe(OH) precipitation (Fendorf, 1995). However, the foliar Cr accumulation was higher in the T1 treatment compared with all amended soils. Thus, it can be noticed that all BSP addition rates significantly decreased the foliar Cr accumulation compared to the untreated contaminated soil (T1).

Zinc

The foliar Zn concentration significantly decreased with the application of BSP in all treated soils compared to the untreated contaminated soil (T1) and control soil (CTRL). The foliar Zn concentration ranges between 2.9 to 10.91 g/kg DW. The lowest value was for the T4 treatment and the highest value occur for the CTRL plants. Mench *et al.* (2000) reported that an increase in soil pH decreases Zn availability in the soil solution while changes in the leaf yield affect the foliar Zn concentration causing a decreased foliar Zn concentration. The best lowest concentrations of Zn in the primary leaves of beans plants occurs when the addition of BSP 4% (T4) with an decreases were 3.5 and 3.8 times compared with the untreated contaminated soil (T1) and control soil (CTRL) respectively. The application of Thomas phosphate basic slag (TBS) in contaminated soils can decrease the mobility and bioavailability of Zn (Mench *et al.*, 1994a,b). While the combination of basic slag and steel shots were more effective in reducing Zn mobility than when used separately in contaminated soils (Mench *et al.*, 1998). The foliar Zn accumulation increased with the application of BSP in all treatments with an exception decreased when the addition 4% BSP compared with the untreated contaminated soil (T1). However a decrease of the foliar Zn accumulation occurred in all amended soil compared with the control plants (CTRL).

8.4. Mineralogical form of copper in the particle-size fractions of the soil

Soil stabilization with the addition of BSP to reduce the metal mobility and bioavailability of copper contaminated soil was investigated by XRD. Analysis was performed for the silt and clay fractions BSP-soil. The diffraction patterns and the principal crystalline metal-containing phases from silt and clay fractions of soil treatments are presented in Figures 8.5 and 8.6 and Tables 8.5 and 8.6.

8.4.1. Copper in the particle-size fractions of the contaminated soil

In our study, the results of the XRD analysis of the silt fraction of the contaminated soil (T1) indicate that the copper was detected in the form of cuprite (Cu_2O), arsenic copper (AsCu_9), and plancheite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$). While in the clay fraction in the contaminated soil (T1) shows that copper and other trace elements such as As and Cr were observed in the form of cuprite (Cu_2O), arsenic copper (AsCu_9), malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$), magnesium chromium oxide (MgCr_2O_4) and chromium arsenate (CrAsO_4). In general copper is distinctly more soluble under oxidised condition than under reduced in the pH rang 5.4-6.5 (Bhattacharya *et al.*, 2002). Thus, an increase in the pH soil caused Cu to be strongly adsorbed at the colloidal surfaces by decreasing the exchangeable form, which is the highly mobile form (Lindsay, 1979). According to changes the soil pH, alkaline materials may be effective treatment chemicals to induce metal hydrolysis reactions and/or co-precipitation with carbonates, acting as a precipitating agent for metals in the soil solution acid (Tylar and McBride 1982; Mench *et al.*, 1998; Singh and Oste, 2001; Bes and Mench, 2008). Our results confirm that BSP increased the soil pH in relation with the addition rate, from 5.7 in the untreated contaminated soil (T1) to 7.0, 7.4 and 7.9 in the amended soils at 1%, 2% and 4 % BSP addition rate respectively. The increase in soil pH in all amended soils is possibly due to the composition of BSP in particular the Ca content in this alkaline product. Liming increases the pH (increase of surface charge) and enhances sorption of heavy metals by reducing the solubility by adsorption or precipitation in the soil (Singh and Oste, 2001).

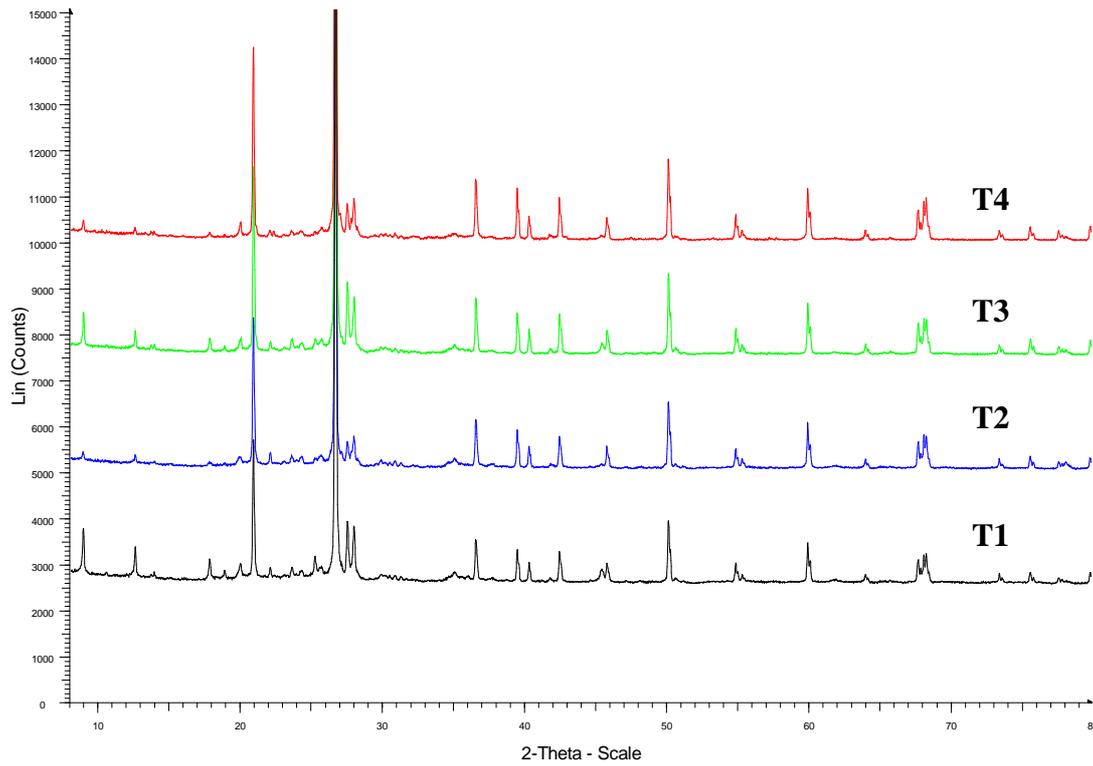


Figure 8.5: XRD diffraction patterns of the silt fractions for each treatment

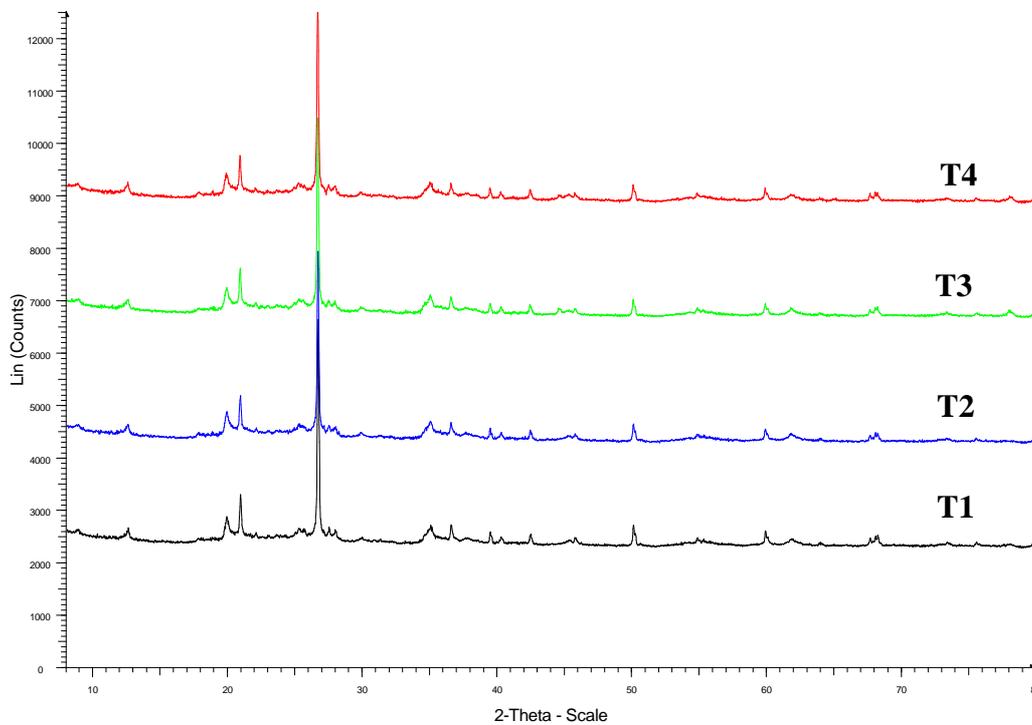


Figure 8.6: XRD diffraction patterns of the clay fractions for each treatment

Table 8. 5: Forms of metals in the silt fractions for each treatment

Treatments BSP	Mineral compound	Formula
T1 (0%)	Cuprite Arsenic copper Plancheite Silicon oxide	Cu_2O $AsCu_9$ $3CuSiO_3 \cdot H_2O$ SiO_2
T2 (1%)	Cuprite Azurite Arsenic copper Plancheite Silicon oxide Arsenic oxide Copper hydrogen nitrogen phosphate chloride Hentschelite Copper oxide phosphate Barium calcium copper thallium oxide Aluminum phosphate silicate	Cu_2O $Cu_3(CO_3)_2(OH)_2$ $AsCu_9$ $3CuSiO_3 \cdot H_2O$ SiO_2 As_2O_3 $Cu_{4.72}H_{3.2}(P_{12}N_{18}O_6)Cl_2$ $CuFe^{3+}_2(PO_4)_2(OH)_2$ $Cu_4O(PO_4)$ $TlBa_2Ca_3Cu_4O$ $Al_2O_3 \cdot 0.90P_2O_5 \cdot 0.22 SiO_2$
T3 (2%)	Cuprite Arsenic copper Plancheite Silicon oxide Copper hydrogen nitrogen phosphate chloride Hentschelite Copper oxide phosphate Dachiardite Aluminum phosphate silicate Calcium phosphate Sodium copper oxide hydroxide	Cu_2O $AsCu_9$ $3CuSiO_3 \cdot H_2O$ SiO_2 $Cu_{4.72}H_{3.2}(P_{12}N_{18}O_6)Cl_2$ $CuFe^{3+}_2(PO_4)_2(OH)_2$ $Cu_4O(PO_4)$ $(Ca,Na_2,K_2)5Al_{10}Si_{38}O_{96.25}(H_2O)$ $Al_2O_3 \cdot 0.90P_2O_5 \cdot 0.22 SiO_2$ $Ca_2P_2O_5$ $Na_5(CuO_2)(OH)_2$
T4 (4%)	Cuprite Arsenic copper plancheite Silicon oxide Copper hydrogen nitrogen phosphate chloride Hentschelite Copper oxide phosphate Dachiardite Aluminum phosphate silicate Calcium phosphate Portalandite Arsenic oxide	Cu_2O $AsCu_9$ $3CuSiO_3 \cdot H_2O$ SiO_2 $Cu_{4.72}H_{3.2}(P_{12}N_{18}O_6)Cl_2$ $CuFe^{3+}_2(PO_4)_2(OH)_2$ $Cu_4O(PO_4)$ $(Ca,Na_2,K_2)5Al_{10}Si_{38}O_{96.25}(H_2O)$ $Al_2O_3 \cdot 0.90P_2O_5 \cdot 0.22 SiO_2$ $Ca_2P_2O_5$ $Ca(OH)_2$ As_2O_3

Table 8. 6: Forms of metals in the clay fractions for each treatment

Treatments BSP	Mineral compound	Formula
T1 (0%)	Cuprite Malachite Arsenic copper Silicon oxide Magnesium chromium oxide Chromium arsenate	Cu_2O $Cu_2(CO_3)(OH)_2$ $AsCu_9$ SiO_2 $MgCr_2O_4$ $CrAsO_4$
T2 (1%)	Cuprite Azurite Plancheteite Malachite Silicon oxide Hentschelite Copper oxide phosphate Copper nikle phosphate Calcium copper hydrogen phosphate Calcium copper titanium oxide Calcium copper germanium oxide	Cu_2O $Cu_3(CO_3)_2(OH)_2$ $3CuSiO_3.H_2O$ $Cu_2(CO_3)(OH)_2$ SiO_2 $CuFe^{3+}_2(PO_4)_2(OH)_2$ $Cu_4O(PO_4)$ $Cu Ni_2(PO_4)_2$ $Ca Cu HPO_4$ $CaCu_3Ti_4O_{12}$ $CaCu_3(Ge_4)O_{12}$
T3 (2%)	Cuprite Azurite Plancheteite Malachite Silicon oxide Hentschelite Pseudomalachite Copper oxide phosphate Calcium copper germanium oxide Copper hydrogen nitrogen phosphate chloride Sodium copper oxide hydroxide	Cu_2O $Cu_3(CO_3)_2(OH)_2$ $3CuSiO_3.H_2O$ $Cu_2(CO_3)(OH)_2$ SiO_2 $CuFe^{3+}_2(PO_4)_2(OH)_2$ $Cu_5(PO_4)_2(OH)_4$ $Cu_4O(PO_4)$ $CaCu_3(Ge_4)O_{12}$ $Cu_{4.72} H_{3.2} (P_{12}N_{18}O_6) Cl_2$ $Na_5(CuO_2)(OH)_2$
T4 (4%)	Cuprite Azurite Plancheteite Malachite Silicon oxide Hentschelite Pseudomalachite Copper oxide phosphate Copper hydrogen nitrogen phosphate chloride Sodium copper oxide hydroxide	Cu_2O $Cu_3(CO_3)_2(OH)_2$ $3CuSiO_3.H_2O$ $Cu_2(CO_3)(OH)_2$ SiO_2 $CuFe^{3+}_2(PO_4)_2(OH)_2$ $Cu_5(PO_4)_2(OH)_4$ $Cu_4O(PO_4)$ $Cu_{4.72} H_{3.2} (P_{12}N_{18}O_6) Cl_2$ $Na_5(CuO_2)(OH)_2$

8.4.2. Copper in the particle-size fractions of the BSP- soil

Stabilization of copper in the soil by clays, organic matter, carbonates, phosphates and Fe oxides amendments was reported with precipitation of Cu carbonates and oxy-hydroxides, ion exchange and the formation of ternary cation–anion complexes on the surface of Fe and Al oxy-hydroxides (Kumpiene *et al.*, 2008). Copper was strongly associated with organic matter and was homogeneously distributed on the clay fraction surface (Adamo *et al.*, 1996). Our study indicates that the application of BSP in the contaminated soil (T1) can reduce the copper mobility by adsorption or precipitation on the BSP surface. The addition of alkaline materials in a highly Cu-contaminated soil can be decreased Cu concentration in the soil (Bes and Mench, 2008). In addition the mechanism of copper removal using slag may be is precipitation with hydroxide dissolved from slag rather than adsorption on slag surface (Kim *et al.*, 2008).

Silt fractions

In the silt fraction, it seems that in all amended soils, copper was observed in the forms of cuprite (Cu_2O), arsenic copper (AsCu_9), in associated with silicate such as plancheite ($3\text{CuSiO}_3 \cdot \text{H}_2\text{O}$) and in associated in the form of complex precipitation with iron and phosphate such as copper hydrogen nitrogen phosphate chloride ($\text{Cu}_{4.72}\text{H}_{3.2}(\text{P}_{12}\text{N}_{18}\text{O}_6)\text{Cl}_2$), hentschelite ($\text{CuFe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2$) and copper oxide phosphate ($\text{Cu}_4\text{O}(\text{PO}_4)$). Only in addition of 1% BSP copper was detected in associated with carbonate and oxy-hydroxides in the form of azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$), and also in associated with calcium in the form of barium calcium copper thallium oxide $\text{TlBa}_2\text{Ca}_3\text{Cu}_4\text{O}$. The stabilization of trace elements contaminated soil by amended soil does not reduce the total content of contaminants but lower the amounts of mobile and bioavailability of the fractions (Kumpiene *et al.*, 2006).

Clay fractions

Soil clay mineralogy is influences chemical adsorption and coprecipitation, thereby affecting contaminant solubility and mobility (Hesterberg, 1998). In general, the soils having highest amounts of clay content showed the highest values for metal adsorption (Singh and Oste, 2001). Our study indicates that several phases were observed in the clay fractions compared with the silt fractions. Generally, it seems that

from all soil treatments BSP addition rate, copper was observed in the form of cuprite (Cu_2O), associated with silicate including plancheite ($3\text{CuSiO}_3\cdot\text{H}_2\text{O}$), associated with carbonate and oxy-hydroxides in the form of azurite ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$) and malachite ($\text{Cu}_2(\text{CO}_3)(\text{OH})_2$) and associated in the form complex with calcium, iron and phosphate including hentschelite ($\text{CuFe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2$) and copper oxide phosphate ($\text{Cu}_4\text{O}(\text{PO}_4)$). The presence of inorganic anions (carbonate, phosphate, sulphate) in the soil water can influence the soils ability to fix metals chemically. These anions can form relatively insoluble complexes with metal ions and cause metals to desorb and/or precipitate in their presence (Evanko and Dzombak, 1997).

Sorption of metal cations onto hydrous oxides generally increases sharply with pH (Evanko and Dzombak, 1997). For pH above 7, copper tend to precipitate in the form of carbonate and hydroxide (Gagnon, 1998). The mechanism of copper retention were precipitation of Cu carbonates and oxy-hydroxide, ion exchange and formation of ternary cation-anion (SO_4 , PO_4) complexes on the surface of Fe and Al oxy-hydroxides (Kumpiene *et al.*, 2008). Therefore, in the level of 1% BSP addition rate, copper was observed in association with calcium and phosphate in the form of copper nickel phosphate ($\text{Cu Ni}_2(\text{PO}_4)_2$), calcium copper hydrogen phosphate (Ca Cu HPO_4), calcium copper titanium oxide ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$). Calcium copper germanium oxide ($\text{CaCu}_3(\text{Ge}_4)\text{O}_{12}$) was only observed in the level of 1% and 2% BSP addition rate. In the level of 2% and 4% BSP addition rate copper was detected in the form complex in association with phosphate and sodium hydroxide such as copper hydrogen nitrogen phosphate chloride ($\text{Cu}_{4.72}\text{H}_{3.2}(\text{P}_{12}\text{N}_{18}\text{O}_6)\text{Cl}_2$), sodium copper oxide hydroxide ($\text{Na}_5(\text{CuO}_2)(\text{OH})_2$) and pseudomalachite ($\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$). Our results are in line with Kim *et al.* (2008). They found that the precipitation amount of copper was highly depending on pH and slag compounds. These results indicate that most of copper mobile was precipitated on the surface slag causing by the compound of BSP in particularly the high Ca and P contents which able to make of it a potential liming agent to sorb and precipitated metals in soil.

8.5. Conclusion

Remediation with BSP improved soil properties and reduce the trace elements mobility and bioavailability in soil and metal uptake by plants. BSP is an alkaline by-product in steel making process with potential properties to ameliorate physical and chemical soil properties and metal stabilization from chromated copper arsenate (CCA) contaminated soil. BSP was mixed at increasing addition rates (1%, 2% and 4%) in an acid sandy Cu-contaminated soil 630 mg/kg from a wood treatment facility with solutions of Cu sulphates and chromated copper arsenate. Analysed soil samples showed that the soil pH was increased from 5.68 in the untreated contaminated soil to 7.04, 7.42 and 7.95 in the 1%, 2% and 4 % BSP addition rate respectively. At the same time, BSP also influenced the soil EC which increased from 0.15 mS cm⁻¹ in the untreated soil to 0.47 mS cm⁻¹, 0.51 mS cm⁻¹ and 1.17 mS cm⁻¹ in the 1%, 2% and 4% BSP addition rate respectively. The pot experiment showed that the addition of BSP resulted in an increased in the root and shoot DW yield for all treatments compared with the untreated contaminated soil (T1). Foliar Al concentration decreased with an increased Al accumulation in plants from all BSP-amended soils compared with the untreated contaminated soil (T1). Foliar Ca concentration was enhanced for all treated soils with increased in Ca accumulation compared to the untreated contaminated soil (T1). The foliar Mg, K and P concentrations were not enhanced by the BSP addition into the Cu-contaminated soil. All addition rates of BSP-amended soil decreased foliar Cu concentration compared with the untreated contaminated soil (T1). The foliar Cr and Zn concentrations and accumulation was not increased with the application BSP into the soil. We conclude that the incorporation of 2% to 4% BSP into the copper contaminated soil can promoted highest root and shoot DW yields with the highest Ca concentrations and lowest foliar Cu concentration. The mineralogical form of copper and other trace elements in silt and clay fractions of contaminated soil (T1) were observed in the form of cuprite (Cu₂O), arsenic copper (AsCu₉), plancheite (Cu₂(CO₃)(OH)₂), malachite (Cu₂(CO₃)(OH)₂), magnesium chromium oxide (MgCr₂O₄) and chromium arsenate (CrAsO₄). The application of BSP addition rate in contaminated soil (T1) can reduce copper mobility by adsorption or precipitation on the BSP surface. Therefore, it seems that in all amended soil BSP, copper observed in association with silicate, carbonate and oxy-hydroxides and complex precipitation with calcium, sodium, iron and phosphate.

SUMMARY

New Technique for Soil Reclamation and Conservation: *In Situ* Stabilization of Trace Elements in Contaminated Soils

Soil contamination by trace elements is a widespread problem in many parts of the world. The accumulation of toxic metals in soil is mainly inherited from parent materials or inputs through human activities. In fact, one of the sources of soil contaminations is very important resulting from chemical widely used wood preservative industries in aquatic environments and storing the wood after treatment by chromated copper arsenate (CCA). Elements such as As, Cu, Cr, and Zn can be found in excess in contaminated soils at wood treatment facilities, especially when Cu sulphates and chromated copper arsenate (CCA) were used as a preservative against insects and fungi, which may result in soil phytotoxicity as well as toxic to plants, animals and humans. The mobility and exchangeable fractions of trace elements in soils are the most important associated to toxicity and bioavailability in contaminated soils. Therefore, it is very important to removal /uptake or reduces metals contaminated soils by the application of assisted natural remediation processes. Currently there are several technologies that can be used to clean up or remove these metals from the contaminated soils and the mining wastes, such as thermal treatments, biological and physical/chemical procedures. These removal technologies are generally require the uptake of contaminated soil, its subsequent treatment and either replacing it *on-site*, or disposed in specific landfills and it is costly to practice and destructive to the application sites, and only partially effective for the total removal of toxic metals, or for the sufficient reduction of their mobility and bioavailability.

In the past few decades, new techniques are being developed to remediate trace elements in contaminated soils such as phytoremediation and *in situ* stabilization. *In situ*

stabilization technique or *in situ* immobilisation is one of the common practices for reducing negative effects of metals and metalloids such as As, Cr, Cu, Pb, Cd and Zn in contaminated soils by adding amendments. *In situ* immobilisation is generally non-disruptive for the natural landscape, hydrology, and ecosystems than conventional are excavation, treatment, and disposal methods. It is considered as a simple and cost-effective approach for the treatment of metals in contaminated soils, when these soils are difficult or costly to be removed and treated *ex situ*. This technique can be used *in situ* and *ex situ* to reclaim and re-vegetate industrially devastated areas and mine-spoils, restore the physical, chemical, and biological soil properties, and reduce the contaminant mobility and bioavailability with various chemical and mineralogical agents. It is able to enhance one or several processes such as metal adsorption through increased surface charge, formation of organic and inorganic metal complexes, sorption on Fe, Mn, and Al oxides, and precipitation. In addition the main goal of this technique is not to reduce the total content of contaminants but help to lowers the fraction of toxic elements or compounds, which are potentially mobile or bioavailable.

Several application studies have demonstrated that *in situ* immobilisation of contaminated soils by using inexpensive soil amendments, such as alkaline materials (calcite, lime, dolomite and slag), phosphate minerals (phosphoric acid, phosphate rocks, synthesized apatites), aluminosilicates mineral (clay and zeolites), Iron and manganese oxides and hydroxides (zerovalent iron), organic matter and alkaline biosolids (waste by-products) were found to be suitable for the remediation metal-contaminated soil. The amendments significantly reduced the mobility of metals in soil, metal uptake by plants, and metal phytotoxicity. Therefore, alkaline materials are usually added to acidic soils to improve soil chemical and physical properties and also to reduce the mobility and bioavailability of contaminant. Slag, which consists of calcium oxide, phosphorus oxide, silicon oxide, iron oxide, and other metal oxides, is an alkaline by-product of metallurgical processes or a residue of incineration processes. Slags have been successfully used to soil reclamation and soil fertiliser. It has been used as a soil additive to remove various metals contaminated soil by precipitation and adsorption on the surface of metal oxide.

The objectives of this Ph.D study were to evaluate the physical, chemical soil properties and the distribution of trace elements in contaminated soil. Also to evaluate the characteristics of two different slags samples, a basic slag (BS) and a basic slag phosphate (BSP) which are alkaline by-products of the French steel industry and which used as a soil amendments to improve soil properties and for the *in situ* immobilisation of copper and metals in chromated copper arsenate (CCA) contaminated soil. Topsoil (0-25 cm) samples were collected from a former wood preservation site, south Bordeaux, France. Four soil treatments (1 kg air-dried weight) were prepared and mixing with 0 %, 1 %, 2 % and 4 % of BS and BSP. The BS and BSP effects on physical, chemical and mineralogy soil properties were investigated. In addition, the concentration and accumulation of metals in biomass beans plants were also evaluated to change the availability and mobility of these metals in contaminated soil and metal uptake by plants.

The following main results have been achieved:

1. Physico-chemical soil properties and distribution trace elements in the soil

The results indicate that the soils of the study area are mostly coarse in texture (mainly sand and loamy sand), the sandy texture dominates in most soil samples followed by loamy sand and all soil samples were very low contents in fine materials (silt + clay). The gravel contents of the soil study ranged between 12 to 87 % by weight. In some cases, very gravely soil texture (gravel content > 50%) occurs in the surface, subsurface and deepest layer of soil profiles. Organic matter content in soil samples ranges between 0.67 to 3.01%. Most soil profiles show a clear decrease of OM with depth indicated that little amount accumulation in the surface soil and the low amounts of OM in most soil samples are the result of poor vegetation cover and indicating poor soil fertility. Calcium carbonate distribution in soil samples showed that the range is between 1.34 and 2.3% and the decrease of calcium carbonate in soil samples may be due to the absence of the basic cations such as Ca, Mg, and K. The pH soil varied from 4.04 to 7.11 and decreases with depth. All soil samples are extremely acid, slightly acid and very slightly alkaline. Thus, extremely and strongly acid soils (pH 4.0-5.0) can have

high concentrations of soluble metals which may be toxic towards the growth of some plants and also effect on the availability of some nutrients such as phosphorus, potassium, calcium, sodium and magnesium. The EC values of the soil study ranged from 0.02 to 0.44 dS/m and all soil samples are non saline (0-4 dS/m). The much lower salinity level in soil profiles study may be causing by the effect of rainfall and leaches basic cations (*e.g.*, Ca, Mg, K) into drainage water. Cation exchange capacity (CEC) indicates that the soil study ranged between 1 and 10.6 cmol (+)/kg and decreased with depth. The low value of CEC in soil study is probably due to the high content of coarse texture and low clay and organic matter contents.

The distribution of trace elements in our study indicate that, from all soil samples study, Cu is the dominate followed by Cr, Zn, As, Ni then Co and they ranged from 4.2 to 1970, 10.9 to 114, 15.4 to 95.7, 1.93 to 51.1, 5.22 to 14 and 1.66 to 4.81 mg/kg respectively. The concentrations of many contaminants tend to accumulate in the soil surface. Therefore, the distribution of Cu, Cr, As and Zn increases in the surface layer of soil profiles and then decreases with depth in all soil profiles. In contrast Co and Ni were decreased in the surface layer of soil profiles and then increased with depth in all soil profiles. In general As, Cu, Cr, and Zn can be found in excess in contaminated soils at wood treatment facilities, especially when Cu sulphates and chromated copper arsenate (CCA) were used as a preservative against insects and fungi, which may result in soil phytotoxicity. Our study indicates that copper is highly phytotoxic at higher concentrations above 30 mg/kg. Therefore, this is probably causing a problem of toxicity to plants then animals and humans. Higher concentration of Cu found in all surface layers of soil profiles and then decreases with depth. It can be noticed that, Cu concentration was exceeded 100 mg/kg in all surface soil profiles and some subsurface and deepest layers of soil profiles indicating that all soil profiles were contaminated. The results of PCA indicates that there was a relationship between copper concentration and clay content for the soil samples but it is weak causing by the low clay content in soil profiles ($r^2= 0.24$). In fact, copper was low strongly associated with OM of soil samples ($r^2= 0.22$) due to the low amount of OM in studied soil. There was no relationship between copper content and pH soil. This is possibly resulted from the anthropogenic contamination influence probably related to the input of CCA-C in the

soil study. The top layer (0-25 cm) has been mainly contaminated by Cu originated mainly from Cu sulphate and in a lesser extent from standard CCA type C (copper oxide 11.1 % w/w, chromium trioxide 30 % w/w, arsenic pentoxide 19.9 % w/w) used as wood impregnation from an industrial site.

2. Slags characteristics used as remediation technology for contaminated soils

Two different type of slags, basic slag (BS) and basic slag phosphate (BSP) were used as soil amendments to remediate trace elements contaminated soil. Slag characterization was carried out using the following analytical techniques: chemical composition analyzed by an atomic adsorption spectrophotometer, mineralogical analysis examined by X-ray diffraction (XRD), microstructure observed by optical microscope, scanning electron microscope (SEM) coupled with an energy dispersive(EDX) and electron microprobe analysis (EMPA). The results indicate that the major compound of BS is mainly consists of Ca (60.69 wt % CaO), Fe (14.61 wt % Fe₂O₃), Si (12.54 wt % SiO₂), Al (5.91 wt % Al₂O₃) and Mg (2.51 wt % MgO). Other compounds such as TiO₂, MnO, P₂O₅ and K₂O are low contents; they represent respectively 1.47, 1.06, 1.05 and 0.15 wt%. The major compound of BSP is mainly composed of Ca (30.71 wt % CaO), Fe (21.4 wt % Fe₂O₃), Si (14.63 wt % SiO₂), P (14 wt % P₂O₅), Mg (9.55 wt % MgO), Al (5.56 wt % Al₂O₃) and Mn (2.53 wt % MnO₂). Other compounds such as, TiO₂ and K₂O are observed in few amounts; they represent respectively 1.09 and 0.53 wt %. It can be noticed that the amounts of phosphorus oxide in the BSP is very much higher than in the BS indicating that BSP is rich in phosphorus oxide.

The results of XRD analysis of both slag samples revealed that many phases such as larnite, wustite, brownmillerite, calcite and merwinite are generally found in both slag samples. Some phases were observed in BS compared with BSP such as mayenite, portlandite, melilite, grossular, imandrite and calcium silicate oxide. In addition, some crystallized compounds were detected in BSP than BS phases such as rodolicoite, calcium silicon, calcium aluminum iron oxide, calcium phosphate, titanium hydrogen phosphate, amonium hydrogen phosphate oxide and whitlockite. Similar

results were obtained by SEM and EDS analysis and electron microprobe analysis (EPMA) reported that the level of P in BS is very low compared with the P content in BSP indicating that the BSP is rich in this element.

3. Effect of the basic slag addition on soil properties, growth and leaf mineral composition of beans in a Cu-contaminated soil

Basic slag (BS) is an alkaline by-product of the steel industry with potential properties to ameliorate nutrient supply and metal stabilization in contaminated soils. The BS effects on soil pH, soil conductivity, growth and chemical composition of beans were investigated using an acid, sandy soil from a wood treatment facility containing 630 mg Cu kg⁻¹. Pot experiments were carried out on a 2-week period with *Phaseolus vulgaris* L. An uncontaminated, sandy soil was used as a control (CTRL). BS was added into the soil (1 kg soil/pot) to constitute four treatments in triplicates: 0 % (T1), 1 % (T2), 2 % (T3) and 4 % (T4) BS/kg air-dried soil.

The results indicate that the soil pH, soil conductivity, and plant growth increased compared to the untreated soil. The soil pH was increased from 5.6 in the untreated soil up to 9.8 for the 4 % BS-amended soil. The soil conductivity rose from 0.14 mS/cm in the untreated soil to 0.38 mS/cm, 0.46 mS/cm, and 0.82 mS/cm in the 1%, 2%, and 4% BS-amended soils respectively. These increases in soil pH and EC in all BS-amended soils likely resulted from the BS composition and in particular its high Ca content. At 1 % and 2 % BS addition rate, highest shoot yields (dry weight, DW) occurred. Foliar Cu concentration varied from 5.6 mg kg⁻¹ to 53.1 mg kg⁻¹ in the treatments. The foliar Cu concentration likely caused a phytotoxic effect in plants grown in the untreated, Cu-contaminated soil. The highest decrease in the foliar Cu concentration, 2.3 times was obtained for the T2 plant. BS addition at 1% rate into the Cu-contaminated soil promoted beans growth with the lowest foliar Cu concentration. Foliar Ca concentration was enhanced in the T2, T3 and T4 treatments whereas the foliar P concentration was not promoted by the BS incorporation into the Cu-contaminated soil. Instead, foliar K accumulation in primary leaves was restored up to control level. Therefore this by-product was effective at 1% addition rate as a liming

material but not as a P fertilizer in this short-term experiment. The BS incorporation in the contaminated soil did not increase the foliar concentrations and accumulations for Cd, Cr, and Zn.

4. In situ remediation of trace elements in chromated copper arsenate (CCA)-contaminated soil using a basic slag phosphate (BSP)

Basic slag phosphate (BSP) which consists of calcium oxide, phosphorus oxide, iron oxide and other metal oxides, is an alkaline by-product from the steel manufacturing. BSP was used as a soil additive for improve physical and chemical soil properties and for the in situ immobilisation of copper and other trace elements in a chromated copper arsenate (CCA) contaminated soil to change the availability and mobility of trace elements in soil and metal uptake by plants. The effect of BSP on soil pH, soil conductivity, growth and biomass of beans plant were investigated using an acid, sandy topsoil (0-25cm). The soil was strongly Cu-contaminated ($630 \text{ mg Cu kg}^{-1}$) from a wood treatment facility using solutions of Cu sulphates and chromated copper arsenate. The pot experiments was carried out with dwarf beans (*Phaseolus vulgaris* L.) grown on the contaminated soil. BSP was added into the pots (1 kg soil) with four different treatments in triplicates: 0 % (T1), 1 % (T2), 2 % (T3) and 4 % (T4) BSP/kg air-dried soil. An uncontaminated, sandy soil was used as a control (CTRL). After a two weeks period, soil and plant samples were collected to determine soil pH and EC, growth and mineral analysis of plants. The mineralogical of clay and silt fractions of soil treatments were also determined by X – ray powder diffraction analysis (XRD) to identify the form of copper in soil.

The results show that BSP increased soil pH in relation with the addition rate, from 5.7 in the untreated contaminated soil to 7.0, 7.4 and 7.9 in the soils amended at 1%, 2% and 4 % BSP addition rate respectively. The BSP incorporation increased the soil electrical conductivity (EC) from 0.15 mS/cm in the contaminated soil to 0.47 mS/cm, 0.51 mS/cm and 1.17 mS/cm in the 1%, 2% and 4% BSP addition rate respectively. All BSP addition rates to the copper contaminated soil increased the root and shoot DW yield compared with the untreated contaminated soil (T1). The foliar Al concentration decreased in plants from all BSP-amended soils. The foliar Ca

concentration was enhanced in the all treatments BSP-amended soils whereas the foliar Mg, K and P concentrations were not increased by the BSP addition. The foliar Cu concentration decreased with the application of BSP for all treatments compared with the untreated contaminated soil (T1). The foliar Cu concentration varied from 6.23 to 35.73 mg kg⁻¹ DW with lowest and highest values for the CTRL and T1 treatments respectively. This indicated that the beans plants were not able to grow on the excessive copper contaminated soil (630mg/Kg). Similar results indicated that the Zn and Cr availability decreased with the incorporation of the BSP into the soil. According to these results, we conclude that the BSP addition at 2% and 4% rate incorporation into copper contaminated soil promoted highest root and shoot DW yields with the highest Ca concentrations and lowest foliar Cu concentration.

The mineralogical form of copper in soil fractions by XRD analysis indicated that copper was detected in the form of cuprite (Cu₂O), arsenic copper (AsCu₉), and plancheite (Cu₂(CO₃)(OH)₂) in silt fraction contaminated soil (T1). While in the clay fraction contaminated soil (T1) shows that copper and other trace elements such as As and Cr were observed in the form of cuprite (Cu₂O), arsenic copper (AsCu₉), malachite (Cu₂(CO₃)(OH)₂), magnesium chromium oxide (MgCr₂O₄) and chromium arsenate (CrAsO₄). The stabilization of metals contaminated soil by amended soil does not reduce the total content of contaminants but lower the amounts of mobile and bioavailability of the fractions. According to changes the soil pH, the application of BSP addition rate in copper contaminated soil (T1) can reduce copper mobility by adsorption or precipitation on the BSP surface. The mechanism of copper removal using BSP may be is precipitation with hydroxide dissolved from slag rather than adsorption on slag surface. Thus, the presence of carbonate, silicate, oxy-hydroxides and phosphate in the soil-BSP can form relatively insoluble complexes with metal ions and cause metals to precipitate in their presence. Therefore, it seems that in all amended soil BSP addition rate, copper was observed in the forms of silicate, carbonate and oxy-hydroxides and complex precipitation with calcium, sodium, iron and phosphate in the soil fractions. We conclude that the precipitation amount of copper was highly depending on pH and slag compounds. These indicate that most of copper mobile was precipitated on the surface slag causing by the compound of BSP in particularly the

high Ca and P contents which able to make of it a potential liming agent to sorb and precipitated metals in soil.

From all achieved results, it can be concluded that the soil studied is an acid sandy soil with a low in organic matter, clay, and cations exchange capacity and a high level of metals contaminated soil. Thus the application of alkaline materials such as basic slag and basic slag phosphate in soil is promising tool for reduction the mobility and bioavailability of trace elements contaminated soil by adsorption or precipitation on the slag surface as well as for remediation of the soil to improve their physical, chemical and mineralogical properties and also to improve plant production.

RÉSUMÉ

Nouvelle Technique Pour L'amélioration Et La Conservation Des Sols: Stabilisation In Situ De Métaux Trace Dans Les Sols Contaminés

Les objectifs de cette étude étaient d'évaluer la phytoremédiation assistée dans le cas de sols pollués par des métaux traces en plus ou moins forte teneur. Par phytoremédiation assistée, il s'agit de coupler les capacités de remédiation offertes par les plantes à celles d'un amendement de synthèse qui peut avoir un effet dual (sur la pousse végétale en agissant comme un engrais mais aussi en adsorbant ou en manifestant des capacités d'échanges entre le milieu et la matrice. L'étude a donc été réalisée sur un site contaminé, en l'occurrence il s'agit d'une ancienne exploitation de traitement de bois au Cuivre-Chrome-Arsenic (CCA) sur lequel différentes stratégies de remédiation ont été testées (Bes et Mench, 2008; Mench et Bes, 2009). Le traitement CCA de type C est un produit à base d'oxyde de cuivre (11,1% w / w), trioxyde de chrome (30% w / w), et de pentoxyde d'arsenic (19,9% w / w). Ainsi une partie de la thèse a porté sur les caractéristiques géologiques, pédologiques et physico chimiques de la zone contaminée d'une part, et d'autre part sur l'étude et le test de l'emploi d'amendements inorganiques (matrice minérale) vis-à-vis d'un protocole de phytoremédiation en vue de d'infirmer ou non l'intérêt de ce type d'apport pour aider à la dépollution de sols contaminés par des éléments traces types métaux. Les amendements testés sont tout deux des matrices minérales issues des coproduits de l'industrie sidérurgique en l'occurrence des scories de laitiers. Le premier produit est une scorie de base (BS) type scorie Thomas®, tandis que le second est un laitier de centrale thermique qui a été soumis à un traitement de phosphatation en vue de le doper en phosphates pouvant jouer un double rôle (BSP). Ce produit de synthèse ou matrice duale doit en principe, du fait de sa richesse en minéraux phosphatés avoir un impact positif sur la pousse végétale (engrais) mais aussi capter et intégrer dans son réseau cristallin certains métaux traces ; améliorant ainsi l'efficacité du traitement par les

plantes de sols pollués par des Métaux Traces (MT). Le couplage amendement et plantes ayant un potentiel d'extraction et de fixation des métaux traces du sol dans leur système végétatif est une alternative au traitement de type physique ou chimique pour des sols contaminés. L'intérêt de la démarche de ce travail est d'aborder les aspects caractérisations du site, des amendements et des plantes lors d'une campagne qui aura duré un peu plus de trois ans. L'approche envisagée est originale en proposant d'apporter un amendement, considéré comme un déchet de l'industrie « lourde », qui pourrait avoir un aspect bénéfique pour la remédiation de sites pollués. Cela permettrait de valoriser ce type de coproduits autrement qu'en tant que source potentiel de granulats. Néanmoins et c'est une des grosses limites de cette étude, car si la phytoremédiation assistée (scories Thomas) bénéficie d'un retour d'expérience de plusieurs dizaines d'années, la durée de l'expérimentation avec nos laitiers phosphatés est trop courte pour pouvoir conclure définitivement sur leur capacité duale (amendement et rétention des MT). Il est nécessaire de poursuivre l'étude sur dix ans afin d'avoir un retour suffisant sur la pérennité et la viabilité des espèces végétales se développant sur ce type de sols pollués.

La thèse est divisée en chapitres dont le premier porte sur la pédologie du site, le second sur la caractérisation des amendements type scorie, le troisième et quatrième chapitre traitent respectivement des essais pour évaluer l'impact des deux amendements testés, respectivement les scories de base (BS) et les scories phosphatés (BSP) vis-à-vis de la contamination dans le sol mais aussi dans la plante test : *Phaseolus vulgaris L.* (ou haricots). Le choix de cette plante a plusieurs raisons mais les principales sont ses capacités à immobiliser des quantités de MT dans son système racinaire et aérien d'une part mais aussi son cycle végétatif assez court qui permet de mesurer rapidement l'évolution de la plante vis-à-vis des conditions expérimentales. L'ensemble des tests ont été réalisés dans les règles de l'art en se référant lors de chaque campagne de tests à un sol de contrôle (nommé control ou CTR) non contaminé, en l'occurrence un sol sablonneux proche du point de vue pédologique du sol issu du site. Le plan d'expérience est le suivant : constituer quatre traitements en triple exemplaire: 0% (T1), 1% (T2), 2% (T3) et de 4% (T4) BS / kg de sol séché à l'air.

1. Caractéristiques du sol contaminé et distribution des métaux traces

L'objectif de cette recherche a été (1) d'étudier les propriétés physico-chimiques, la pédologie d'un sol contaminé par le CCA et (2) d'identifier la répartition des métaux traces du site en vue (3) d'évaluer les zones contaminées et notamment apprécier le gradient vertical de la pollution par le CCA et son évolution en fonction de paramètres comme la distribution granulométrique des particules, la matière organique, le pH du sol et la capacité d'échange cationique. Ces paramètres sont connus pour être les principaux facteurs pédologiques contrôlant la diffusion des métaux traces dans le sol. Les résultats indiquent que les sols de la zone d'étude sont des sables limoneux à texture grossière avec de faibles teneurs en matières fines (limon + argile). Il existe également un peu de calcaire sous forme de carbonate de calcium avec des teneurs allant de 1,3 à 2,3 %. Les teneurs en Matières Organiques (MO) varient de 0,67 à 3,01% avec une nette diminution avec la profondeur, de même que le pH variant de 4,04 à 7,11) et diminuant avec la profondeur. Les sols fortement acides (pH 4.0-5.0) ont présenté de fortes concentrations de métaux solubles. La Conductivité Electrique (CE) a varié de 0,02 à 0,44 dS/m. La capacité d'échange cationique (CEC) diminue avec la profondeur (valeurs allant de 1 à 10,6 cmol/kg). La distribution des éléments traces indique une abondance en ET tels que Cu (4,2 à 1970 mg/kg), Cr (10,9 à 114, 15), Zn (4 à 95.7), As (1.9 à 51.1), Ni (5.22 à 14) et Co (1,66 à 4,81 mg/kg). L'accumulation de métaux toxiques dans le sol est héritée de l'usage du site pour le traitement du bois par le CCA. La distribution des métaux traces, suivant un gradient vertical dans le sol, n'est pas la même pour tous les métaux. En effet, Cu, Cr, As et Zn augmentent dans la couche superficielle du sol et diminuent ensuite en profondeur. En revanche, Co et Ni diminuent dans la couche superficielle du sol et augmentent avec la profondeur. La mobilité du cuivre dans le sol est contrôlée par différentes caractéristiques physico-chimiques du sol comme le pH et la Force Ionique par exemple. En outre, le cuivre est complexé avec la MO et est adsorbé à la surface de la fraction argileuse, influençant fortement la mobilité et la biodisponibilité du Cu dans le sol (Adamo *et al.*, 1996; Chaignon *et al.*, 2003; Sterckeman *et al.*, 2006).

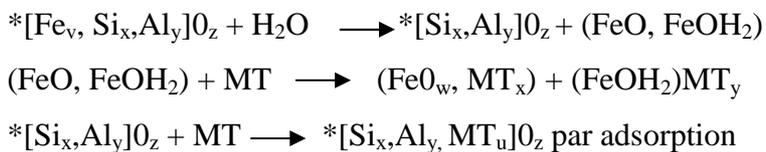
2. Caractérisation des scories utilisées comme technologie d'assainissement de sols contaminés

Deux types d'échantillons de laitier : une scorie de base (BS) et un laitier phosphaté (BSP), ont été utilisés comme amendement et ainsi assainir le site contaminé par des Métaux Traces (MT). Cette partie vise à évaluer les propriétés chimiques et minéralogiques des scories par plusieurs techniques d'analyse spectroscopique et d'imagerie. La composition chimique a été déterminée par un spectrophotomètre d'absorption atomique sur scorie dissoute dans l'acide et par microsonde électronique de Castaing (EMPA) sur lame mince. La minéralogiques a été obtenue par diffraction des rayons X (XRD) sur poudres et microscopie optique polarisante sur lame mince. Cette approche couplant analyse spectroscopique statistique, et analyse directe et ponctuelle (imagerie) permet de corrélérer et de valider les résultats obtenus d'une part mais aussi de préciser la microstructure associée à la chimie locale des phases minérales. Cette microstructure a été étudiée par microscopie électronique à balayage (MEB) couplée à l'énergie dispersive (EDX).

Les résultats indiquent que les principaux composés de BS sont Ca (60,69% en poids de CaO), Fe (14,61% en poids Fe_2O_3), Si (12,54% en poids de SiO_2), Al (5,91 wt% Al_2O_3) et de Mg (2,51% en poids MgO). D'autres éléments comme Ti, Mn, P et K sont présents à des teneurs pondérales (en poids d'oxydes) respectivement de 1,47, 1,06, 1,05 et 0,15 %. Comparée aux scories d'acier classiques qui sont principalement composées des oxydes suivants: CaO, Fe_2O_3 , SiO_2 , Al_2O_3 , MgO, MnO et P_2O_5 (Cha *et al.*, 2006, Shen et Forssberg, 2003, Shi et Qians, 2000; Tossavainen *et al.*, 2007; Tsakiridis *et al.*, 2008), notre matériau est appauvri en P. Cette composition se traduit minéralogiquement par des cristaux d'opaques comme l'Ilménite, la Magnétite, l'Hématite et la Limonite pour les formes oxydes mais aussi par de la Pyrite pour les formes sulfures. Ils représentent environ 80% de l'ensemble des cristaux tandis que les 20% restants sont des microlites de Feldspaths (Plagioclase et Orthoclase), du Quartz, des Grenats de la Calcite, quelques Rutilés et Tourmaline. L'ensemble est pris dans une mésostase aphanitique majoritaire. Les XRD ont confirmé l'aspect cryptocristallin du matériau avec comme phases identifiables sous forme de microcristaux submillimétriques : Larnite, Wurstite, Brownmillerite, Calcite, Merwinite, Mayenite,

Portlandite, Mésosilite, Grossulaires, Imandrite et un composé d'oxyde de calcium et de silice non identifié. Cet ensemble minéralogique rend compte de la chimie du matériau de type calco-silicate riche en métaux traces mais aussi des conditions d'élaboration qui sont de type haute température (>1400°C) et moyenne pression en condition plutôt oxydante comme l'atteste la présence de Wurstite, de Brownmillérite, de Mésosilite, de Portlandite et du Grossulaire.

Les résultats obtenus par SEM/X-EDS et EPMA confirment que le matériau BS est composé de Ca, Fe et Si pour 90% et le plus souvent sous forme d'une mésosilite aphanitique dans laquelle baignent des microcristaux calco-silicatés et des oxydes de fer essentiellement, traduisant un refroidissement rapide. Il semble que l'ensemble des éléments traces soient présents dans les formes cristallines comme l'atteste les nombreux minéraux différents (Wurstite, Brownmillérite, Mésosilite, Grossulaire) observés par XRD, MO et SEM. En revanche, la phase amorphe est calco-silicatée et plus ou moins riche en Fe. Cet ensemble de caractéristiques rapproche ce type de laitiers BS d'une scorie Thomas fortement appauvrie en P mais riche en métaux. A priori cette composition peut être un handicap pour leur utilisation en tant qu'amendement sur des sols de sites pollués par des métaux traces. Néanmoins le fait que les métaux traces soient inclus dans le système cristallin des phases cristallisées réduit fortement l'hypothèse d'un transfert depuis la matrice BS vers le sol, et a fortiori l'existence d'une phase aphanitique riche en Fe permet d'envisager soit un piégeage des métaux traces du sol par cette phase par le biais des oxydes de Fe ou la capacité supposée et espérée de l'inertage des MT par la phase cryptocristalline selon le schéma suivant (* mésosilite amorphe).



Ce matériau dérivé de BS est enrichi en phosphore (par réaction de phosphatation en milieu acide). Les résultats de l'analyse chimique montrent effectivement que la composition chimique de BSP est Ca (30,71 wt % CaO), Fe (21,4

wt % Fe₂O₃), Si (14,63 wt % SiO₂), P (14 wt % P₂O₅), Mg (9,55 wt % MgO), Al (5,56 wt % Al₂O₃), Mn (2,53 wt % MnO₂) et quelques traces de Ti et K (1,09 wt% TiO₂ et 0,53 wt% de K₂O). Comparativement à BS, BSP est enrichie en P et se traduit du point de vue minéralogique en microscopie optique polarisante par la présence de Zircons et d'Épidotes (non observés dans BS) et bien sûr par des minéraux phosphatés pris dans une mésostase aphanitique. On retrouve les microlites de Feldspaths, de Quartz, des Grenats, de la Calcite, du Rutile et des Tourmalines. Les DRX ont permis d'identifier du phosphate de calcium, du phosphate hydrogéné de titane, de la whitlockite associée à des phases de rodolicoïte, des silicates de calcium et des oxydes calco-alumino-ferreux. L'analyse SEM/X-EDS et par EPMA de la mésostase montre que sa composition est à plus de 95% (masse pondérale) formée de Ca, P, Fe et Si confirmant donc l'enrichissement net en P comparé au laitier BS. Les éléments Mn, K, Mg et Al ont été identifiés mais à de faibles teneurs de l'ordre du pourcent. La présence de minéraux phosphatés sub-millimétriques dans BSP permet d'envisager une double action vis-à-vis de sols pollués par des MT. En effet, ces minéraux phosphatés vont participer à l'apport en nutriment phosphoré pour le sol mais sont connus comme étant d'excellents capteurs de MT lors des réactions d'hydrolyse (Pierzynski and Schwab, 1993; Mench *et al.*, 1994a, b; Mench *et al.*, 1998 ; Hettiarachchi *et al.*, 2001 ; Wang *et al.*, 2001; Liu and Zhao, 2007 ; Bes and Mench, 2008). On peut donc attendre, lors de l'apport de quelques pourcents (de 2% à 10% pondéral par kilogramme de sol) de laitier BSP broyé sur les parcelles une meilleure pousse végétale tout en observant une décroissance des teneurs en MT dans le sol mais aussi au niveau de la plante. C'est ce que ce travail doit mettre en évidence c'est-à-dire l'effet dual de la matrice de laitier enrichie en P.

3. Effet des scories de base sur le sol et la mobilité des métaux traces du site pollué

Cette étude vise à enquêter sur l'intérêt ou non (aspect positif) d'amender un sol contaminé par une pollution de type CCA. Le seul ajout d'un amendement ne suffisant pas bien sûr à dépolluer un sol contaminé par des MT, mais associé à une stratégie de phytoremédiation, l'apport de scories (BS et BSP) peut modifier certains paramètres pédologiques et contribuer ainsi au succès (rendement de phytoremédiation amélioré ou pas). Il permet aussi de vérifier si l'apport de scorie peut également abaisser le cortège

des métaux traces labiles (fraction mobile) par sa seule présence. Il sera alors possible de considérer un double effet de l'apport de scorie sur un site pollué. Cet apport joue sur certaines caractéristiques du sol telles que le pH et la conductivité électrique (CE) et donc sur la mobilité potentielle du pool de métaux labiles du sol et captés par la plante (analyse des racines et du cortex supérieure de la plante (tige et feuille). De plus, il est important de réduire ce pool labile de MT au niveau de l'environnement proche de la rhizosphère (réseau racinaire du sol) afin de minimiser le transfert depuis ce système vers les tiges de la plante (type haricot dans nos tests). Les expériences en pots ont été réalisées sur une période de deux semaines avec *Phaseolus vulgaris* (plants de haricots). Un sol sablonneux a été utilisé comme contrôle (CTRL). Sur une série de quatre traitements (en triple) en pots de 1 kg de sol chacun, nous avons ajouté le laitier BS à raison de : 0% (T1), 1% (T2), 2% (T3) et de 4% (T4) BS / kg de sol séché à l'air. Le pH, la CE, la croissance des plantes, la production de biomasse foliaire et les concentrations des éléments nutritifs et les métaux traces dans les feuilles primaires ont été suivis. Les résultats indiquent que l'incorporation de BS dans le sol se traduit par une augmentation du pH tout comme de la CE. Cette augmentation est la conséquence de la nature alcaline des scories qui se dissolvent en partie dans le sol assurant leur fonction d'amendement. L'effet de BS sur la biomasse des feuilles primaires des haricots varient selon les traitements. Si la croissance végétative est maintenue dans ce contexte de sol pollué pour certains tests, la répartition des MT dans les haricots suivant les tests sont complexes, traduisant des mécanismes antagonistes entre éléments. De manière générale, l'apport de BS (au taux de chaulage de 1% pondéral) se traduit par une augmentation de la concentration du Cu dans les extrémités foliaires sans impact notable sur les concentrations de métaux tels que Cd, Cr, et Zn. Il y a là une sélectivité des MT traduisant une sorte de spéciation biologique complexe ou affinité sélective de la plante vis d'un cortège de MT présent dans un sol, qui reste à étudier sur le long terme.

4. Effet de l'ajout de base de phosphate de scories sur les métaux trace dans un sol contaminé

Dans cette étude, un laitier d'aciérie a été enrichi en phosphate (BSP) et testé comme adjuvant ou amendement pour l'assainissement de sols contaminé par des MT

(issus du traitement au CCA). Les objectifs de cette étude étaient les suivants: (1) évaluer l'influence de BSP sur les fonctions pédologiques du sol (pH et la CE), (2) évaluer l'effet de BSP sur le rendement végétatif des plantes tests et (3) déterminer le potentiel de BSP pour réduire le cuivre et les autres métaux traces dans le sol. Les résultats montrent que l'apport de BSP augmente le pH du sol de 5,7 à 7,9, ainsi que la conductivité électrique (CE) de 0,15 mS/cm à 1.17 mS/cm. Les plants de haricots ne sont pas en mesure de se développer dans des sols contaminés par de fortes teneurs en Cu comme par exemple celui ou des teneurs de plus de 630mg/Kg ont été mesurées, même si l'apport de BSP induit une baisse de la teneur en Cu dans le sol et une augmentation dans la masse foliaire. Des résultats similaires ont été observés pour le Zn et Cr labile et dont les teneurs dans le sol ont diminué avec l'apport de BSP. Les fortes teneurs en Cu dans le sol se traduisent par la précipitation, en milieu pédologique légèrement acide, de phases minérales telles que la cuprite (Cu_2O), associée à l'arsenic de cuivre (AsCu_9), la planchéite [$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$], la malachite [$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$] comme l'ont démontré les analyses par DRX. Lorsque les teneurs en CCA sont importantes (certaines zones sur le terrain), le chrome peut également précipiter pour donner des oxydes type oxyde de chrome magnésium (MgCr_2O_4) et d'arséniate de chrome (CrAsO_4). La répartition de ces phases dans le sol contaminé est complexe. Ainsi dans le cas du test T1 (sol contaminé sans apport d'amendement), la distribution de phases néoformées est fonction de la minéralogie du sol et l'on ne trouve pas tout à fait les mêmes formes entre les fractions argileuses et silteuses. L'apport de BSP sur le sol contaminé se traduit par un changement de pH et de la CE qui affecte la mobilité du cuivre labile. Ce dernier se retrouve ainsi précipité ou adsorbé à la surface du laitiers BSP broyé. Ainsi le Cu, quel que soit la teneur en BSP, se retrouve, au niveau de la fraction silteuse sous forme de cuprite (Cu_2O), d'arsenic de cuivre (AsCu_9), associés avec les carbonate et les oxy-hydroxydes sous forme d'azurite [$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$], avec les silicates tels que la planchéite ($\text{Cu}_3\text{SiO}_3\cdot\text{H}_2\text{O}$), mais également sous forme de complexe de fer et de phosphate tel que le chloro phosphate hydro-nitrogéné de [$\text{Cu}_{4.72}\text{H}_{3.2}(\text{P}_{12}\text{N}_{18}\text{O}_6)\text{Cl}_2$], l'hentschélite [$\text{CuFe}^{3+}_2(\text{PO}_4)_2(\text{OH})_2$] et de phosphate d'oxyde de cuivre [$\text{Cu}_4\text{O}(\text{PO}_4)$]. Dans la fraction argileuse les formes observées en DRX sont similaires avec l'existence d'un plus grand nombre de variétés comme la malachite [$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$], la pseudomalachite [$\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$], le phosphate de cuivre nickel

[Cu Ni₂(PO₄)₂], le phosphate hydrogéné de cuivre calcium (Ca Cu HPO₄), ou bien l'oxyde de calcium cuivre titane (CaCu₃Ti₄O₁₂). Ces phases minéralogiques rendent compte des mécanismes chimiques complexes et variés qui se produisent à l'interface sol contaminé et amendement BSP. Ces résultats confirment que la plupart du Cu labile, du Cr labile et de l'As labile précipite à la surface de l'amendement par sorption ou co-précipitation associée au Ca et au P (apportés par l'amendement).

Conclusion

De tous les résultats obtenus, il peut être conclu que l'apport d'un amendement alcalin comme les scories de base ou d'un laitier phosphaté dans un sol sablo limoneux aquitain contaminé par des métaux traces issus d'activités industrielles de traitement du bois par imprégnation au Cuivre Chrome Arsenic (CCA) est intéressant. Cet amendement est un outil prometteur pour la réduction de la mobilité et la biodisponibilité des métaux traces (MT) des sols contaminés. Les mécanismes qui contrôlent cette baisse des teneurs en MT sont des réactions d'adsorption-précipitation de phases minérales riches en MT. Elles se traduisent par la précipitation de phases minérales néoformées en surface des scories. La présence de phosphates sous forme de minéraux submillimétriques dans les scories semble améliorer ces réactions. Les teneurs en MT sur le site étudié sont à certains endroits (tâches de léopard sur le site) tellement élevées que l'on observe des formes minéralisés - comme la Cuprite, la Malachite, des Arséno-cuivre, des oxydes de chrome - révélant donc des mécanismes de précipitation et de croissance cristalline suffisants pour être détectées en DRX. La présence de ces phases minérales traduit que le traitement par le CCA de bois conduit à des teneurs telles que les capacités pédologiques d'un sol sont fortement dégradées et conduisent par la rémanence des apports à une sur-saturation en MT (Cu, Cr et As) qui avec le temps va conduire à ces précipitations. Cependant, aux échelles de temps auxquels le site est confronté (activité industrielle sur un demi-siècle) il est étonnant de trouver ces minéraux. Cela suppose que d'une part les résidus de CCA sont faiblement mobiles suivant le gradient vertical, ce qui est étonnant sur ce type de sol (grave sablo limoneuse à faible horizon humique) connu pour leur capacité drainante. Mais d'autre part, le

passage de MT labile sous forme d'oxydes, d'hydroxydes traduit une activité bactérienne capable de catalyser les réactions minéralogiques conduisant à la précipitation de ces phases. En effet les seuls mécanismes physico chimiques sont insuffisants, étant donné l'échelle de temps, pour générer des phases cristallisés. Les cinétiques chimiques, sur la base d'une approche classique (équation d'Arrhénius, de Fick) ou plus récente (Lasaga & al), ne peuvent à elles seules expliquer la nucléation et la croissance cristalline. Il est donc nécessaire d'évoquer des réactions biologiques (activité bactérienne par exemple) pour obtenir de tels cristaux comme pour les lixiviats de déchets miniers par exemple où l'on observe des minéraux néoformés en présence de bactéries (Exemple du site de Rio Tinto en Espagne ou de Carnoulès en France). Il faudrait donc pouvoir continuer sur de plus longues périodes ce type d'approche de phytoremédiation assistée par des matrices minérales issues de l'industrie sidérurgique pour valider le procédé. Les essais sont en cours et devront permettre de valider ou d'invalider les premières conclusions de ce travail.

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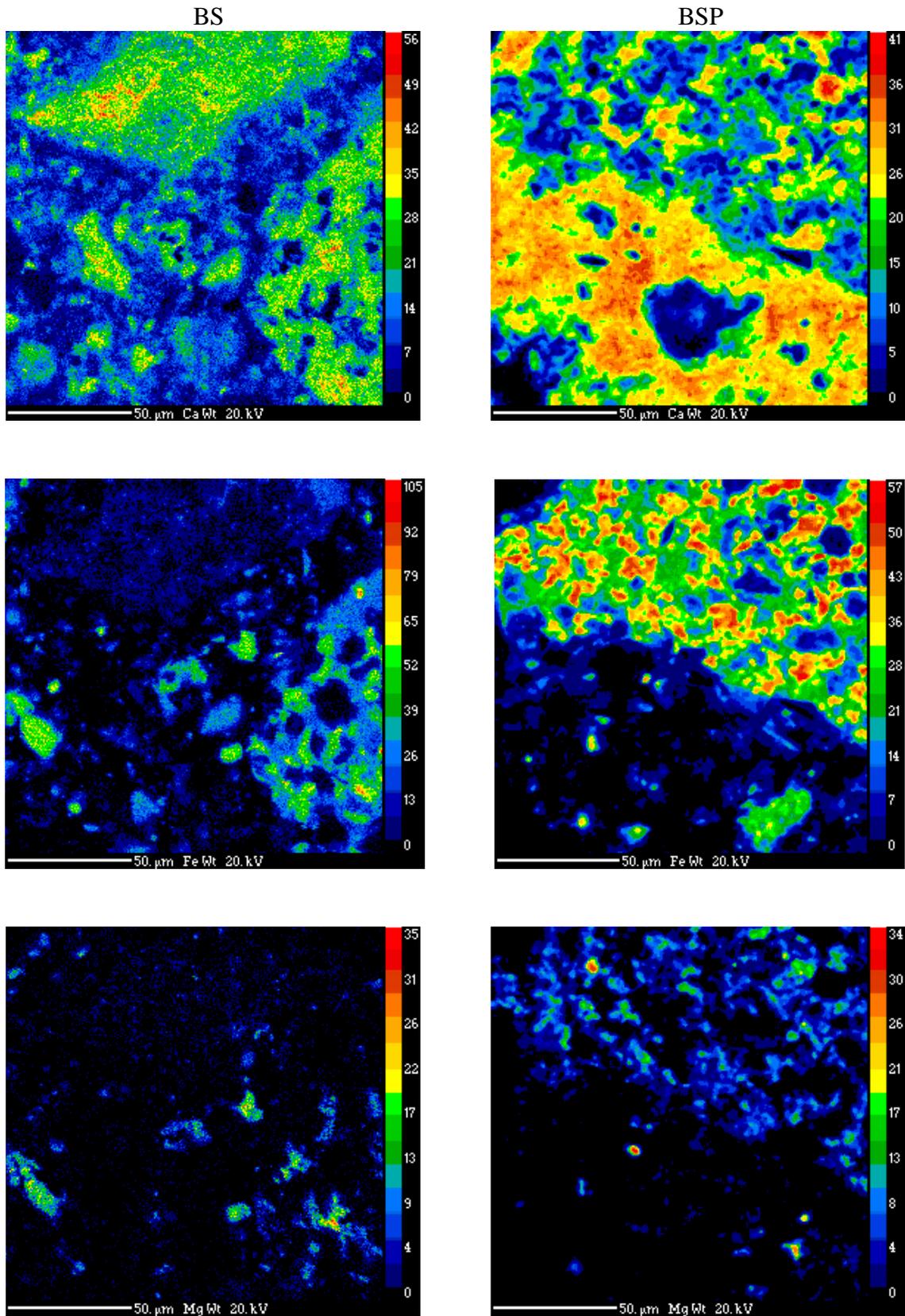
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Appendixes

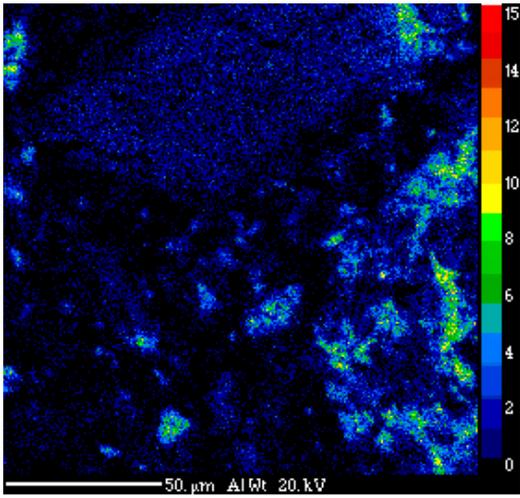
Appendix 1: EPMA analysis composition of BS and BSP

Elements (wt. %)	BS (1)	BS (2)	BS (3)	BS (4)	BSP (1)	BSP (2)	BSP (3)	BSP (4)
Al	3.76	1.54	0.16	0.22	0.29	6.31	0.33	0.62
Ca	20.91	31.78	8.44	5.45	34.95	28.77	3.51	23.17
Cr	0.04	0	0	0	0	0.41	0	0.11
Fe	37.36	6.6	3.08	11.27	2.72	33.05	1.27	14.55
Mg	2.37	1.48	0.77	4.48	0.06	2.35	0.15	0.05
Mn	3.45	2.8	0	1.02	0.02	1.52	0.43	0.77
P	0	0.23	0.28	0	10.23	0	0	1.62
Si	1.7	11.49	1.13	4.18	3.71	17.01	0.9	1.84
Ti	0.04	0.16	0	0	0.06	3.26	0	0.89
C	6.77	18.32	64.46	62.4	11.83	0.41	83.54	3.13
O	23.6	25.6	21.68	10.98	36.11	6.71	9.87	53.25
Total	100	100	100	100	100	100	100	100

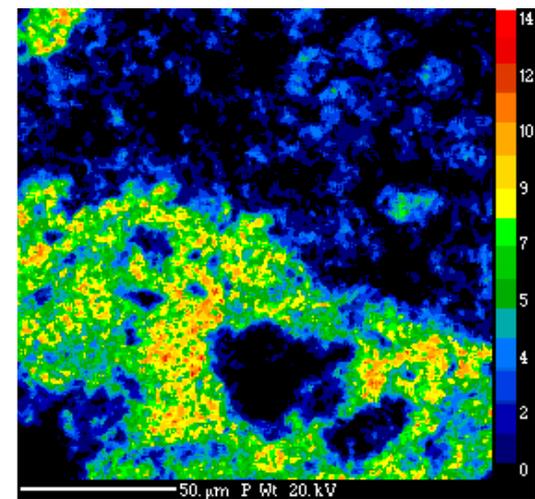
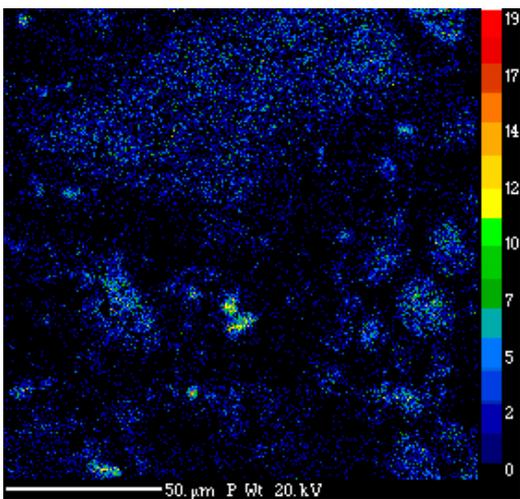
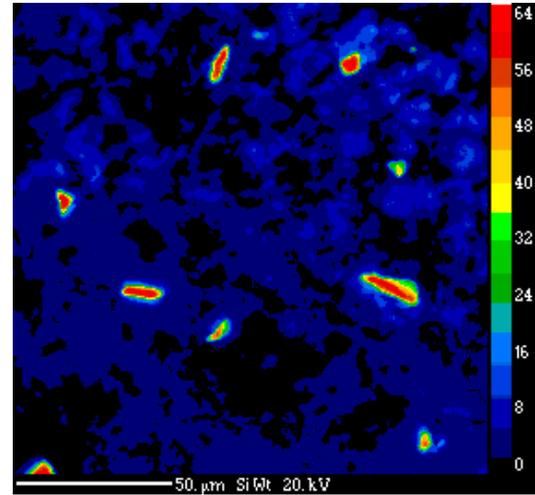
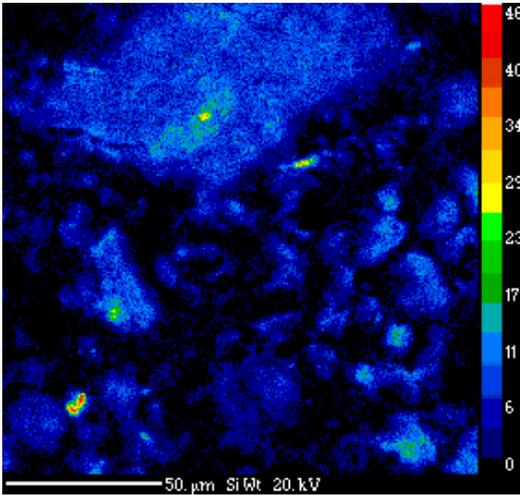
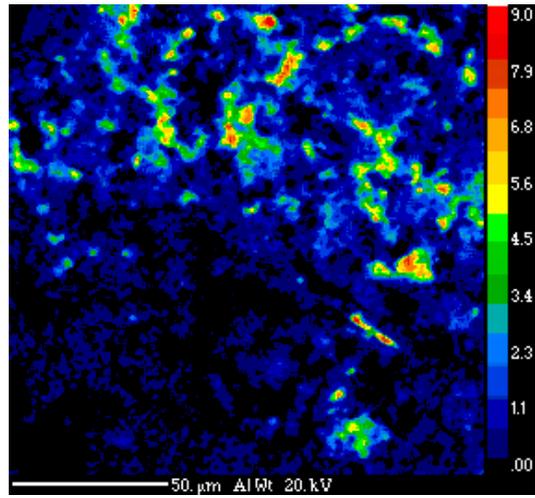
Appendix 2: Elemental distribution of BS and BSP by EPMA analysis



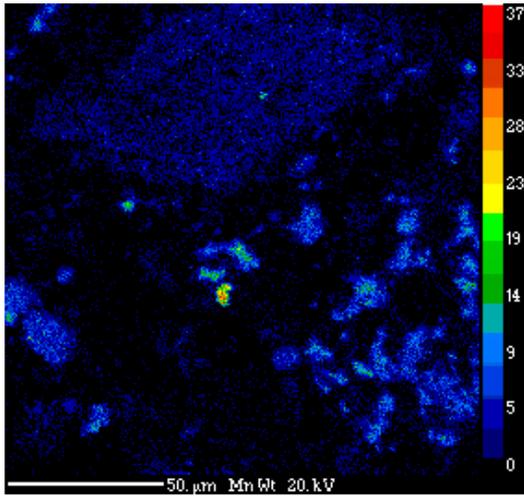
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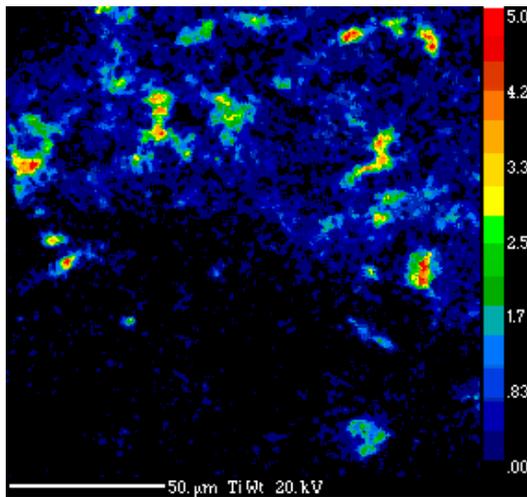
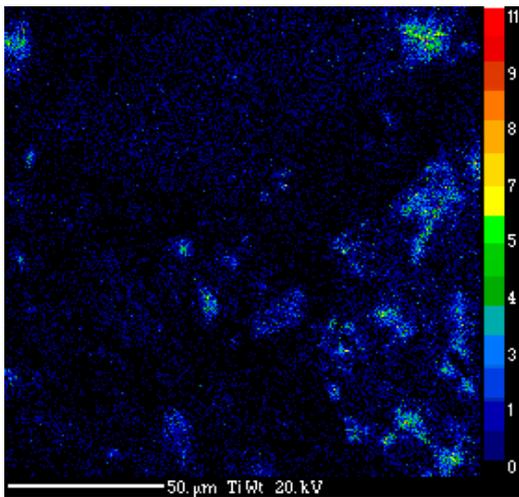
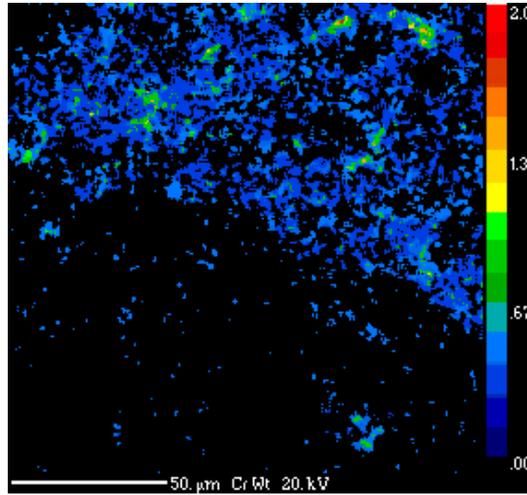
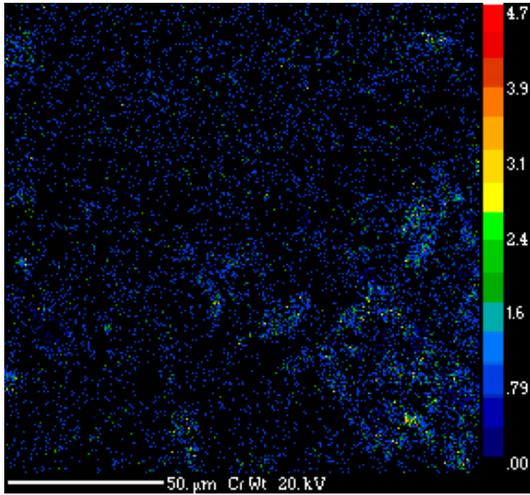
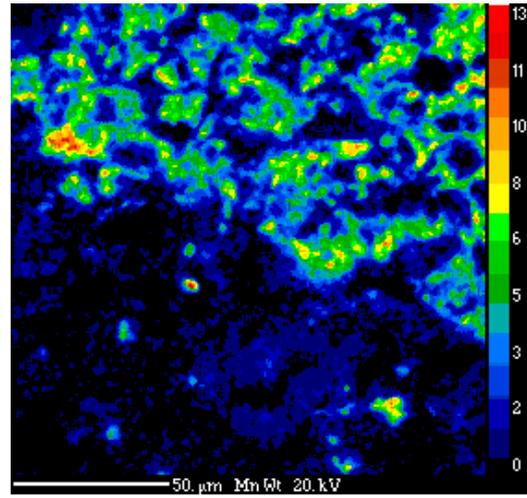
BSP



BS



BSP



SCIENTIFIC DISSEMINATION

Communications

1- Negim, O., Eloifi, B., Mench, M., Le Coustumer, P. “Phytoremediation assisted dual matrix for stressed soil (hydrous and trace elements contamination type)” - Poster. Pnetox, Colloque De Restitution Du Programme National d’Ecotoxicologie. Lille, 13-14 Octobre **2008**.

2- Negim, O., Eloifi, B., Mench, M., Bes, C., Le Coustumer, P. “Effects of Basic Slags on Soil Properties and Plant Biomass in a Trace Element-Contaminated Soil. Environmental Technologies-Sediment and Landfills.” (ECOR-5, EC-DNAPL-3 and EC-RSSG-1), Amsterdam October 21-23, **2008**.

3- Negim, O., Mench, M., Motelica-Heino, M., Guegan, R., Le Coustumer, P. “In Situ Remediation of Trace Metals in a Cu-Contaminated Soil by Addition of Basic Slag Phosphate”. The Second International Environmental Best Practices Conference. Cracow, Poland (**Septembre 2009**)

Articles

1- Negim O., Eloifi B., Mench M., Bes C., Gaste H., Motelica-Heino M., Le Coustumer P. 2009. “Effect of basic slag addition on soil properties, growth and leaf mineral composition of beans in a Cu-contaminated soil.” International Journal of Soil and Sediment Contamination. (BSSC-2009-0044.R1).

2- Negim O., Eloifi B., Mench M., Bes C., Motelica-Heino M., Le Coustumer P. “In situ remediation of trace metals in chromated copper arsenate (CCA)-contaminated soil using basic slag phosphate”. International Journal of Soil and Sediment Contamination (**accepted, under revision, 2009**)

3- Negim O., Mench, M., Motelica-Heino M., Fabre R., Gauthier A., Le Coustumer, P. “Physico-chemical soil properties and trace elements distribution in contaminated soil”. International Journal of Soil and Sediment Contamination (**Submit 2009**).

4- Negim O., Amin F., Huneau F., Motelica-Heino M., Le Coustumer, P. “Slag characteristics used as an alternative technology for copper contaminated soil remediation” .Waste Journal (**Submit 2009**).