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Les effets d'amendements sur la fonctionnalité des sols de potagers contaminés par les éléments métalliques et sur la réduction des dangers environnementaux et sanitaires

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Résumé

Le besoin de nature en ville, l'engouement pour le « manger sain » et le contexte socio-économique difficile contribuent au développement du jardinage en milieu (péri)-urbain. Les collectivités sont régulièrement sollicitées pour la création de jardins collectifs. Or, de par leurs contextes environnementaux et historiques, les sols de potagers sont des milieux complexes, encore peu connus ; leurs fonctionnements peuvent être fortement perturbés par des dégradations physiques, chimiques et biologiques. Leur contamination peut même présenter un danger sanitaire notamment, en lien avec l'ingestion de particules de terre ou de légumes. Parmi les techniques pouvant améliorer le fonctionnement des sols et influer sur le comportement des polluants, notamment métalliques, l'ajout d'amendements tels que le compost de déchets verts, les produits phosphatés et carbonatés, les zéolites naturelles ou synthétiques, ou les sous-produits industriels (boues rouges, grenailles de fer, oxy-hydroxydes de fer) sont cités comme pouvant réduire la mobilité et la biodisponibilité des éléments métalliques. Se posent néanmoins les questions de l'efficacité de ces amendements et sa pérennité. La gestion des amendements, qu'ils soient organiques ou minéraux, pose toutefois question puisque ces derniers peuvent présenter des contaminants métalliques et/ou organiques. Or, le recours aux amendements comme méthode de gestion des sols de potagers et les risques sanitaires sur sols amendés restent encore assez peu étudiés.

Le sujet de la thèse vise à étudier l'intérêt d'amendements organique et minéraux, pour gérer des sols de potagers urbains présentant des contaminations anthropiques modérées. Il s'agit d'évaluer le potentiel de ces amendements (utilisés seuls ou en mélange) pour réduire de façon durable la phytodisponibilité des polluants métalliques ainsi que l'exposition des jardiniers et de leur famille. Des expérimentations *in situ* seront réalisées dans différents contextes environnementaux et urbains et s'appuieront en amont sur des expérimentations *ex situ* visant à sélectionner le choix des amendements étudiés.

Abstract

The need for nature in the city, the craze for "healthy eating" and difficult socio-economic contexts contribute to the development of gardening in (peri-)urban areas. Communities are regularly solicited for the creation of collective gardens. However, due to their environmental and historical contexts, the soils of vegetable gardens are complex environments, still little known; their functioning can be strongly disturbed by physical, chemical and biological degradation. Their contamination can even present health hazards, particularly in connection with the ingestion of soil particles or vegetables. Among the techniques that can improve the functioning of soils and influence the behavior of pollutants, especially metallic ones, the addition of amendments such as green waste compost, phosphate and carbonate products, natural or synthetic zeolites, or industrial by-products (red mud, iron shot, iron oxy-hydroxides) are cited as being able to reduce the mobility and bioavailability of metallic elements. However, the effectiveness of these amendments and their durability are still in question. The management of amendments, whether organic or mineral, raises questions since they may contain metallic and/or organic contaminants. However, the use of soil amendments as a method of managing vegetable garden soils and the health risks on amended soils are still relatively unstudied.

The subject of this thesis is to study the interest of organic and mineral amendments to manage urban vegetable garden soils with moderate anthropogenic contamination. The aim is to evaluate the potential of these amendments (used alone or in mixtures) to reduce in a sustainable way the phyto-availability of metallic pollutants as well as the exposure of gardeners and their families. In situ experiments will be carried out in different environmental and urban contexts and will be based on ex situ experiments aimed at selecting the choice of the studied amendments.

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Preamble

The work carried out in the framework of this thesis was performed at the Laboratoire de Génie Civile et géo-Environnement (LGCgE) located at JUNIA – ISA Lille. The thesis was financed by JUNIA – ISA Lille during the three years of enrollment at University of Lille's doctoral school of Science de la Matière, du Rayonnement et de l'Environnement (SMRE).

The research carried out during this work is based upon the POTAGERS project, financed by ADEME since 2019 for a duration of 3 years (APR Graine 2017, grant n° 1972C0018). This project brings together LGCgE of JUNIA – ISA Lille as the coordinator, the University of Lille, AgroParisTech-INRAe, IRSTV (FR CNRS 2488), Ineris, and Groupe Agriopale, in the general objective of evaluating the remediation potential of a wide variety of mineral and/or organic amendments in vegetable garden soils in various French pedoclimatic and contamination contexts. To valorize this research, the article entitled "Effects of inorganic and organic amendments on the extractability of As, Cd, Pb and Zn in kitchen garden soils" was written with these project partners and published in 2022 in the journal Advances in Environmental and Engineering Research (Schnackenberg et al., 2022).

Another part of this thesis work focusing on contaminated composts was subject of an article entitled "Is the co-application of self-produced compost and natural zeolite interesting to reduce environmental and toxicological availability in metal-contaminated kitchen garden soils?," written with Madeleine Billmann, Géraldine Bidar, Francis Douay, and Aurélie Pelfrêne. This article was submitted in 2022 to the journal Environmental Geochemistry and Health, where it is currently under review. Two additional articles are currently in preparation.

The work carried out in this thesis has also been presented at two conferences. A poster entitled "Effects of amendments on the extractability and phytoavailability of As, Cd, Pb, and Zn in contaminated urban kitchen garden soils" was presented at the World Soil Science Congress in Glasgow in August 2022, and another entitled "Effects of amendments on the mobility, bioaccessibility, and phytoavailability of As, Cd, Pb, and Zn in contaminated urban kitchen garden soils" was presented at the 11th Conference on Soils of Urban, Industrial, Traffic and Mining Areas in Berlin in September 2022.

It is also important to note that the health crisis caused by the COVID-19 pandemic had non-insignificant impacts on this dissertation work begun in October 2019. *Ex-situ* experiments and associated analyses have been affected as their implementation has been delayed.

Introduction

A recent increase in urban sprawl, the consequential desire for nature in cities, increasingly uncertain socio-economic conditions, and a need for food security has led to the spike in popularity of urban and peri-urban small-scale food growth for personal and familial consumption (Clavin, 2011; Church et al., 2015; Loopstra et al., 2015; Scheromm & Mousselin, 2017; ADEME, 2019). Consequently, increasingly more people are cultivating their own crops produced on in ground small parcels, also known as kitchen gardens (Edmondson et al., 2014; Palau-Salvador et al., 2019; Torres et al., 2018). This includes both private gardens, most commonly adjoining homes, and community gardens. The self-produced foods hailing from these gardens can have the advantage of contributing to both healthy eating habits and environmental and ecologically sustainable practices (Cameron et al., 2012; Clavin, 2011; Draper & Freedman, 2010; Martin et al., 2017).

In this urban and peri-urban context, kitchen garden (KG) soils can be affected by past and present human activities in various ways. Some KG are built on available or abandoned space, or on marginal areas close to railways, main roads, nearby industrial areas, and other heavily used sites. In comparison with agricultural or forest soils, urban soils are more complex, often very heterogeneous, and depending on their history and/or environment, may have poor agronomic qualities (El Khalil et al., 2008; Nehls et al., 2013). These soils are also affected by inorganic contaminants (such as As, Cd, Pb) of various origins and in variable concentrations (Pruvot et al., 2006; Antisari et al., 2015; Bretzel et al, 2018). Contamination of soils may result from geogenous origins where contaminants are linked to geochemical backgrounds and the erosion of bedrock containing mineralized metal(loid)s), and from anthropogenic origins. This includes past and/or present discharges of industrial or urban origins (*e.g.*, combustion of fossil fuels, automobile traffic, incineration of household waste) (Kabata-Pendias, 1993; Bruand, 2002; Szolnoki et al., 2013; Amato-Lourenco et al., 2017(Alloway, 2004; Ashrafzadeh et al., 2018; Kandic et al., 2019; Norra et al., 2001; Turnbull et al., 2019; Yu et al., 2018). Cultivation practices used by gardeners (*e.g.*, use of phytosanitary products, mineral fertilizers, contaminated irrigation water) and the unregulated manipulation of these areas also contributes to anthropogenic soil contamination (Huq et al., 2006; Meuser, 2010; Burghardt et al., 2018; Gupta et al., 2019; Joimel et al., 2016; Morel et al., 2005; Rai et al., 2019).Metal(loid)s in soils can present sanitary risks which vary by element, exposure pathway, vector, and receptor (Laidlaw et al., 2017). Regarding KG, humans can be exposed via ingestion/inhalation of soil particles and consumption of contaminated vegetables (Bacigalupo and Hale, 2012; Hough et al., 2004; Izquierdo et al., 2015; Pelfrêne et al., 2013; Warming et al., 2015). Among these pathways, ingestion can present the main exposure route associated with the cultural practices of gardening (Fernandez-Caliari et al., 2019). In humans and other living organisms, some metallic elements such as Co, Cu, Cr, Fe, Mg, Mn, Mo, Ni, Se and Zn are required for normal biological functions in low concentrations (Tchounwou et al., 2012). However, in higher concentrations, they have the potential to pose varying health risks. Non-essential metallic elements include As, Cd, and Pb, which pose risks at any concentration. Over exposure can lead to anemia, cardiovascular disease, cancers, osteoporosis, and damage to various organs including the kidney, brain, and skin (Jarup, 2003).

Metallic contamination of KG soils can also result in effects on vegetables, including low yields and poor product quality, as well as potentially negative impacts on the environment (Ure, 1996; Das et al., 2016; Liénard et al., 2016 Tang et al., 2016; Szolnoki et al., 2013). Metal(loid)s can enter the food chain via root and/or foliar uptake and translocate into edible parts of vegetables (Rai et al., 2019; Bidar et al., 2020). Several studies have shown that vegetables grown in metal(loid)-contaminated soils may not show any visible signs of contamination, although the concentration of metals in its edible part could pose risk for consumers (Gupta et al., 2019; Joimel et al., 2016; Morel et al., 2005; Rai et al., 2019). Notably, some commonly grown garden vegetables are capable of accumulating high amounts of metal(loid)s (Bidar et al., 2020). Root vegetables like potatoes and carrots are reported to accumulate Pb (Alexander et al., 2006), herbs are noted for their ability to uptake As, Pb, and Cr (Finster et al., 2004, Saumel et al., 2012), and leafy vegetables like lettuce and spinach tend to accumulate the high concentrations of Cd, Pb, Zn, As, Cr, and Ni (Zhou et al., 2016a; Pourrut et al., 2012; Roba et al., 2016; Warming et al., 2015; Pruvot et al., 2006; Pilgrim & Schroeder, 1997). Plants sold on the market are thus monitored for their quality in order to limit risk for consumers. In Europe, vegetables are regulated by the European Directive of August 2021 modifying the European Directive no. 1881/2006, which defines the maximum permissible concentrations of metals such as Cd and Pb in sellable fruits, legumes, and vegetables by their type and tendency to uptake metal(loid)s. However, these regulations do not apply to unsold kitchen garden vegetables grown by individuals or communities grown for personal use.

Physico-chemical parameters of the soils including but not limited to pH, cation exchange capacity, organic matter, nitrogen, phosphorous, carbonates, clay content, and biological activities are among the main factors that influence the accumulation of metal(loid)s in crops (Hough et al., 2004; Nabulo et al., 2011; Zhang et al., 2018). According to these parameters and their temporal evolution, only a fraction of the metal(loid)s is available for the biota in the soil. In general, reducing the availability of pollutants can play a key role in limiting their phytoavailability and potential toxicity via ingestion (and to a lesser extent, inhalation) of dust/soil particles and via consumption of vegetables (Clarke et al., 2015; Izquierdo et al., 2015; Zagury et al., 2016; Waterlot et al., 2017).

There are various potential remediation strategies to limit the availability of metal(loid)s in soils and these management methods depend upon the degree of contamination of the soil. Remediation technologies for contaminated soils can thus be divided into different intensities, including (i) gentle *in situ* remediation, (ii) harsh *in situ* restrictive soil measures, and (iii) harsh *in situ* or *ex situ* destructive soil measures (Gupta *et al.,* 2013). In selecting appropriate remediation options, several factors are to be considered, such as: (i) cost, (ii) long-term effectiveness/permanence, (iii) commercial availability, (iv) general acceptance, (v) applicability to high metal concentrations, (vi) applicability to mixed wastes (metal(loid)s and organics), (vii) metal(loid) toxicity reduction, (viii) metal(loid) mobility reduction, and (ix) metal(loid) quantity reduction (Wuana & Okieimen, 2011). Until the 1980's, highly contaminated French KG soils (10 – 24 mg kg^{-1} Cd and 682 - 3280 mg kg^{-1} Pb) were often excavated partially or fully in order to reduce their total metal(loid) concentrations, and then replaced with uncontaminated soil (Lanphear et al., 2003; Douay et al., 2008; Khalid et al., 2016). This soil replacement technique is not suitable to remediate large areas, due to the inferred costs and logistics of the storage and treatment of the removed soil (Douay et al., 2008; Yao et al., 2012; Khalid et al., 2016). Although this technique effectively reduces environmental contamination very quickly, it is limited regarding (i) costs of soil excavation, transport and disposal, (ii) eventual soil re-contamination from the surrounding soils, and (iii) the risk of soil fertility loss.

The most sustainable remediation strategies, however, maintain and/or restore soil functions and improve their agronomic potential while minimizing environmental and human risk. A feasible way to do this is via gentle remediation options (Puschenreiter et al., 2018), among which exists the relatively rapid and easily applied technique of applying amendments to soil (Kumpiene et al., 2008; Khan et al., 2017; Puschenreiter et al., 2018). This can be a cost-effective, environmentally friendly, and sustainable way of reducing metal(loid) availabilities while maintaining a low environmental footprint (Hou & Al-Tabbaa, 2014; Tajudin et al., 2016; Wiszniewska et al., 2016). Additionally, gardeners can easily employ this technique, because many commercialized amendments are already regularly used to improve soil quality. In addition to stabilizing soil and adding macro- and micro-nutrients, inorganic and organic soil amendments can act as *in situ* metal(loid)-immobilizers (Kumpiene et al., 2008; Sharma and Nagpal, 2018). Thus, amendments might limit the risk of food chain contamination by reducing metal(loid) uptake by crops (Wang et al., 2014; Khan et al., 2017; Sharma and Nagpal, 2018). The effect of high rates of industrial products used as amendments (sludges, red muds, iron grit, furnace slag) on contaminated soils is well documented (Simon et al., 2015; Clemente et al., 2019; Bes & Mench, 2008; Li et al., 2014; Gertler et al., 2013). These amendments, however, can be contaminated themselves or invoke environmental issues, and are thus not appropriate for KG soils. Kitchen garden soils are characterized by distinct physicochemical properties (*e.g.*, pH, organic matter and carbonates contents) and require to be of a certain quality in order to be able to produce food (Joimel et al., 2016; Burghardt et al., 2018).

Thus this thesis consists in studying a range of amendments to manage urban KG soils with moderate geogenic and/or anthropogenic contamination and assessing the effects of these amendments on the physico-chemical characteristics of soils, the mobility of metal(loid)s and more generally on their efficiency to reduce the environmental and toxicological availabilities of metal(loid)s.

This manuscript is composed of seven chapters:

- Chapter 1 describes relevant information pertaining to soil and metal(loid) characteristics in kitchen garden soils, as well as a selection of amendments used to manage metal(loid)s in soils. This is followed by a presentation of the objectives of the thesis;
- Chapter 2 details a general presentation of the approach, materials, and methods used to meet the objectives;
- Chapter 3 presents and discusses the results of the effects of several soil amendments on physicochemical soil parameters and metal(loid) environmental availability;
- Chapter 4 is dedicated to the study of the amendments identified as the most relevant in Chapter 3 in combination with a vegetal model, and their effects on environmental availability and phytoavailability of metal(loid)s;
- Chapter 5 is devoted to the specific study of the environmental and toxicological availability of Cd, Pb, and Zn hailing from a self-produced compost, applied to KG soil alone or in co-application with a natural zeolite;
- Chapter 6 focuses on the effects of the proposed soil management on human health through the assessment on population exposure related to the non-intentional ingestion of soil particles in moderately contaminated KGs by using the oral bioaccessibility of metal(loid)s;
- Chapter 7 is devoted to a general discussion of the results obtained, in order to provide a global view of amendment efficacy for As, Cd, Pb, and Zn. The amendments' environmental, agronomic, and toxicological interest for the three moderately-contaminated kitchen garden soils is summarized and links among soils and common effective amendments are made. Perspectives for future considerations and studies are also discussed.

Chapter 1: Management of metal(loid)-contaminated kitchen garden soils

Chapter 1: Management of metal(loid)-contaminated kitchen garden soils

1. Behavior of metal(loid)s in soils

Metal(loid)s are metallic chemical elements that have a high relative density greater than 5 g/cm^3. Because of their density and solubility, metal(loid)s are most commonly found in the soil and water rather than the air. The most commonly found metallic elements are As, Cd, Cu, Cr, Hg, Mn, Ni, Pb, and Zn (Wuana & Okieimen, 2011). In humans and other living organisms, essential metal(loid)s such as Co, Cu, Cr, Fe, Mg, Mn, Mo, Ni, Se and Zn are required for normal biological functions in low concentrations (Tchounwou et al., 2012). However, in higher concentrations, they pose varying health risks. Non-essential metallic elements include As, Cd and Pb, which pose risks at any concentration. These metal(loid)s, among others, have the potential to accumulate in soil and living organisms, as they are non-biodegradable (Ali et al., 2019; Gu & Ruei-Lung Lin, 2010; Järup, 2003).

Metal(loid)s occur naturally in the environment and soil matrix as a result of the weathering of underlying bedrock, and volcanic eruptions (Wuana & Okieimen, 2011; Palansooriya et al., 2020). In France, bedrock and its composition vary greatly by nature (granite, gneiss, chalk, schist…), and thus the background levels of metal(loid)s and their reactivity also highly vary according to region. Though natural, geogenous metal(loid) concentrations can still be mobilized and pose a risk. Furthermore, human activity can render the metal(loid)s in the surface layers of soil more accessible. In urban and peri-urban areas, metallurgy (mines, smelters), industry and industrial waste (batteries, paints), construction, district heating, road traffic, manufacturing, agriculture, and cultural practices (pesticides, fertilizers, and irrigation) are contributors to elevated anthropogenic metal(loid) concentrations and their redistribution from atmospheric and waste deposits (Tchounwou et al., 2012; Li et al., 2019; Palansooriya et al., 2020; Rai et al., 2019).

Metal(loid) concentrations, expressed in term of total or pseudo-total concentrations, do not directly indicate mobility or the potential transfer to organisms (Ullrichet al., 1999; Ure & Davidson, 2007). In soils, metal(loid)s are linked to soil constituents. Depending upon the strength of this link, some of these elements become more or less mobile. Soil physico-chemical parameters (*e.g.* pH, carbonates, organic matter content) and climatic conditions determine metal(loid) distribution and mobility in the soil, and availability in the environment and for man. The risk linked to the presence of metal(loid)s in the environment also depends on the quantity and nature of this elements.

1.1 Distribution of metal(loid)s in soils

An element's distribution is determined by its proclivity to shift to different soil fractions with more or less energetic binding strength (Juste, 1988). This distribution is linked to the chemical form or phase of the metal(loid) in question (Figure 1-1). This division of metal(loid)s in different forms is not static, and changes with shifts in soil physico-chemical parameters and environmental conditions (*e.g.* pH, organic matter content, available phosphate content, moisture content, temperature). These characteristics help determine their distribution in different forms. In order from least to most mobile, metal(loid)s can be found (i) in crystalline, residual mineral structures resulting from either bedrock or secondary transformation processes, (ii) adsorbed to iron, aluminum, and/or manganese oxides or hydroxides, (iii) sequestered in vegetal or animal residue, (iv) complexed or part of organic macro-molecules, (v) as cations or anions adsorbed to clay minerals or organic matter (OM), and (vi) a colloids dissolved in the soil solution (Baize, 1997). **Sequential extractions** are a commonly used successive chemical extraction that allows for the determination of these different soil fractions. These are used to help determine the different phases to which soil metal(loid)s are fixed, defined as different soil fractions determined by a series of complex successive sequential reactions first described by Tessier (1979) and normalized by a BCR protocol. These phases correspond to a 4-step chemical method for determining some the different theoretical soil metal(loid) forms as determined by Baize (1997).

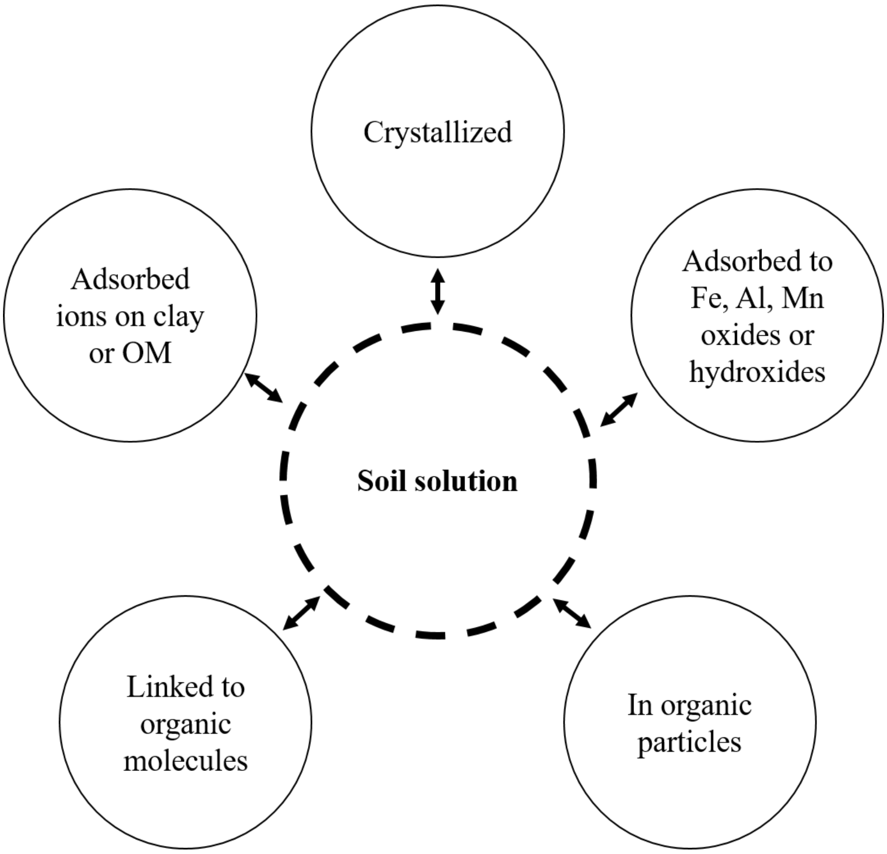

Figure 1-1. Chemical distribution of metal(loid)s in soils (adapted from Baize, 1997)

1.2 Mechanisms of metal(loid) mobilization in soil chemical fractions

The behavior of metal(loid)s in soil depends on their chemical form and speciation, which depend on agronomic conditions (Wuana & Okieimen, 2011). Generally, elements trapped in a crystalline network or in their mineralized form have a low migration ability. In other chemical fractions, according to agronomic conditions (*e.g.* pH), metal(loid)s can undergo a series of complex interactions with soil constituents (*e.g.* clay, carbonates, organic matter, and oxides of Fe, Mn and Al) which can impact their mobility in the soil (Wuana & Okieimen, 2011; Huang et al., 2016; Kachova, 2016; Chaw et al., 2018) (Figure 1-2). This mobility is enhanced with erosion, anthropogenic activity (*e.g.* mining, smelting), when the metal(loid) retention capacity of the soil is overloaded, or when metal(loid)s interact with the disposed waste or soil additives (McLean et al., 1992). Although, metal(loid)s are not degradable, some of them (As, Mn, Cr) can be transformed to other oxidation states in the soil which reduce their toxicity and mobility (McLean et al., 1992; Palansooriya et al., 2020). The reactions incurring metal(loid) immobilization include precipitation, adsorption, and complexation (Figure 1-2).

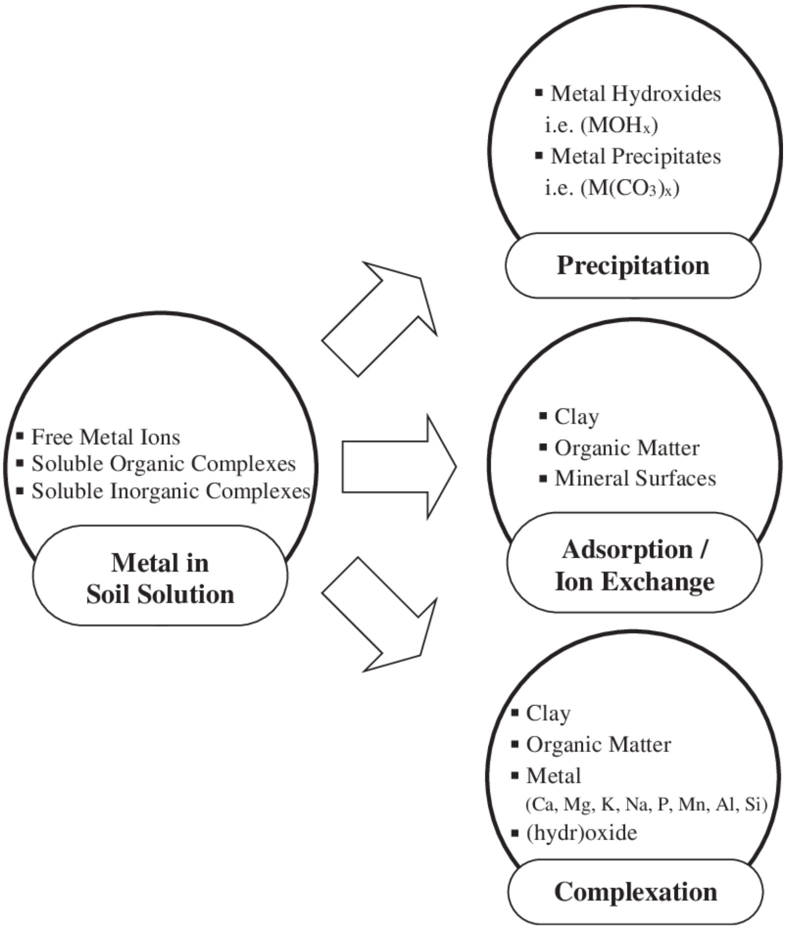

Figure 1-2. **Mechanisms of metal(loid) immobilization via interactions with soil constituents (Chaw et al., 2018)**

1.2.1 Precipitation

Precipitation appears to be the predominant process of metal immobilization in soils with a nearly neutral pH in the presence of anions. These anions include sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), hydroxide (OH^-), and phosphate ($H_2PO_4^-$). Precipitation forming the hydroxides and carbonate compounds noted in Figure 1-2 occurs especially when the concentration of metal ion is high (Adriano, 1986; Bolan et al., 2003). Metalloids that form anionic species, such as Cr and As, have been reported to form precipitates with cations, such as Ca^{2+} at a pH near 6 (Cui et al., 2019).

1.2.2 Adsorption

Adsorption is the process by which charged ions are attracted to the charged soil surface by electrostatic attraction and through the formation of specific bonds. When electrostatic attraction controls metal adsorption, the adsorption capacity of the soil is determined by its cation-exchange capacity (CEC), determined by soil minerals, clay, and organic matter (Figure 1-2). Cation exchange is important because most metals occur in cationic form in the soil (Adriano, 1986). However, there is also a corresponding anion exchange for elements that bind with oxygen (*e.g.*, Se, As, Cr, Sb, V, Mo) and thus occur as oxyanions (Adriano, 1986). According to Bolan et al. (2003), the effect of inorganic and organic anions on the adsorption of metal(loid)s could be explained by, (i) the complexation of anions and metals, thereby reducing their adsorption onto soil particles, (ii) the increase of the negative charge on soil particles due to the specific adsorption of ligand anions, thereby increasing the adsorption of metal cations, and (iii) the anion sorption, such as phosphate $H_2PO_4^-$, which strongly compete with metal anions, such as arsenate and selenate, resulting in their desorption.

1.2.3 Complexation

Complexation is the reaction of a metallic ion and a molecular or ionic ligand containing at least one atom with an unshared pair of electrons. In complexation processes, individual atom groups, ions or molecules combine to form one large ion or molecule. This atom or ion is the central atom of the complex that helps in bonding with other atoms as well as unshared electrons (Tewari et al., 2018). As seen in Figure 1-2, soil constituents such as OM and clay help complex metal(loid)s. Metal(loid) mobility can also be highly influenced by ligand concentration and properties. Ligands that complex metal(loid)s can include chelating agents (e.g. amino acids), partially oxidized biodegradation products, and humic materials (Speight, 2018).

1.3 Availability of metal(loid)s in soils

Availability of metallic elements in soils can be more specifically defined in terms of environmental availability, environmental bioavailability, toxicological bioaccessibility, and toxicological bioavailability (ISO 17402) (Figure 1-3).

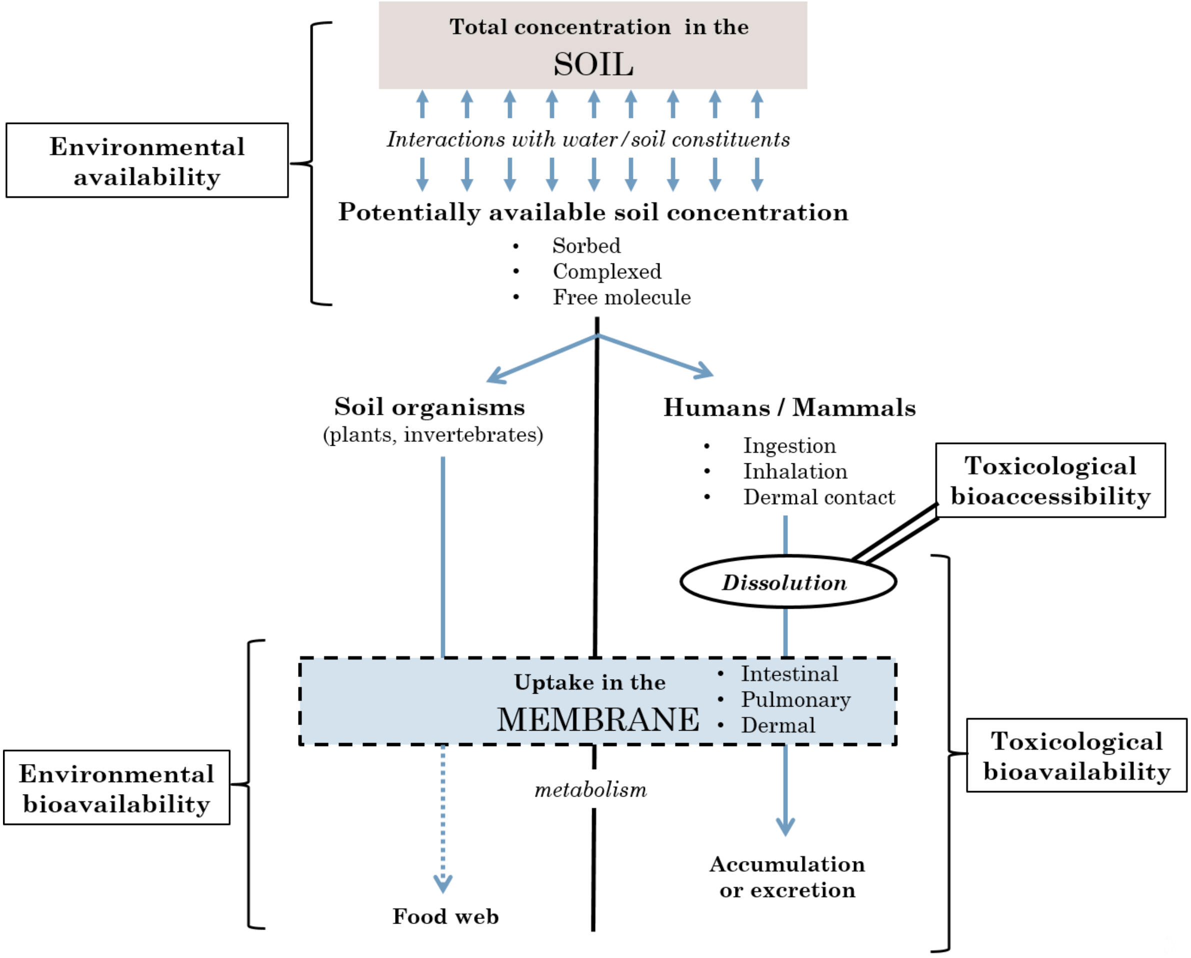

Figure 1-3. **Links between the different notions of availability (environmental availability and bioavailability, and toxicological bioaccessibility and bioavailability) (adapted from EN ISO 17402)**

1.3.1 Definitions

Environmental availability can be defined as the fraction of pollutant physico-chemically driven by desorption processes potentially available to organisms. It includes the fraction of metal(loid)s in any environmental matrix that can be physically, chemically, and biologically influenced (Fernandez-Caliari et al., 2019).

Environmental bioavailability is specific to soil organisms and corresponds to the environmentally available metal(loid) which a plant or invertebrate uptakes through physiologically driven processes. Specifically, **phytoavailable metal(loid)s** are that which are environmentally bioavailable in plants, and are measured in the organism (DTSC, 2019). Metal(loid)s can enter a plant via root and/or foliar uptake.

These pollutants can enter roots in their ionic or chelated forms dissolved in soil pore water, and these elements are either stored via compartmentalization or sequestration in underground plant parts, or transported to aerial parts through the xylem (Kabata-Pendias, 2011; Saraswat and Rai, 2011; Kumar & Aery, 2016; Mukherjee et al., 2016; Shahid et al., 2017; Antoniadis et al., 2017; Gupta et al., 2019). Leaves can also uptake metallic elements after their deposition from the atmosphere, specifically for leafy plants with high surface area. This is because cuticles adsorb pollutants through stomatal openings (Schreck et al., 2014; Shahid et al., 2017). When a metal(loid) enters plant tissues, it can cause physiological, morphological, and biochemical toxic effects resulting from disrupted nutrient- and water- uptake and transport, altered nitrogen metabolism, disrupted ATPase activity, and reduced rates of photosynthesis. At the cellular level, excessive metal(loid) exposure can increase the production of reactive oxygen species (ROS), thereby altering cell cycles, division, and chromosomal aberrations (Yadav, 2010). This can interfere with plant growth, interrupt plant photosynthetic apparat in chloroplasts, and cause stomatal closure (Shahid et al., 2014). These disruptions can cause physical signs of plant injury such as browning of roots, necrosis, chlorosis, leaf rolling, and reduced biomass production (Gupta et al., 2013). Thus, the amount of uptaken metal(loid) in a given plant can have implications on both plant health.

Toxicological bioaccessibility and **bioavailability** are specific to humans, who can be exposed to contaminated soil via different routes, including ingestion and inhalation of soil particles and dust, and dermal contact. Bioaccessibility corresponds to the fraction of a contaminant released or dissolved from the soil that can cross a biological membrane. This can happen under *in vitro* conditions in physiological fluids (*i.e.*, digestive fluids for ingestion, lung fluids for inhalation, and sweat fluid for dermal contact). Of these, ingestion is the main exposure route for metal(loid)s (Paustenbach, 2000). Specifically, oral bioaccessibility refers to the fraction of a contaminant that is soluble in the gastrointestinal environment and potentially available for absorption through the intestinal membrane (Ruby et al., 1999). This type of bioaccessibility includes all physical, chemical and microbiological processes in the human organism, from mastication in the mouth to the precipitation process in the intestine. Bioavailability is defined as the internal concentration of metal(loid)s accumulated in the systemic circulation and/or organs (Oomen et al., 2002) (Figure 1-4).

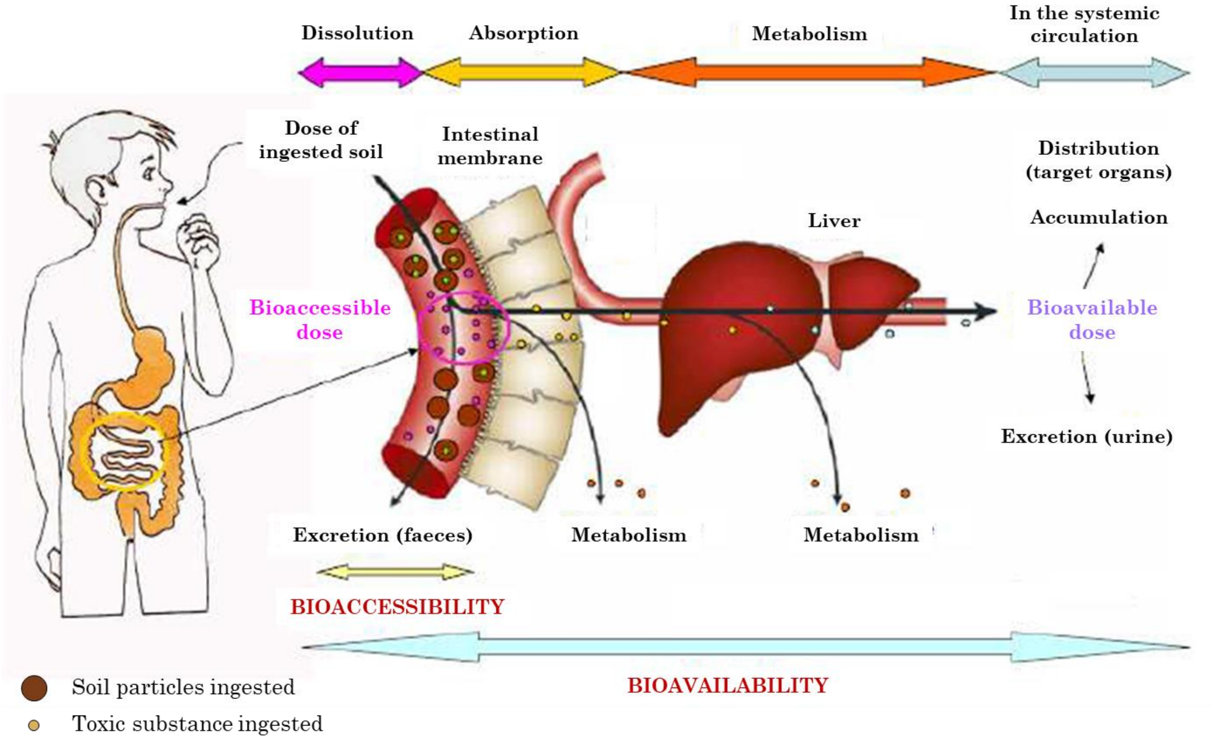

Figure 1-4. Toxicological bioaccessibility and bioavailability of ingested soil metal(loid)s (Dabin et al., 2012)

1.3.2 Measurements

Chemical and biological methods allow for the assessment of availability of metal(loid)s in soil (Figure 1-5). Chemical measurements examining environmental availability and bioaccessibility consider processes before the passage of metal(loid)s through the membranes. The objective of these methods is to predict the amount of contaminants taken up by organisms. Biological methods correspond more directly to the exposure of organisms to soil or soil eluates and thus provide a way to monitor effects on the exposed living organisms. These methods measure processes after the passage of metal(loid)s through the membranes, as in the case of environmental and toxicological bioavailabilities. Biological methods consist of measuring the contaminant found directly in the organism (*e.g.*, plants). In case of environmental bioavailability, the concentration of metal(loid)s is evaluated in the biomass of these plants (phytoavailability), which allows for the determination of a bioconcentration factor. The measurement of toxicological bioavailability requires the use of *in vivo* tests on animals or humans. However, these methods are often time-consuming, expensive, difficult to implement, and may raise ethical issues. Their measurement will thus not be included in this chapter. Chemical measurements, however, may replace biological testing with a reasonable amount of accuracy, if a correlation between the resulting chemical values and effect or accumulation has been demonstrated (e.g., *in vivo* availability of ingested Cd, Pb and UBM oral bioaccessibility). These measurements and will be detailed in this section in terms of environmental availability and bioaccessibility methods.

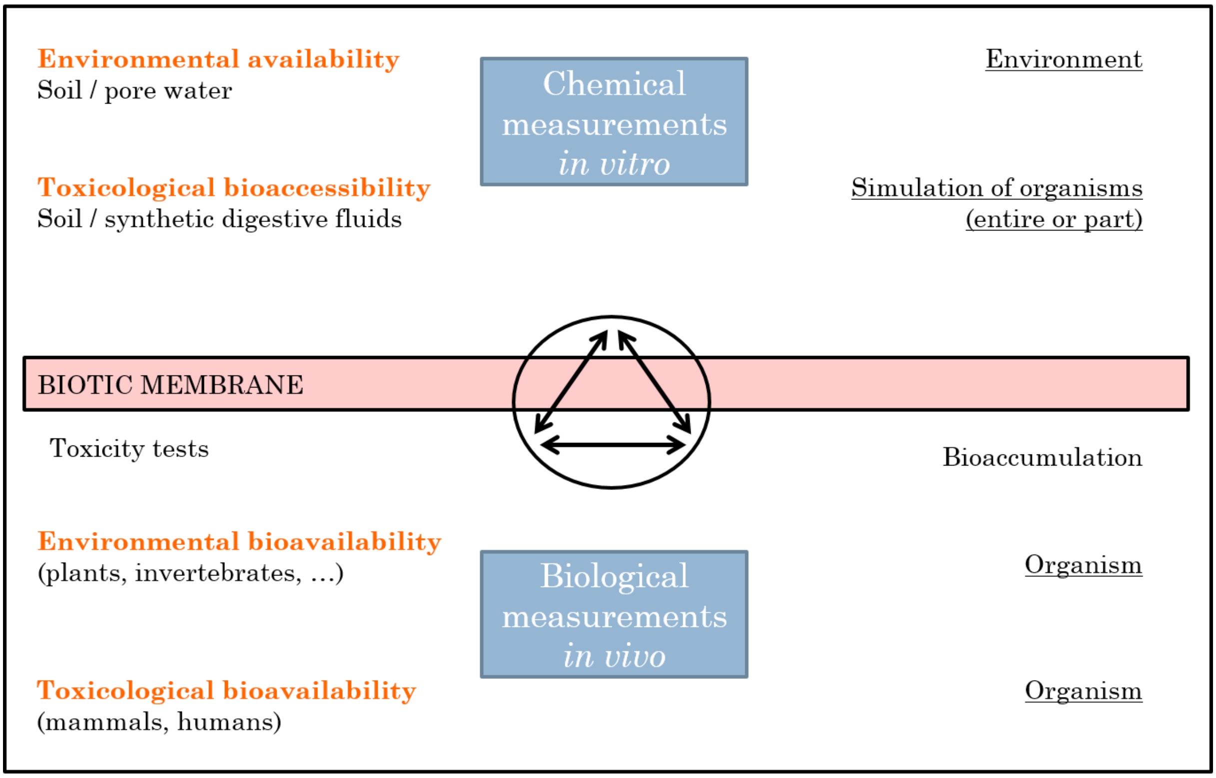

Figure 1-5. **Metal(loid) availability and accessibility methods by their chemical and biological measurements (adapted from EN ISO 17402)**

Environmental availability measurements

The fate and behavior of metal(loid)s are highly dependent upon their availability, which can be assessed in soils using sampling systems, simple extractions (with water, diluted salts, chelating agents or diluted salts), or successive chemical extractions (Figure 1-5) (Vijver, 2022).

Sampling systems can allow for the assessment of the environmental availability of metal(loid)s for plants. Specifically, **pore water extractions** carried out over time with porous microsampling needle *in situ* have been shown to correlate with plant uptake, as it is linked with readily available soil metal(loid)s (Vijver, 2022). The use of **passive extractions** such as diffusive gradients in thin films (DGT) help mimic pore water concentration according to the amount of metal(loid)s accumulated in a resin covered with a diffusive gel placed in the pore water in the soil (Zhang et al., 1998). This allows for the investigation of the soil pore water compartment, and the mimicry of the absorption of metal(loid)s by biological membranes.

Similarly, **water extractions** simulate this soil fraction, but via an extraction which favors the displacement of metal(loid)s. Other simple extractions include **diluted salt extractions**, globally, allow for the estimation of easily available and/or exchangeable metal(loid)s, particularly cationic metals bound to negatively charged soil particles. Unbuffered $CaCl_2$ and NH_4NO_3 solutions are favored in order to avoid interference with soil pH, and for their correlations with uptake in soil invertebrates and sometimes plants (Gupta & Aten, 1993; Novozamsky et al., 1993; Zhang et al., 2019). These relatively weak extraction types are also examples or measures of chemical solubility. Thus they are useful indicators of metal(loid) reactivity in typical environmental conditions, especially considering that soils have wide ranges of physical chemical properties that impact uptake. **Chelating agents**, specifically those which are buffered at a specific pH such as EDTA or DTPA in their sodium or ammonium salt forms, can provide an estimate of less available metal(loid)s. This can sometimes correspond with the bioavailability for some plants, and humans, as this destroys bonds between metal(loid)s and organic matter as would some *in vitro* conditions. Extractions with **diluted acids**, like HCl for example, can help determine labile or anthropogenic metal(loid)s (Snape et al., 2004; Andrews & Sutherland, 2004).

Oral bioaccessibility measurements

To mimic the availability of metal(loid)s in the human gastrointestinal tract (*i.e.*, bioaccessibility), many *in vitro* extraction procedures were developed to be applied to soils and to inorganic pollutants (in particular As, Cd, and Pb). These tests can be grouped into three categories:

- <u>Simple chemical tests, which correspond to</u> acid extraction processes and consist of a single phase (the stomach phase). The protocols use inorganic chemical reagents (mainly hydrochloric acid) without any physiological conditions (no regulation to body temperature of 37°C);
- <u>Simple physiological tests, which</u> consist of a single phase (usually the gastric phase) and use few chemical reagents (notably glycine, phosphate, HCl), but a physiological condition is set (body temperature regulated to 37°C);
- <u>Physiological tests with gastrointestinal analogues, which</u> consist of several phases (salivary, gastric and/or intestinal) and require a greater number of reagents, but especially complex reagents corresponding to intestinal analogues (*e.g.*, enzymes, bile salts). Physiological conditions are maintained as well.

Frequently used oral bioaccessibility tests include PBET (Physiologically Based Extraction Test, Ruby et al., 1993), SBET (Simplified Bioaccessibility Extraction Test, Medlin, 1997), DIN (German standard 19738, Hack and Selenka, 1996), RIVM (Rijksinstituut voor Volksgezondheid en Milieu in vitro digestion model, Sips et al, 1998), TIM (the TNO Gastrointestinal Model, Minekus et al., 1995), and UBM (Unified Bioaccessibility Method, ISO 17924, Denys et al., 2012).

1.4 Influence of soil physico-chemical parameters on soil-metal(loid) behavior

Metal(loid) mobility and (bio-)availability in soils are mainly influenced by their physico-chemical parameters (texture, pH, organic matter content, carbonate content, phosphate content, cation exchange capacity, biological activity, and oxidation-reduction potential) (McLaughlin et al., 2011). However, anthropization, disturbance, diverse contamination sources, and diverse cultural practices of garden management can contribute to the large variability in kitchen garden soil physico-chemical characteristics (Morel et al., 2005; Pruvot et al., 2006; Bretzel et al., 2018). These particularities influence soil-metal(loid) interactions by impacting the availability of metal(loid)s for uptake in plants and ingestion in humans.

1.4.1 Soil type/ texture

The capacity of soils to retain metal(loid)s partly lies with their texture which is typically classed by particle size into sand (0.05 – 2 mm), silt (0.002 – 0.05 mm), or clay (<0.002 mm) (Sheard, 1991) . Soils high in clay minerals (*e.g.,* kaolinite, smectite, montmorillonite) exhibit higher metal(loid) adsorption capacities due to the small size of the clay particles, the presence of clay minerals (*i.e.,* hydrous aluminosilicates), organic matter, Fe–Mn oxides and sulfides (Rieuwerts et al., 2015; Bradl, 2004; John & Leventhal, 1990; Palansooriya et al., 2020). The large surface areas and negative layer charge of tetrahedral and octahedral sheets of phyllosilicates explain the adsorbent proprieties of clays. Chemical species such as metallic cations interacts generally with clay through ion exchange or adsorption, both being reversible (Otunola et al., 2020). Regarding adsorption processes, these can be specific or non-specific (Gupta & Bhattacharyya, 2012; Du et al., 2019). Non-specific adsorption takes place primarily at permanently charged sites on mineral surfaces. This in turn forms complexes bound by electrostatic forces. Specific adsorption is stronger, and typically takes place at variable charge sites (e.g., Si-OH and Al-OH sites) to form complexes on mineral surfaces (Uddin, 2017; Zhu et al., 2019; Li et al., 2022). Thus metal(loid) (*e.g.*, Pb, Zn) migration down the soil profile can also be slowed by the attenuative properties of clays (Rieuwerts et al., 2015). Kitchen garden soils are cited as containing between 1-39% of clay (Bidar et al., 2020). in urban and peri-urban environments, anthropogenic materials such as bricks, glass, plastic, and pavement might be found in various amounts in garden soils greatly contributing to soil physicochemical and contamination diversity (Bretzel et al., 2018; Morel et al., 2005; Pruvot et al., 2006).

1.4.2 pH

Due to its strong effects on solubility and speciation of metal(loid)s, pH is the main factor affecting the availability of metal(loid)s in the soil (John & Leventhal, 1990; McLean et al., 1992; Mühlbachová et al., 2005; Rieuwerts et al., 2015; Zeng et al., 2011; Zhang et al., 2018; Palansooriya et al., 2020). At a pH above 6, metal(loid)s tend to form insoluble metal mineral phosphates and carbonates, whereas at a lower pH they tend to be found as more bioavailable free ionic species or as soluble organometals. Generally, when pH increases, adsorption, mobility and stability of metals increases due to the formation of complexes and dissolution of organic matter. The trend is opposite for anionic elements such as As, Se, and Cr due to their increasing desorption with a reduction of positive charge on soil surfaces with increasing pH. Adsorption reactions of cationic metals is partly dependent on the pH due to the preferential adsorption of the hydrolyzed metal species in comparison to the free metal ion. As the pH decreases, the number of negative sites for cation adsorption diminishes while the number of sites for anion adsorption increases (Bradl, 2004). Also, as the pH becomes more acidic, metal cations also face competition for available permanent charged sites by Al^{3+} and H^{+}(Sparks, 2003; Rieuwerts et al., 2015; Draszawka-Bołzan, 2017). Kitchen garden soils typically have a pH ranging from between 3.4 to 8.6 (Bidar et al., 2020). Different cultivation practices (liming, fertilization) could explain this heterogeneity, as well as leaching effects related to the potential presence of anthropogenic carbonated materials which raise soil pH when weathered such as cement, plaster, and bricks in urban kitchen garden soils (Townsend et al., 1999; Halim et al., 2003; Hale et al., 2012; Scheromm, 2015; Bidar et al., 2020).

1.4.3 Organic matter

Organic matter (OM) accumulates at the soil surface, mainly as a result of decomposing plant material. Organic matter is important because it has the potential for the retention of metal(loid)s inputs in the surface humic layer of soils. This has important implications for metal(loid) mobility down the soil profile and for the availability of metal(loid)s plants. In addition to decomposing plant material, other organic components, such as soil fauna and microbiota (dead and alive) may also be important sinks for metal(loid)s. In terms of organic carbon, French garden soils contain of average 2.62%, as compared to an average of 1.49% for agricultural soils (Joimel et al., 2016). Adsorption and complexation are the mechanisms by which metal(loid)s are retained by OM in the soil (Rieuwerts et al., 2015). A publication by Zeng et al. (2011) showed that metal adsorption onto soil constituents declined with decreased OM content in soil. Because of organic matter's link to improved soil fertility and increased yield, kitchen garden soils are typically rich in added OM, averaging 4% (up to 10%) in comparison to an average range of 1 to 3% in agricultural soils (Morel and Schwartz, 1999; Edmonson et al., 2014; Burghardt et al., 2018; Bidar et al., 2020).

1.4.4 Carbonates

Carbonates (-CO_3) can be present in soil in many forms, the most commonly found including $MgCO_3$, $FeCO_3$, $MnCO_3$, calcium and magnesium carbonates, (($CaMg)CO_3$, dolomite) and calcium or calcite carbonates ($CaCO_3$) (Baize & Jabiol, 1995). Of these, calcium carbonates have a strong acid neutralizing property which can lead to increased soil pH and decreased metal bioavailability (Zachara et al., 1991; Rouff et al., 2006; Han et al., 2007). Studies show that many metals are more soluble, mobile and bioavailable in acidic soils (Bolan et al., 2003; Han et al., 2007). A study conducted by Wang et al. (2015) on the effect of carbonate content on the transfer of metals from soil contaminated with Cd and Ni to plants, showed that wheat harvested from soil with a depleted carbonate content had 2-3 times more Ni and Cd than wheat harvested from carbonate-enriched soil. A typical kitchen garden soil contains 0 -18% of carbonates (Joimel et al., 2016; Bidar et al., 2020). The presence of cement, bricks, and plaster in some kitchen garden soils can also increase the amount of carbonates present in a given garden (Hale et al., 2012).

1.4.5 Phosphates

Some research has shown that, phosphate ions have the capacity to immobilize metals like Pb and Cd in the soil by enhancing metal adsorption through anion-induced negative charge (*i.e.*, cation exchange capacity) and metal precipitation (Bolan et al., 2003; Nzihou & Sharrock, 2010). Some publications have also shown that the application of some phosphorous compounds in the form of phosphate fertilizers mobilizes metallic elements, such as Cd, in the soil (McLaughlin et al., 1996; Bolan et al., 2003). This could be explained by the acidification of the soil when NH_4^+ is released from ammonium phosphate $(NH_4)_3PO_4$ in the fertilizer (Bolan et al., 2003). Therefore, the metal species and the phosphorous compound present in the soil will determine phosphate ion to mobilize or immobilize metal(loid)s in the soil. Garden soils typically exhibit a range in extractable phosphorous as P_2O_5 between 0.04 and 7.6 g/kg (Bidar et al., 2020). Exacerbated applications of fertilizer increase its contents in comparison to agricultural soils (Kabala et al., 2009). This exaggerated application might result in the uptake of anions like As and Cr by garden plants (McLaughlin et al., 2011).

1.4.6 Cation exchange capacity

Cation exchange capacity (CEC) is important in the determination of the mobility of metal(loid)s in soil because it determines the capacity of soil to bind to ions. A higher soil CEC implies a higher binding capacity for cations and consequently, a reduction of metal(loid) mobility in the soil. Other factors such as clay minerals, metal oxides and organic matter could increase CEC and create a greater surface area for sorption with metal(loid)s. Higher clay contents are associated with higher soil CEC, which is largely proportional to the surface area of individual components (Adriano, 1986). Kitchen garden soils can have a strong CEC, sometimes exceeding 30 meq per 100 g of soil, and typically ranging from 3.2 to 159 meq per 100 g of soil (Bidar et al., 2020). High inputs of organic fertilizers in unregulated kitchen garden soils contribute to this increase in comparison to agricultural soils.

1.4.7 Biological activity

Microorganisms can be present in soils freely or as associated with plant roots, with most topsoils containing between 1 million and 1 billion bacteria per gram of soil (Deneux-Mustin et al., 2003). These microorganisms can influence the solubility of various elements present in soils. Regarding metal(loid)s, microbes can produce acidic components or complexes, or change redox soil potentials, and oxidize or reduce Fe, Mn, and S (Deneux-Mustin et al., 2003). Microbial action may immobilize soil metals, for example, by aiding the precipitation of sulfides and hydrated ferric oxide and by exuding mucopolysaccharides (Rieuwerts et al., 2015). Microorganism cell walls are known to play an important, though unquantified, role in adsorption of metals from soil solutions due to the presence of surface organic functional groups. Microbial action has also been observed to mobilize Pb, Zn and Cu from the carbonate and oxide forms by aerobically decomposing lucerne or wheat straw added to kitchen garden soils (Rieuwerts et al., 2015). The addition of organic matter to soils can increase microbial action.

1.4.8 Oxidation-reduction potential

Redox potential in soils determine the tendency of a chemical species to acquire (reduce) or lose (oxidize) electrons. A species with a high reduction potential has a tendency to gain electrons, whereas one with a low potential tends to lose electrons. These redox reactions are controlled by the aqueous free electron activity, pE, which can also be expressed in terms of Eh, the redox potential. This parameter is closely linked with pH, and can determine the solubility of metal(loid)s such as As (Masscheleyn et al., 1992). Metal(loid) solubilization can also be closely linked with the dissolution of oxy-hydroxides (Fe, Mn) in reducing conditions (Chaun et al., 1996). This is specifically the case for for Cd, Zn, and particularly Pb, which have a tendency to mobilize in these reducing conditions (Chaun et al., 1996; Charlatchka et al., 2000; Davracnhe & Bollinger, 2001). High redox potentials are often recorded in dry, well aerated soils whilst soils prone to waterlogging and rich in organic matter tend to have low Eh values (Adriano, 1986; Rieuwerts et al., 2015). Several publications reveal that metals and other inorganic constituents are more readily dissolved in reducing conditions (Olaniran et al., 2013; Caporale & Violante, 2016; Palansooriya et al., 2020). Under oxidizing conditions (Eh > 0), metals are more likely to exist in their free ionic form and exhibit increased water solubility (Olaniran et al., 2013). The mobility and toxicity of Cr, Se and As are highly dependent on soil redox conditions (Adriano, 1986; Bradl, 2004). Under reduced Eh soil environments, Cr (VI) can be converted to Cr (III), making it less available and thus less toxic to organisms (Walworth & Sumner, 1989; Bradl, 2004; Caporale &

Violante, 2016; Palansooriya et al., 2020). Kitchen garden soils that are over watered and/or highly fertilized with organic matter additions may be prone to having a low redox potential (Rieuwerts et al., 2015). Few studies evaluate the redox potential of kitchen garden soils, but some redox potential values found in agricultural soils include ranges between 250 and 550 mV (Husson et al., 2016).

2. Role of soil amendments in metal(loid)-contaminated kitchen garden soil management

In the case of moderately contaminated kitchen garden soils, the monetary and environmental costs of harsher remediation methods such as soil replacement outweigh the rewards. The use of soil amendments can thus be a suitable management technique for metal(loid) contaminated kitchen gardens, as multiple have already been studied and proven to have the ability to effect environmental availability, phytoavailability, or *in vitro* bioaccessibility of metal(loid)s (Li et al*.,* 2015; Gunes et al*.,* 2014; McBride et al*.,* 2014; Puga et al., 2015; Obrycki et al., 2016; Zagury et al., 2016; Al Mamun et al., 2016; Liu et al*.,* 2017; Waterlot et al., 2017; Wang et al., 2018; Awasthi et al., 2019; He et al*.,* 2019; Kumpiene et al., 2019). Detailed in this section are the mechanisms of amendment groups that play an active role in metal(loid) immobilization. These groups include additives that are i) organic matter-rich, (ii) phosphate-rich, (iii) calcareous, (iv) siliceous, and (v) mixes between organic amendments and complementary additives.

2.1 Organic matter-rich amendments

Organic matter-rich amendments include composts, manures, biosolids, mulch, peat, and potting soils, among others. The addition of these amendments to soils aims to increase their fertility. This includes the improvement of soil quality in terms of supply of nutrients for crops, stimulation of microbial activity, soil structure, contributions to clay-humus complexes, increase in water retention capacities, and the solubility of trace elements in calcareous soils. Thus organic-matter rich soil amendments are frequently used in vegetable gardens. One survey carried out in the UK showed that 72% of the garden allotment holders in Leicester (East Midland, UK) added manure to their plot soils, and 45% of them added commercial compost (Edmonson et al., 2014). Similarly, 38% of the questioned gardeners in Muscat (Oman) used organic amendments including compost, green manure, animal wastes (goat, cow and chicken manure) (Al-Mayahi et al., 2019). In Montpellier (France), Scheromm et al. (2015) reported that the majority of interviewed gardeners added manure and their own compost to the soil, and occasionally green manure. In the North of France, a survey carried out on 153 private kitchen gardens found that self-produced compost was used on vegetable gardens in 69% of cases (Pelfrêne et al., 2019). The ultimate agronomic value of using amendments rich in organic matter is to provide a stabilized fertilizing material, rich in humic compounds and nutrients (Leclerc, 2001; Kaiser, 1981).

In addition to their agronomic interest, organic matter-rich amendments are also known to contribute to the management of soil contaminated by metal(loid)s. Humic substances, mineral ions, and microorganisms present in organic matter can reduce metal availability in agricultural soils through adsorption, complexation, precipitation, and redox reactions (Palansooriya et al., 2020). Regarding complexation specifically, humic substances and other natural ligands can reduce metal(loid) availability in the soil. This can happen through contact with organic functional groups (carboxyl, carbonyl and phenols of humic substances) (Shuman et al., 2001; Madrid et al., 2007; Achiba et al., 2009; Paradelo et al., 2011; Al Chami et al., 2013; Ahmad et al., 2017; Khan et al., 2017; Welikala et al., 2018; Pennanen et al., 2020) or more broadly dissolved organic matter (DOM) (Madrid et al., 2007; Achiba et al., 2009; Ahmad et al., 2017; Welikala et al., 2018; Pennanen et al., 2020). For example, in Cd contaminated soil, OM can often convert the exchangeable Cd into a stable, non-hydrolyzable organic bound fraction, thus reducing uptake into various garden plants, specifically bok choi and wheat (Garcia-Mina, 2006; Khan et al., 2017). Table x summarizes the effects and mechanisms of metal(loid) immobilization or mobilization in scientific literature for different organic matter-rich soil amendments.

Composts are comprised of organic matter of vegetal origins decomposed by bacteria working in aerobic conditions. Composts can be classified according to their origins, contents, and the way by which the organic matter was degraded. They can (i) hail from both industrial and domestic sources and scales, (ii) be composted in a commercialized composter, a heap, a lombricomposter, a home-made, an electromechanical composter, or a high-technology composter, or (iii) be composed of kitchen waste, grass clippings, wood shavings, garden waste, manures, green waste, dead leaves, household waste, industry by-products, and sludge. Industrial-scale composts are often composed of green waste, manure, livestock effluent, food industry by-products, methanization digestion products, mineral fertilizers, and/or water treatment plant sludge. To be placed on the market, composts must comply with the NF U 44-051 standard for organic amendments, which defines threshold values in terms of agronomic characteristics (dry matter content, N, P_2O_5, K_2O, C/N), inorganic remains (glass, plastics), chemical pollutants (metal(loid)s, organic compounds), and biological safety hazards (helminth eggs, salmonella) (Lopez, 2002). Self-produced domestic composts are not subjected to EU- or country-based regulations, and consist mainly of garden and kitchen waste (leaves, prunings, lawn clippings, manure, food waste) composted under various conditions (*e.g.* temperature, moisture, in heaps or in composters). Therefore, quantities and qualities of produced domestic composts, as well as the practices of their producers, are variable. These composts can differ greatly in terms of agronomic quality, contamination, maturity, and application rate (Lopez, 2002), and the latter two both often fall outside of the range that is recommended (4-8 months and 20 to 40 t ha^{-1}y^{-1}, respectively) in agriculture and horticulture.

Nevertheless, composts have been used to successively limit the amounts of available metal(loid)s such as Cr, Ni, Cu, Pb, Zn, and As in garden soils and plants for several soils types and garden vegetables (Szolnoki et al., 2013; Gunes et al., 2014; McBride et al., 2014; Li et al., 2015; Al Mamun et al*.,* 2016; Das et al., 2016; Liénard et al., 2016; Awasthi et al., 2019; He et al., 2019; Kumpiene et al., 2019). As composts can be highly personalized and variable, it is important to note the qualities of compost in these studies. It has been found that different compost parameters can influence the behavior of specific metal(loid)s, and lead to either mobilization or immobilization of these elements. Specifically, compost maturation, compost components, and compost pH have distinct impacts according to scientific literature.

Compost maturation is particularly important when considering metal(loid) mobility and soil health. During composting, temperature rises, and organic matter stabilizes, resulting in a product which is rich in nutrients and humic acids (Kaiser, 1981; Leclerc, 2001). As seen in Figure 1-6, the composting process consists of three predominate stages: the initial mesophilic decomposition, the thermophilic decomposition (50 to 70°C), and after cooling the final "stable" mesophilic maturation (Francou, 2003; Cornell University, 2010). The footprint of this maturation curve depends upon numerous factors, including but not limited to the biomass composition and the season during which the degradation takes place.

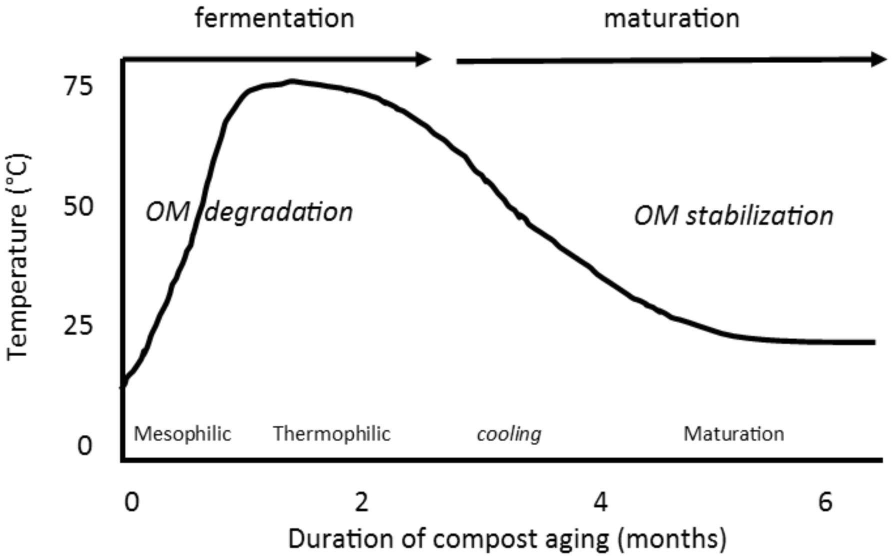

Figure 1-6. Compost temperature evolution curve (adapted from Francou, 2003)

Fermentation of the waste products (first steps of the composting process) takes place for several weeks and is followed by at least several months of maturation. At the end of the process, compost should be stable, free from pathogens and viable weed seeds, and ready to use for plant culture (St Martin and Brathwaite, 2012). Maturity and stability of compost plays an important role in its effectiveness to reduce metal availability, because it directly concerns the content and type of soluble organic matter in compost (Huang et al., 2016). Mature compost contains more aromatic structures and organic matter, which mainly occurs in the relatively stable humic acid fraction (Huang et al., 2016). The application of stable and mature compost to soil can lead to metal(loid) immobilization via the formation of stable complexes with surface functional –OH and –COOH groups of organic polymers (Madrid et al., 2007; Achiba et al., 2009). Because mature compost is the most homogenous, physically, and chemically stable, it retains the fewest metals in available forms. Conversely, immature compost has a relatively high content of soluble organic matter. Its application on agricultural soils could facilitate the mobility of metal(loid)s and decreased crop growth (Madrid et al., 2007; He et al., 2011).

Inorganic components in composts such as Fe, Mn, Al oxides also impact metal(loid) mobility. These oxides can immobilize metal(loid)s through complexation or adsorption processes (Hettiarachchi et al., 2003). Metal(loid)s can also be biosorbed and biomineralized by microorganisms in composts enhancing their immobilization (Vargas-García et al., 2012). In arsenic-contaminated environments, it was showed that various bacteria groups inhabiting the spent mushroom compost were able to counteract the toxicity of both inorganic forms of As by oxidizing As(III) and reduce As(V) through respiratory metabolism (Dabrowska et al., 2021). The physicochemical characteristics of compost can also determine its efficiency in affecting the mobility and (bio) availability of metal(loid)s (Mudhood et al., 2020).

A compost's pH can influence its metal immobilizing efficacy . Mature compost should have a pH that is neutral or slightly alkaline, and has thus the capacity to increase the pH of acid soils. Several publications show that soil pH increases with addition of compost (Zhou et al., 2016; Strachel et al., 2017; Li et al., 2019). This pH change is associated with the immobilization of some metals like Pb, but not uncommonly the mobilization of As (Udovic & McBride, 2012). Specifically, the complexation and precipitation of Pb occurs under higher pH, and this immobilizes Pb in the soil. Arsenic is more soluble and mobile at higher soil pH levels, because chemisorption is not favorable for anions such as AsO_4^{3-} and AsO_3^{3-}. For example, an *in situ* experiment on phytoavailable As and Pb conducted by Paltseva et al. (2018) found that for an acidic soil (pH = 6.0) containing 304 mg/kg of Pb and 73 mg/kg of As, the application of 33% compost increased phytoavailable As by more than 50%. Other possible reasons for the increase of pH after application of compost may be due to mineralization of carbon, OH^- ions produced by ligand exchange, and the release of basic cations such as Ca^{2+}, K^+, and Mg^{2+} (Mkhabela &

Warman, 2005). Realistic successful application rates for a soil of mid-range pH fall between 0.3 and 6 percent by dry mass, and have also been shown to reduce availability of Zn and Cd alone or mixed with fertilizer (Das et al., 2016; Agriopale, 2019).

Manure consists of animal excrement and bedding (*e.g.*, straw, shavings), and is traditionally added to garden soil either in fresh (self-produced, farmyard manure) or dehydrated (commercial manure) form. Pure manure as a waste has a very high nitrogen and moisture content and is thus not too useful alone for composting or as a soil amendment, as it can bring pathogens and ammonium toxicity to soils. Composting provides more degraded organic matter and increases its efficiency in metal(loid) immobilization, as well as reduces the number of pathogens in the manure due to the increase in temperature during the composting process.

When mixed and composted with straw, wood residues, sawdust, or leaves, however, the carbon to nitrogen ratio and moisture content stabilizes (Sterrett et al., 1996; Angelova et al., 2004; Wardynski, 2015). In order for a manure mixture to be commercialized or effective in compost or soil, certain characteristics must be achieved. A carbon to nitrogen ratio of 25-30:1 is ideal, and a ratio of 20-40:1 is acceptable. Moisture content should be between 50-60%, though 40-65% is acceptable. The vast majority of that which is commercialized is bedded manure pack, which reaches appropriate carbon to nitrogen ratios and moisture content (Wardynski, 2015). The composition of these manures varies greatly depending on its nature, the conditions under which they the animals providing the product were raised, and the degree of degradation. Waste is mainly from cattle, horse or sheep sources; which are rich in minerals, trace elements, carbon, and humic substances. These organic waste products from livestock farming also represent an important source of nitrogen, which is present in mineral and organic forms. Thus its availability for crops is highly variable (Bouthier et al., 2007). Nitrogen can stay in a particular mineral form for a few days, specifically in the case of ammonia-rich nitrogen, up to several years for organic forms. Organic nitrogen, the main form of nitrogen contained in cattle, horse, or sheep manure, contributes to the long-term modification of the organic status of the soil and acts on the mineralization potential of soil organic matter. This product is cited as effectively being able to decrease their presence of metal(loid)s analyzed by various extractions and phytoavailability studies, particularly in the case of Cd, at application rates between 1 and 3% for composted manure (Gunes et al., 2014; Hamid et al., 2019).

Specifically, **poultry droppings** are rich in N, P, and K, and are thus considered as complete organic fertilizers. In France, their marketing must comply with the NF U42-001-2 standard. They must meet at least one of the following two conditions: (i) contain a minimum of 3% of one of the major constituents (N, P_2O_5, K_2O) in the raw material, or (ii) have a sum of 7% or more of N + P_2O_5 + K_2O. Thus the addition of chicken manure to acidic soil can increase pH and total phosphorus contents of soils (Li et al., 2016). The standard also requires the analysis of metal(loid) contents (As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Se and Zn) and a regular assessment of the risks that may result from the possible presence of pathogenic germs for humans and animals, and phytotoxic substances for crops. The particularity of nitrogen in poultry manure or droppings is that it is mainly present in its ammoniac form (70%), which is very quickly available to the plant. The fertilization modifies the composition of the soil solution and the states of ionic balance. It should also be noted that while some constituents of poultry manure provide nutrients, they may also contain metal(loid)s. Repeated inputs could enrich soils with As, Cu and Zn (Toor et al., 2007).

In scientific literature, poultry litter or manure is cited as an effective soil amendment to decrease metal availability, specifically that of Cd, at application rates between 1% and 3% for composted manure (Sato et al., 2010; Kim et al., 2012; Gunes et al*.,* 2014; Mubemba et al., 2014; Hamid et al., 2019). A study by Li et al. (2016) found that the amendment of soils with poultry manure resulted in the decrease of acid-extractable Cd by 8.2 - 37.6%, and an increase of the reducible and oxidizable Cd by between 9.2% to 39.5%, and 8.2% to 60.4%, respectively. Another study found that 8% of poultry litter by mass reduced by approximately 13% the *in vitro* bioaccessibility of Pb in a polluted urban sandy loam soil with a pH of 6.8. This happened when the amount of available P in the amended soil corresponded to a 5:1 phosphate to Pb molar ratio (Obrycki et al., 2016). Additionally, Gunes et al. (2014) characterized the effects of poultry manure on the metal composition of *Latuca savita L*. leaves in a greenhouse, and found that when the amendment was applied at 20 g kg^{-1} on alkaline soil (pH 7.98), minimal leaf contamination was seen, but there was an increase in yield explained by the N and K contents of the amendment.

Peat is the product of the accumulation of decomposed organic matter in anoxic hydromorphic conditions over the span of several thousand years, and a pre-product of coal. It consists of debris made up of bryophytes (mosses, sphagnums) and various vascular plants such as sedges and reeds. Peat is classified into three different categories (blonde, brown, or black) according to its age, formative environment, and the type of plant from which it is derived. The youngest is blonde peat (3,000 – 4,000 years of maturation) derived from sphagnum moss, and the one most used in the garden. This matter is acidic and has a high cellulose and carbon content, as well as a fibrous texture, a high capacity to absorb water, a low density, and a low ash content. Agronomically, sphagnum peat moss is recommended to make clay soils less dense, enrich soils with humus, improving their permeability, and encouraging plant rooting. It is a good growth medium, either alone or mixed with other products. However, its use is largely dissuaded, particularly in large quantities or alone, as it is detrimental to peat bog ecosystems which act as carbon sinks.

In their review, Singh & Oste (2001) report that the addition of peat to contaminated soils can reduce the extractability (by using DTPA as chemical extractant) and phytoavailability (*Lolium perenne* L.) of Cd, Cu, Ni and Zn. This immobilization of metal(loid)s is in connection with the formation of insoluble metal-organic complexes and the increase of the cation exchange capacity of the soil. Peat's immobilizing effect, however, reduced one year after application, due to a release of metal(loid)s following organic matter degradation. McBride et al. (2013) found no effect of peat (amount) on the accumulation of Pb and As in lettuce leaves grown on vegetable garden soils contaminated with lead arsenate, lead paint and petrol. This finding is explained by low solubility of Pb. Nwachukwu and Pulford (2009) studied the effects of peat applied at different doses (1, 10 and 20%) on a Cu, Pb, and Zn- contaminated mine soil in a greenhouse. The study found that the EDTA extractability of Cu and Zn, as well as their concentrations in the aerial parts of *Lolium perenne,* increased at doses higher than 10%, whereas pH decreased. In all cases, peat application increased biomass yield. Studies have also tested the effects of combining peat with stabilizing amendments. Kumpienne et al. (2007) showed that peat (pH = 3.9) combined with fly ash from coal combustion could significantly reduce the mobility of Cu and Pb in contaminated soils.

2.2 Phosphate-rich amendments

Phosphate-rich amendments include apatites, phosphates, bone meal, and crushed horn, among others. The addition of these amendments to soils aims to increase and improve the supply of nutrients for crops, thus increasing yield (Khalil, 2013; Zhao et al., 2019). Thus P-rich soil amendments are frequently used in vegetable gardens. Their slow degradation and demineralization provide gradually available nutrients for plants. This is beneficial as the rapid availability of P can lead to eutrophication in water supplies, so slowly degradating P avoids this issue (Sun et al., 2018). A survey, carried out in Leicester (Eat Midland, UK) showed that 42% of the garden allotment holders used mineral fertilizers and chicken manure respectively, and 27% supplemented their soils with bone (Edmonson et al., 2014). In Montpellier (France), Scheromm et al. (2015) reported that some gardeners added ground horn to their soil.

The interactions between metal(loid)s and phosphates depend upon adsorption, precipitation, complexation or exchange reactions, and these depend on the solubility of the phosphates and the nature of the metallic element (Bolan et al., 2003). The immobilization of metals (Cd, Cu, Pb and Zn) by insoluble phosphates requires their prior dissolution, and this dissolution rate depends on the nature of the phosphates and the particle size of the soil additive. The effectiveness of water-insoluble phosphates in metal(loid) immobilization is thus facilitated for acidic soils (pH < 6.5). Phosphate-rich amendments have the potential to reduce the availability of metallic elements such as Pb, Cu, and Cd because of their potential to create relatively insoluble metal phosphate compounds (Bolan et al., 2003). Many various metalloids, particularly cationic metalloids, can be precipitated in the form of metal phosphate in the presence of a sufficient amount of phosphorus in soil (Sneddon et al., 2002; Gatimu et al., 2007). Specifically, P compounds are known for their ability to react with Pb in its cationic form over time, to form pyromorphite-like minerals of low solubility, specifically at certain molar ratios. Literature cites a P to Pb molar ratio of 5:3 as the most effective for immobilizing the metal (Ma et al., 2002). However, the efficiency of P amendments in metal immobilization depends on the other metal(loid)s present in a given medium. For example, regarding Al, Cu, Fe, Cd, Zn, and Ni, their immobilization by P-rich compounds is dependent upon the Pb concentration present in a given soil. This phenomenon takes place because of the competition on exchange sites. At high Pb concentrations, Al > Cu > Fe(II) > Cd > Zn > Ni and at low Pb concentrations, Cu > Fe(II) > Cd > Zn > Al > Ni (Ma et al., 1994).

Bone meal is obtained from bones (51% water, 32% minerals, 15% fat and 12% protein) that are heated to extract marrow, nitrogen and various minerals, which can be used in the manufacture of gelatin and glues. The residue from this thermal extraction is then ground and marketed as an organic fertilizer with a slightly acidic pH around 6. Depending on the bones used, and the extraction process of the constituents, the bone meal has a variable NPK composition ranged from low to no N and K content. However, it is rich in calcium and phosphorus (Basta et al., 2001; Chen et al., 2006). As bones are composed of calcium phosphate (85%), calcium carbonate (10%), magnesium phosphate (1.5%), calcium fluoride (0.3%), calcium chloride (0.2%), and sodium salts (2.0%), the phosphates in the bone meal are present in insoluble forms. When the bone is calcined, organic matter is destroyed, and the mineral salts that retain the shape of the bone remain.

Interactions between metal(loid)s and bone meal thus depend heavily on the immobilization of metal(loid)s by the insoluble phosphates present in the amendment. This requires their dissolution, which depends upon both the particle size of the bone meal and the soil pH (Gatimu et al., 2007). Typically, bone meal is most effectively applied to soils with a neutral to acidic pH. In these conditions, it is generally observed that the addition of bone meal reduces the release of metallic elements from soils, decreases the concentration of metals in the soil solution, increases soil pH, and reduces the availability of metallic elements for plants and soil organisms (Sneddon et al., 2002). It is believed that in the case of Cu-contaminated soils, however, bone meal can cause the formation of soluble organo-copper complexes at basic pHs (Sneddon et al., 2002). Metal immobilization by bone meals is attributed to the soil pH rise associated with bone meal dissolution and the formation of P-complexes.

An experiment investigating the impact of bone meal on the immobilization of Cd, Cu and Pb in contaminated soils followed their fractionation. After the soil was amended, the exchangeable Cd significantly decreased from 47.0% to 7.3 % of the total Cd content. The exchangeable Pb decreased from 2.5 % to 0.7%, while the carbonate-bound Pb increased from 3.4 % to 4.6 % of the total. With the addition of the amendment, the exchangeable and carbonate-bound Cu proportions both decreased, whereas the organic-bound Cu proportion increased (Huang et al., 2016). Another study examined the impact of the amendment on oral bioaccessibility of Pb. Bone meal applied at 2% by mass reduced the bioaccessibility of Pb in an urban sandy loam soil (pH = 6.8) contaminated by 807 mg/kg of Pb, 12.5 mg/kg of As, 2.6 mg/kg of Cd, and 448 mg/kg of Zn. This percentage of amendment corresponded to a P:Pb molar ratio of nearly 5:1, and reduced bioaccessibility by 11%. When the quantity of bone meal was increased to 4% by mass, Pb bioaccessibility increased to 12% (Obrycki *et al*., 2016). An *in situ* experiment on phytoavailable As and Pb conducted by Paltseva *et al.* (2018) also found that bone meal was an effective amendment. An acidic soil (pH = 6.0) containing 304 mg/kg of Pb, 73 mg/kg of As, and 728 mg/kg of phosphorus was amended with 0.006% of bone meal. This amendment effectively brought the molar ration of P:Pb to 5:3, as recommended by scientific literature, reducing the phytoavailable Pb by 25%.

2.3 Calcareous amendments

Calcareous amendments are soil additives that consist of or contain calcium carbonate ($CaCO_3$), calcium (Ca^{2+}), or lime or limestone (rich in Ca and Mg carbonates and (hydr-)oxides). Liming is a common practice in agriculture that consists of adding basic products rich in calcium and sometimes magnesium to the soil, in different chemical and granulometric forms, in order to improve plant growth and/or reduce soil acidity (Palansooriyaa et al., 2020). Calcium carbonate, hydrated lime and dolomite are among the common liming materials used as amendments, with each varying in their capacity to neutralize acids (Bolan & Duraisamy, 2003). The range of marketed limestone amendments is wide. Depending on the product, the crop and the use (maintenance or pH correction) and the applied doses can vary. Two main categories can be distinguished: natural or raw products (limestones, magnesium limestones or dolomites) and thermally modified or fired products like hydrated lime. However, they have different rates of action depending on their composition and granulometry. The use of fast-acting soil improvers such as pulverized limestone and especially lime, which are often more expensive, is justified in situations requiring a rapid recovery of the soil pH. It should be noted that the use of quicklime (or calcium oxide) is not authorized in organic agriculture due to its bactericidal, insecticidal and fungicidal effects.

Often, limes, specifically hydrated lime, adds Ca^{2+} to soil. This reinforces the stability of the soil's clay-humus complex, increases the pH of an acid soil, or maintains it at an optimal value in order to promote ionic exchanges and thus facilitate the assimilation of nutrients such as phosphorus and nutrients by plants. Though this optimum value varies according to the nutrient and the vegetable, most nutrients are optimally absorbed by plants in a pH range of 6.5 to 7.5, where the activity of soil microorganisms is also greater (Albert, 2015). Specifically, liming can increase the concentration of exchangeable Ca and/orMg in soils, promotes exchangeable Al's precipitation on clay surfaces (Li et al., 2018). This acts as a cementing agent that binds adjacent soil particles to form aggregates, thereby influencing aggregate stability and improving soil structure (Haynes & Naidu, 1998). This reaction is also linked to an increase in CEC and available soil nitrogen and phosphorous in field conditions. Liming has also been reported to increase microbial biomass content, soil respiration rate (CO_2 evolution), soil enzyme activities and net mineralization of soil organic N and S (Edmeades et al., 1981; Haynes & Swift, 1988; Badalucco et al., 1992). Liming has in particular a stimulatory effect on dehydrogenase activity (an indicator of microbial activity) (Mijangos et al., 2010).

Limes have been adopted as a management tool for reducing metal(loid)s toxicity in metal(loid)s (Kaitibie et al., 2002; Anderson *et al.,* 2013; Lahori *et al.,* 2017; Palansooriyaa et al., 2020). Most of the immobilization mechanisms of these amendments arerelated to precipitation, surface adsorption, and complexation reactions as result of pH increases which alter chemical speciation. It has been shown that calcareous amendments can lead to the shift metal(loid)s in the exchangeable fraction of metal(loid)s to a less available fraction, which consequently decreases their mobility and phytoavailability (Basta et al., 2000; Chen et al., 2000; Kaitibie et al., 2002; Lee et al., 2004; Anderson et al., 2013; Lahori et al., 2017; Palansooriyaa et al., 2020). Calcareous calcium soil improvers added to soils moderately contaminated with As, Cd, Pb and Zn have been shown reduce metal(loid) availability at different application rates. For As, rates between 0.27 and 1.36% are applied and effective. Available Cd is often limited with a dose of 1%. In several studies, rates of both 0.1 and 1% limited levels of available Pb in soil and plants. For Zn, effective rates between 0.45 and 0.9% are applied (Preer et al., 1995; Lehoczky et al., 1995; Lombi, 2002; Szomolanyi et al., 2002; Warren et al., 2003; Hartley et al., 2008; Chaney et al., 2009; Kim et al., 2012; Lu et al., 2014; Hamid et al., 2019). However, the effects can vary considerably depending on the metal ions and the species of calcareous amendment used.

The use of **magnesium carbonate amendments (dolomite or magnesium lime)** which have little effect on soil pH can be recommended in neutral and/or magnesium deficient soils. These amendments can lead to the complexation of cationic metal(loid)s with carbonates and the subsequent release of Mg ions, as with hydrated lime. Dolomite added at 2, 3, or 5% can reduce Cd, Pb and Zn concentrations in onion, Chinese cabbage, red pepper, and lettuce when grown on slightly acidic and heavily contaminated soil (Kim et al., 2012; Lee et al., 2009). It was also shown that efficiency in reducing Cd, Pb and Zn availability can increase with increasing rates of dolomite (Lee et al., 2009). Liming with **calcareous calcium amendments (limes)** on very acidic soils has been linked with the reduction in the toxicity of Cd, Pb, Zn, Al, and Mn (Li et al., 2018), and the increased mobility of As. This metal(loid) is often liberated through the formation of mobile arsenite at pHs above 8 (Lwin et al., 2018). As soil pH is increased by liming, some metal(loid)s may become less available while plant nutrients such as N, P, K, S, Ca and Mg become more available (Bolan et al., 2003; Kostic et al., 2015). Kim et al. (2012) and Lee et al., 2009 showed that agricultural lime added at 1% could reduce Cd, Pb and Zn concentrations in onion, Chinese cabbage, red pepper, and lettuce when grown on slightly acidic soil. Simon et al. (2015) demonstrated a reduction in the extractability and phytoavailability of As metal(loid) for lettuce (*Lactuca sativa L.)* on an alkaline soil after addition of calcareous sludge from the marble industry.

2.4 Siliceous amendments

Silicates are ionic minerals containing silicate anions such as orthosilicates, metalsilicates, and pyrosilicates with the general formula $[\mathrm{SiO}^{(4-2x)-}{}_{4-x}]_n$. Silicates also include non-ionic compounds such as silicon dioxide, and minerals where aluminum or other tetravalent atoms replace some Si atoms, as with aluminosilicates (Greenwood, 1997). These minerals are known for their effect on increased crop growth, and are widely described as molecular sieves because of their structure (Plummer & McGeary, 1993). Silica possesses active surface hydroxyls and a permeable surface area with relatively high porosity. Because of its tendency to form a framework lattice structure, silicates can immobilize cationic metal(loid)s (Figure 1-7).

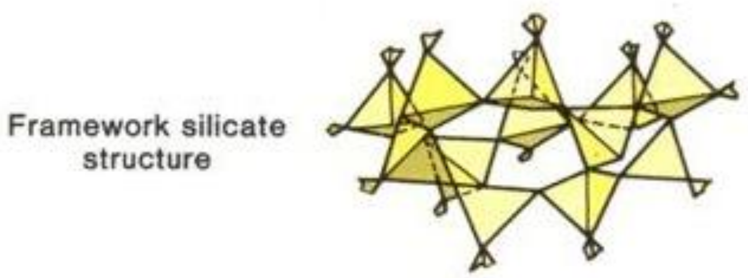

Figure 1-7. Framework silicate structure (adapted from Plummer and McGeary, 1993)

They also favor reactions between metal(loid)s and other agents because of their large surface areas and a high surface activity. This quality can provide space the attachment of various functional groups to the silicate structure. This can also facilitate reactions between metal(loid)s and other agents present in kitchen garden soils (Lian et al., 2019). Thus silicates have commonly been cited to absorb metal(loid)s such as Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+} in solution (Lian et al., 2019).

2.4.1 Tetrated alumino-silicates

This group of silicates includes tectosilicates with a framework of SiO_2 in a 1:2 ratio. Examples include quartz, feldspars, scopolites, and zeolites. **Zeolites** are natural or synthetic crystalline frameworks of alkaline-based aluminosilicates on a three-dimensional structure of a silicate (SiO_4) tetrahedron where some Si are replaced by Al (Auvinet, 2018). The tetrahedron base molecules are linked together to form rings, which induce the internal spaces and channels which give zeolites an open structure (Lallemand-Barrès, 1992). The compound may be represented by the general formula (Kuhn, 2011):

$$[(SiO_2)(AlO_2)_x]M_{x/n}^{\ n+} \bullet H_2O$$

In brief, the crystal has a three-dimensional organization of SiO_4^{4-}, a tetrahedral shape with a Si atom in the center, which is sometimes replaced by Al within a repetitive structure (Figure 1-8).

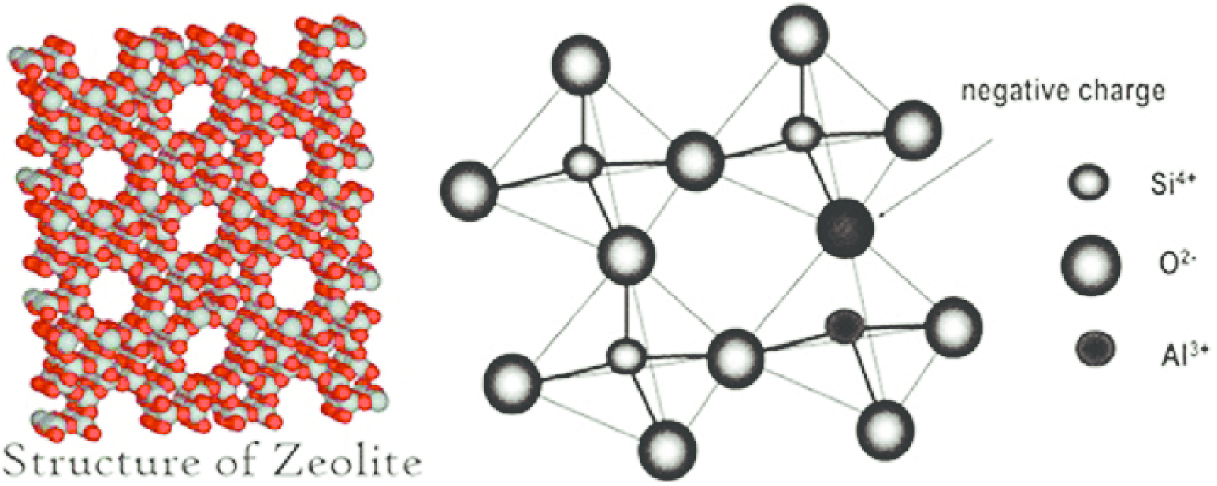

Figure 1-8. Structure of zeolite (Golomeova & Zendelska, 2016)

This replacement can cause a charge deficit, which then attracts ions such as Na, K, Ca and Mg, and subsequently water molecules. These cations typically weakly bond in the zeolite structure and can be exchanged with each other to varying degrees (Golomeova & Zendelska, 2016). The zeolite framework contains channels and interconnected voids occupied by cations and water molecules (Querol et al., 2002). Zeolites functions as molecular sieves because they can selectively adsorb molecules according to their size and/or shape. The adsorption properties of zeolites are determined by a unique crystal lattice, characterized by a developed inner surface and a strictly defined size of the entrance windows. There are at least thirty species of natural zeolites, but in terms of abundance and physical properties, six natural zeolites are of particular interest in terms of their application: i) chabazite, popular for horticultural use because of its high CEC, ii) clinoptilolite, popular for planting cacti, iii) heulandite, iv) erionite, v) mordenite and vi) phillipsite (Rocher, 1995).

All zeolites are marked by their low density, high porosity, capacity to adsorb polar water molecules and cations, their high cation exchange capacity, and their structural stability. Agronomically, these zeolite amendments are known to be able to improve the physico-chemical properties of soils. They can act upon soil CEC, pH, porosity, water retention capacity, ion exchange, contribution of nutrients, the reduction of leaching, and soil fertility. As zeolites have strong adsorptive properties, they can absorb potassium, ammonium, and necessary plant nutrients in the form of ions. This thereby affects and influences the mineral nutrition of plants. Zeolites' noted capacity for adsorption is related to its notable pore space and pore volume. This ample surface area allows for adsorption, which can for example help control the release rate of pesticides and fertilizers (Ming & Allen, 2001). It is also hypothesized that zeolite pore space can trend with increased biological activity in soils, as bacteria can populate and thrive in these spaces under the right conditions (Wu et al., 2020).

All zeolites have adsorptive properties that render them useful as amendments to reduce metal(loid)s availability in the soil. Zeolites can readily uptake almost all metal(loid)s that are bound to the carbonate and the exchangeable soil fractions with a selectivity of Cu > Cr > Fe > Ni > Mn > Pb > Zn (Zorpas et al., 2000; Singh & Kalamdhad, 2012). Nevertheless, particular zeolites are better suited for specific purposes. Synthetic, thermally modified zeolites are the byproduct of various industrial products such as furnace slag or fly ash. Their characteristics are similar to those of natural zeolites, but they have certain limitations for amendment use. These tetrahydrates are formed from various fuels or wastes and may contain metal(loid)s, as some are the result of coal combustion. This can lead to the long term mobilization of metal(loid)s in soils. These zeolites also have high pH, which can easily result in increase in soil alkalinity. Additionally, synthetic zeolites are not easily found by gardeners (Belviso, 2020). Natural zeolites better adsorb monovalent metal(loid) cations than divalent ones (such as Cd^{2+}, Pb^{2+}, and Zn^{2+}) because of a predominantly ionic adsorption mechanism (Phillips, 1998). This sorption is partially dependent on soil pH, so zeolite choice must also take into consideration the acidity of the matrix to which it is added. At a pH less than 4, zeolites can begin to lose the efficacy since their crystal structure begins to disintegrate and weaken. In the pH range of 4 to 6, the main mechanism of metal immobilization is ion exchange (Haidouti, 1997). Zeolites that contain calcium oxide and/or sodium hydroxide, specifically acidic soils, can contribute to soil pH increase (Lin et al., 1998; Xavier Querol et al., 2006).

The persistence of zeolite in the soil and its effect on the immobilization of soil metal(loid)s also depends upon its surface area and pore space, and climatic conditions (Contin et al., 2019). Several studies have shown that adsorption increases with increasing doses of zeolite because of increased pore volume. In one contaminated soil, the introduction of zeolite with 15 and 75 % of the pore volume by mass reduced the available Cd by 12% and 35 %, respectively (Mahabadi et al., 2007). A study evaluating the effects of 1, 2.5, and 5% of natural zeolite on pots of an acidic agricultural soil with a pH of 6.46 contaminated by Cd found that wheat grain yield (*Triticum aestivum L.*) increased with the two higher doses of zeolite (Zhou *et al.*, 2020). With this addition, pH also increased, and Cd extractability (0.01 $CaCl_2$) decreased in the soil with the two highest doses of zeolite, and in the grain with all doses of zeolite. Another study found that 3% of zeolite added to a contaminated sandy loam soil (pH = 6.1) resulted in a slight increase in pH, an increase in dissolved carbon content, and a reduction in both the extractability (1 M NH_4NO_3) and vegetable accumulation (Chinese cabbage, red pepper, spring onion) of Cd, Pb, and Zn (Kim et al., 2012).

Though zeolite has little effect on the pH of alkaline soils, studies have shown that this amendment can still impact metal(loid) mobility (Lahori et al., 2020). On alkaline soils with pH between 7.40 and 8.43 contaminated anthropogenically by Cd, Cu, Pb, and Zn, a pot experiment applying natural zeolite at 20 t ha^{-1}, or 0.6% by mass, found a reduction of all metal(loid)s in the aerial parts of cabbage (*Brassica chinensis L.).* This rate of addition also improved the growth of *Zea mays L* (Lahori et al., 2020). These decreases in mobility for metal(loid)s such as Cd, Ni, Pb, and Zn could be the result of adsorption into Fe/Mn oxides, and/or an increase in cation exchange capacity and organic complexation (Contin et al., 2019). These works further confirm the interest of zeolite in the management of metal(loid) contaminated soils (Lin et al., 1998; Querol et al., 2006).

2.4.2 Expanded alumino-silicates

Some expanded alumino-silicates include perlite and vermiculite. **Perlite** ($Al_2CaFe_2K_2MgNa_2O_{12}Si$) is an amorphous volcanic rock, and an alumino-silicate composed of more than 70% silica, with alumina, iron oxide, lime oxide, magnesia, sodium oxide and potassium oxide. This product is thermally heated which leads to its expansion and the formation of nano- and micro-pores. Perlite has a high-water retention capacity of 4 to 5 times its weight, and a neutral pH, as well as a high CEC. In horticulture, expanded perlite is used pure or mixed as a growing medium. Because of these physico-chemical properties, perlite can be used to treat contaminated solutions and influence the behavior of metal(loid)s in sludge and soils. Ozdemir et al. (2020) evaluated the efficiency of expanded perlite to extract Fe, Mn, Cr, Cu, Zn, Ni, Pb during the composting of sewage sludge. In comparison to the control compost containing no perlite, expanded perlite reduced the concentrations of all available metals in the compost except Cr. Perlite has also been used to treat vineyard soil. Rodriguez-Salgado et al. (2016) studied the effects of a perlite applied at different doses of 0.15%, 0.3%, 0.6% and 1.2% on an acidic wine-growing soil with a pH of 5.4 kept in pots. After 8 months, reduction of available Cu was observed, regardless of the amendment doses. As with zeolite, perlite's main mechanism of metal immobilization is adsorption via ion exchange (Haidouti, 1997).

Vermiculite ($(Mg; Fe^{3+}; Al)_3(Si; Al)_4O_{10}(OH)_2{}^2\ 4H_2O$) is a phyllosilicate clay of basaltic origin, which belongs to the mica group. It consists of a stack of layers, each being composed of two octahedral layers of Mg and Fe oxides, with a tetrahedral layer of silicates inserted between. Cations and water molecules are adsorbed in this interfoliar space to compensate for the charge imbalance. This clay's exfoliation under extreme temperatures causes it to have weak between the laminae of this interfoliar layer. Thus uring creation, this layer becomes occupied by air, which results in an increased volume and low density of the material (Potter, 2000). Vermiculite has a high cation exchange capacity, a neutral to slightly basic pH, low density, and high-water retention. Because of these qualities, vermiculite is used in horticulture to facilitate seed germination and seedling establishment. Due to their high cation exchange capacity, in solutions some vermiculites adsorb metal ions such as Ti, Ni, Cr, Zn, as shown Marwa et al. (2011) with the case of Tanza vermiculites. Malandrino et al. (2011) performed a pot experiment analyzing the effects of vermiculite applied at a dose of 10% to Cd, Cr, Cu, Ni, Pb, and Zn- contaminated soil on the mobility and phytoavailability of metal(loid)s using two vegetable plants, lettuce (*Lactuca sativa* L.*)* and spinach (*Spinacia oleracea* L.*)*. The amendment greatly reduced metal(loid) concentrations in both vegetables, while increasing soil pH from 4.2 to 6.0. This is one explanatory factor for the metal(loid) immobilization. The authors also suggest that this amendment would be suitable to reduce the phytoavailability of metal(loid)s over time. However, because of the light and voluminous nature of the product, some vermiculites contain fibrous materials that can pose health hazards, such as amphiboles, serpentines, and asbestos. Many of these amendments have a high Cr and Ni concentration, and thus exceed limits for agricultural use for these metal(loid)s when used alone as substrate or applied to soils in large quantities.

2.5 Mixes between organic matter-rich amendments and complementary additives

To increase the effectiveness of amendments on metal reduction and/or soil fertilization, as well as the durability of their effects, some studies have evaluated the effects of combining them with stabilizing products. These are applied to soil as a mixture (Singh & Kalamdhad, 2014; Zhang & Sun, 2015; Golia et al., 2017, Hamidpour et al., 2017, Al Mamun et al., 2019; Liu et al., 2019). The association of composts and other organic matter-rich amendments with other stabilizing products, applied as a mixture or composted together, can help reduce availability of metal(loid)s (Lu et al., 2014). These additives can help improve the possible poor quality (*ie.*, pH, CEC) of an organic amendment, and help address multiple metal(loid) soil pollution, and even increase the durability of the amendment. Such additives which are commonly found and applied in kitchen gardens include zeolites (Gadepalle et al., 2009; Najafi-Ghiri & Rahimi, 2016; Golia et al., 2017; Hamidpour et al., 2017), limes (Wong et al., 2006), phosphate-rich amendments (Lu et al., 2014). Other organic matter and additive mixes are marketed directly in the forms of different potting soils.

The addition of **hydrated lime to compost** is a commonly used kitchen garden practice. Gardeners commonly add lime to a maturing compost in order to reduce its smell and prevent rodents and insects. When lime is mixed with a mature compost and added to an acidic soil, the mix can increase soil pH, CEC, available N, P, K, and Mg, microbial biomass, and organic matter content. It can also improve soil density, porosity, and stability (Lwin et al., 2022). Neaman et al. (2012) found that the application of a hydrated lime and compost mix resulted in the decrease in exchangeable Cu and Zn because of a decrease in proton activity in the soil solution which facilitated the adsorption of the metal(loid)s to OM particles. This also decreased their bioavailability. Another study found that the addition of both lime and compost to a soil contaminated by As, Cd, Cu, Pb, and Zn reduced their availability in *Brassica. rapa* L. leaves in comparison to the control soil. The immobilization of the cationic metal(loid)s was attributed to the pH-changing effect of both the lime and compost. The efficacy of the mix was not significantly more than one of the single amendments alone for any metal(loid) (Lwin et al., 2022).

Several studies have mixed **compost and zeolite** either during or after the composting process. This amendment mix has been shown to decrease composting time and favor organic matter maturation (Zang & Sun, 2015, Hamidpour et al., 2017). Zeolite can modify mature compost parameters by buffering pH and increasing electrical conductivity (Waqas et al., 2019). It has also been associated with increased seed germination rates. When applied to soil, this amendment mix has been shown to shift metals from their available forms to a form bound to organic matter and oxides (Zang & Sun, 2015, Hamidpour et al., 2017). Studies have also suggested that the increased application of zeolite to a mature compost can lead to decreases in metal availability in both acidic and alkaline soils containing Cd, Cu, and Zn (Golia et al., 2017). When zeolite is introduced directly in a maturing compost, it is able to reduce available metal(loid)s in the compost itself. Lime and zeolite can also be added during the composting process. This allows to reduce compost acidity. Ozdemir et al (2020) evaluated the efficiency of both natural and artificial zeolites on a Fe, Mn, Cr, Cu, Zn, Ni, and Pb contaminated composting sewage sludge. The results found that zeolite reduced the available concentrations of all elements except Cr.

Potting soils are very commonly used in kitchen gardens as either an amendment or substrate. This product is suitable for sowing, cutting and transplanting young plants, both alone or mixed with garden soil. Multitudes of formulations are commercially available, but most include sand, vermiculite, compost, peat moss, lime and nutrients in varying proportions. A typical mix will contain 60-80% peat rich in organic matter (Burne, 2019). Potting soil compositions, however, depend upon their intended use (MSU Extension, 2013; Gerbeaud, 2014). There are varieties of commercially available potting soils, some of which have specific characteristics, including horticultural purposes, universal purposes, seeding, potting, vegetable patches, cactii, or heather. They are typically designed to hold water and nutrients in a soil.

Although some of its components are cited as metal(loid) immobilizers (Chen et al., 2016; Abbar et al., 2017; Petitgrand, 2019), there is a lack of international scientific literature referring to interactions between seed bedding soil and the behavior of metal(loid)s in soils. Nevertheless, a study on outdoor plots (pH = 6.0) contaminated by 304 mg/kg of Pb and 73 mg/kg of As demonstrated that additions of potting soil decreased available Pb (Paltseva et al*.,* 2018). However, As availability increased by more than 50%, when potting soil was applied at 33% to soil. This rate of addition reflects that which is typically seen in kitchen gardens. Lead was somewhat decreased in soil by a dilution effect, but As was mobilized by the addition of organic matter and the soil pH increase. It is important to note that potting soil is often added to garden soil in large doses. When applied this way, a decrease in the availability of metal(loid) in potting soil amended soils could be induced by a dilution effect, particularly in the case of potting soils containing a high proportion of sand (Paltseva et al., 2018).

2.6 Summary of amendments and their metal(loid) immobilization mechanisms in soils

The categories of soil amendments outlined in this section have different mechanisms of metal(loid) immobilization. These include adsorption on organic matter, complexation with humic acids, OM functional groups, and P-compounds, and precipitation.These reactions are highly dependent upon the metal(loid)s present in soils, as well as the individual characteristics of the amendment and soils. Table 1-1 includes a large overview of amendments, their subsequent effects on soil physico-chemical characteristics and metal(loid) immobility, and mechanisms linked to metal(loid) immobilization.

Table 1-1. **Summary of amendments, their effect on soil physico-chemical characteristics, and mechanism(s) of metal(loid) immobilization associated**

Amendment		Metal(loid)s	Effects	Mechanism
Compost	Solid olive husk compost	Mn, Fe, Zn, Pb	Reduction of the concentration of Pb in shoot tissue of plant	Complexation (a)
	Green waste compost	Pb, Zn	Reduced Pb and Zn accumulated in Rhodes grass	Adsorption and complexation (b)
	Municipal solid waste compost	Cr, Ni, Cu, Pb, Zn	Increase in accumulation of Cr in *Lepidium sativum* L.	Complexation (c)
	Food waste compost	Pb, As	Increased soil pH. Reduction of bioavailability soil Pb. Increased As potential bioavailability because displacement by PO_4^{3-}	Complexation and precipitation (d)
	Composted chicken manure	Cd	Immobilization of Cd in soils and decreased Cd uptake by wheat, increased soil pH	Precipitation with phosphorous compounds (e)
			Increased soil pH, OM, and CEC. Decreased soluble Cd, increased concentration of organically-bound Cd and inorganic Cd precipitates.	Sorption of cation hydroxyls (f)
Peat		Cd, Cu, Ni, Zn	Increase of soil CEC. Decrease of DTPA-extractable and phytoavailable Cd, Cu, Ni, and Zn in *Lolium perenne*	Complexation (g)
		Cu, Pb, Zn	Decrease in soil pH when peat applied at 20% by mass. Increase of EDTA extractable and phytoavailable Cu and Zn in *Lolium perenne*	
Bone meal		Pb	Reduced Pb, Cu, Cd bioavailability. Exchangeable and organic-bound Pb decreased	Complexation and precipitation (h,i,j)
		Pb, Cu, Cd	Reduction of the bioavailability metal(loid)s in soil	
		Cu	Increase in accumulation of Cu in Lepidium sativum L. Exchangeable and carbonate-bound Cu proportions decreased	Complexation (k)
		Cd	Exchangeable Cd significantly decreased	
Porous keratin hydrogel		Pb	Almost 100% efficient	

Continuation of table

Keratin powder		Cd	Increased adsorption with smaller grain sizes	Adsorption (l,m,n,o)
Steamed sheep hooves		Cd, Pb, Zn	Optimal pH for adsorption is 8.5 for Cd, 5.6 for Pb, and 7 for Zn	
Keratin-based material		Cu	Relatively fast adsorption	
Lime	Hydrated	Cd	Reduced available Cd in rice paddy soil by 12.9-18.2% and rice by 28.5-56.2%	Complexation and precipitation (p,q,r,s,t,u,v,w)
		Cu, Cd	Reduced availability, bioaccessibility, leachability of Cu and Cd in ryegrass	
		Co, Cu, Ni, Zn	Reduced levels of bioavailable Co, Cu, Ni and Zn in a previously limed area	
		Ni, Cd, Fe	Reduced solubility, mobility and bioavailability	
		Mo, As	Increased bioavailability	
	Dolomite	Cd, Pb, Zn	Reduced phytoavailability in lettuce, onion, red pepper, and cabbage	
Calcareous sludge		As	Reduced phytoavailability of As for lettuce	
Diatomite		As, Cu, Zn	Increase in shoot biomass of alder and decrease in Cd and Zn in leaves	Adsorption (w,x,y,z, aa,ab,ac,ad)
		Cd, Cu, Pb, Zn	More Cd, Cu, Pb, Zn in less available soil fractions	
		Cd, Cr, Cu, Ni, Pb	More Festuca rubra above ground biomass, increase in soil pH, increase of Cd, Cr in aerial plant parts	
Zeolite	Synthetic	Cd, Co, Cu, Ni, Zn	Soil pH increase from 3.3 to 7.6	
		Cd	Reduction of Cd concentration by up to 99%, soil pH increase due to $Ca(OH)_2$	
	Clinoptilolite		Stabilization of Cd associated with increase in pH and increases in pore volume	
	Natural	Hg	Reduced Hg accumulation in alfalfa seedlings and roots	Adsorption, ion-exchange (ae)
		Zn	Immobilization of Zn ions dependent on pH	Adsorption (af, ag, ah)
	Clinoptilolite	Cd, Pb	Reduced Cd and Pb in corn and barley	
	Natural	Cd	Increased wheat grain yield, increased pH, decreased Cd extractability from soil	

Continuation of table

		Cd, Cu, Pb, Zn	Reduction in aerial parts of cabbage, increased biomass, increased pH and CEC	Adsorption on oxides, complexation (ai)
			Increase in pH, increase in dissolved C, decrease in extractability, decrease in vegetable accumulation for Cd, Pb, and Zn	Adsorption (aj, ak, al, am,an)
Perlite		Cr, Cu, Fe, Mn, Ni, Pb, Zn	Reduced availability of all available metal(loid)s in maturing compost except Cr	
		Cu	Increased C, N, P2O5, and exchangeable K and reduced available Cu	
Vermiculite	Tanza	Cr, Ni, Ti, Zn	Decrease of all metal(loid)s available in solution	
	-	Cd, Cr, Cu, Ni, Pb, Zn	Reduced phytoavailability of all metal(loid)s in lettuce and spinach, increase in soil pH	
Potting soil		As, Pb	Decrease in extractable Pb, increase in extractable As, increase in soil pH	Pb dilution, As desorption (ao)
Compost	Green waste + hydrated lime	Cu, Zn	Increase in soil pH and decrease in exchangeable Cu and Zn, reduced bioavailability	Adsorption to OM (ap, aq)
	Green waste + hydrated lime	As, Cd, Cu, Pb, Zn	Reduced availability of all metal(loid)s in B. rapa leaves, pH increase	
	80% *Posidonia oceanica* + 20% zeolite	Cd, Zn, Cu	Decrease in H_20- and DTPA- extractable Cd, Zn, Cu	Binding to OM (ar)
	Vermicompost + zeolite	Cd, Pb, Zn	Decrease in soil pH, increase in EC, and less carbonate bound Pb, less exchangeable, and less carbonate-bound Cd and Zn	Fixation to OM related to pH change (as)

a. De la Fuente et al., 2011 ; b. Zhou et al., 2012 ; c. Carbonell et al., 2011 ; d. Udovic & McBride, 2012 ; e. Liu et al., 2019 ; f. Huang et al., 2018 ; g. Singh & Oste, 2001 ; h. Nwachukwu & Pulford, 2009 ; i. Huang et al., 2016 ; j. Gatimu et al., 2007 ; k. Carbonell et al., 2011 ; l. Bolan et al., 2003 ; m. Cao et al., 2022 ; n. Chen et al., 2019 ; o. Souag et al., 2009 ; p. Kar & Misra, 2004 ; q. Shi et al., 2019 ; r. Cui et al., 2016 ; s. Nkongolo et al., 2013 ; t. Wang et al., 2015 ; u. Rowley et al., 2020 ; v. Lwin et al., 2018 ; x. Kim et al., 2012 ; x. Li et al., 2009 ; y. Simon *et al.,* 2015 ; z. Whitbread-Abrutat, 1997 ; aa. Piri et al., 2020 ; ab. Radziemska et al., 2020 ; ac. Querol et al., 2006 ; ad. Lin et al., 1998 ; ae. Mahabadi et al., 2007 ; af. Haidouti, 1997 ; ag. Ören & Kaya, 2006 ; ah. Chlopecka & Adriano, 1997 ; ai. Zhou et al., 2020 : aj. Lahori et al., 2020 ; ak. Kim et al., 2012 ; al. Ozdemir et al., 2020 ; al. Rodriguez-Salgado et al., 2016 ; am. Marwa et al., 2011 ; an. Malandrino et al., 2011 ; ao. Paltseva et al., 2018 ; ap. Neaman et al., 2012 ; aq. Lwin et al., 2022; ar. Golia et al., 2017 ; as. Hamidpour et al., 2017

Continuation of table

3. Objectives and thesis approach

The general objective of the thesis is to evaluate the effect of culturally-relevant doses of easily available, applicable, and affordable amendments on the environmental and toxicological availability of metal(loid)s (specifically As, Cd, Pb, and Zn) in moderately contaminated kitchen garden soils and the plants grown upon them. The present research also aims to limit human exposure to metallic pollutants linked with the ingestion of soil particles and contaminated garden plants. The main working hypothesis of the thesis focuses on whether **culturally-relevant doses of soil amendments can reduce metal(loid) mobility, (bio)availability and oral bioaccessibility in multi-contaminated soils.** Several experiments were carried out on various physico-chemically distinct soils, where the effects of amendment dose and nature on metal(loid) behavior in soils and plant models were investigated (Figure 1-9). These experiments made it possible to answer to the following questions:

- What are the effects of several soil amendments on physico-chemical soil parameters and on environmental availability of metal(loid)s? To answer this question, investigations were carried out on a selection of 14 modalities (*i.e.* inorganic and organic amendments alone or in mixture) applied on three different moderately-contaminated kitchen garden soils with different contamination origins (Chapter 3);
- Does the establishment of a crop in combination with amendments influence the environmental availability and phytoavailability of metal(loid)s? To answer this question, an experiment consisted in studying the most relevant amendments identified in Chapter 3 in combination with lettuce (Chapter 4);
- Does the use of soil amendments as a management technique for moderately contaminated soils reduce population exposure? To answer this question, the oral bioaccessibility in case of non-intentional ingestion of soil particles was assessed for the different amended conditions studied in the thesis (Chapter 5);
- Can we manage vegetable garden soils with contaminated self-produced compost? What is the environmental and toxicological interest of the co-application of such compost and a natural zeolite to manage a metal-contaminated soil? (Chapter 6).

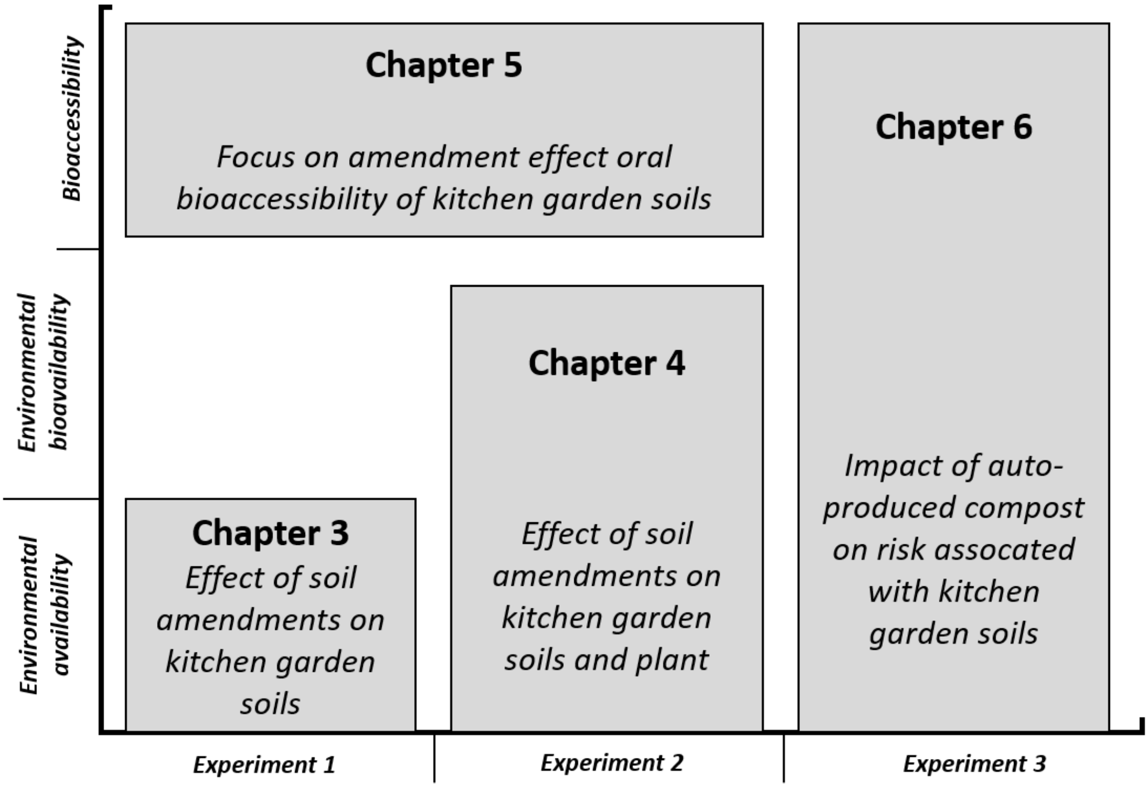

Figure 1-9. Thesis manuscript chapter explanations

Chapter 2: Materials & Methodology

Chapter 2: Materials & Methodology

The work done within the framework of this thesis seeks to study the effects of soil organic and mineral amendments on the environmental and toxicological availability of As, Cd, Pb, and Zn in three diverse kitchen garden (KG) soils with both anthropogenic and geogenous sources of contamination. The thesis consists of three main pot experiments, conducted in semi-controlled and controlled conditions (Figure 2-1).

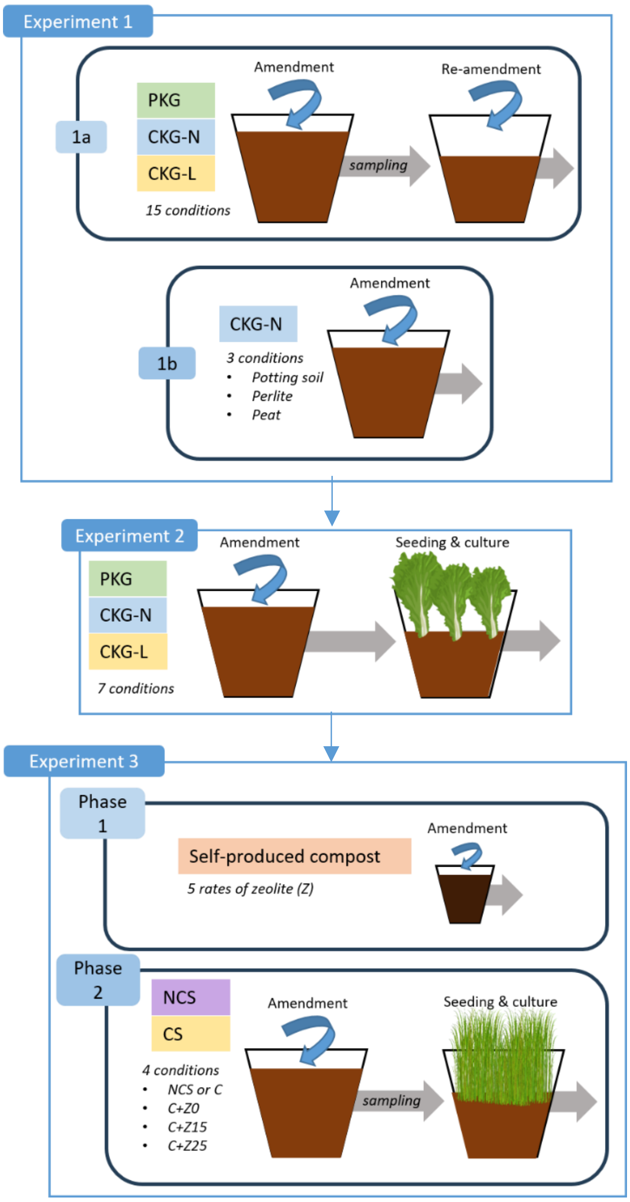

Figure 2-1. **Overarching experimental design schema. PKG: private kitchen garden; CKG-N: community kitchen garden in Nantes; CKG-L: community kitchen garden in Lille; NCS: non-contaminated control soil; CS: contaminated control soil; Z: zeolite; C+Z0, C+Z15, and C+Z25: contaminated compost applied at 20 t ha^{-1} without zeolite, and mixed with 15% and 25% of zeolite (w:w), respectively.**

The first experiment tests the effects of several amendments on the physico-chemical parameters of these three KG soils and on the metal(loid) behavior based on chemical extractions. The second experiment studies the most pertinent conditions from Experiment 1 on their metal(loid) immobilizing efficiency, implemented one the same three KG soils in combination with a plant model. The last experiment focuses on the potential risk of releasing the metals contained in a contaminated material-based self-produced compost, and evaluates the environmental and toxicological interest of the co-application of this compost and a natural zeolite to manage a metal-contaminated KG soil.

1. Materials

1.1 Kitchen garden soils studied

1.1.1 Presentation of soils studied

Experimental *ex situ* assays were conducted on soils from three moderately metal(loid)-contaminated kitchen gardens in France: a private kitchen garden (PKG) in Evin-Malmaison and two community kitchen gardens, one in Nantes (CKG-N) and one in Lille (CKG-L). These gardens have been studied during prior scientific projects, including REPJAR[1], financed by ARS Hauts-de-France, and the ANR-supported JASSUR[2] project (Pelfrêne et al., 2015; Schwartz et al., 2016; Pelfrêne et al., 2019). The main physico-chemical parameters and the degree of contamination in metal(loid)s) are given in Table 2-1 and Table 2-2. Thus these soils were chosen for study because of their moderate contamination, variability in terms of physico-chemical parameters, environmental contexts, and contamination sources.

[1] REPJAR: “**R**éduire l’**E**xposition aux métaux des **P**opulations en lien avec le **JAR**dinage et la consommation de denrées autoproduites" (2013-2015), gardens investigated including 115 in the megasite Metaleurop

[2] JASSUR: “**J**ardins **ASS**ociatifs **UR**bains et villes durables : pratiques, fonctions et risques" (2013), gardens investigated in Lille, Lyon, Marseille, Nancy, Nantes, Paris, and Toulouse

Table 2-1. Preliminary selected kitchen garden soil characterizations (data from REPJAR and JASSUR projects) and comparisons to other French kitchen garden soils and their agronomically optimal ranges

	PKG (n=25)[a]	*CKG-N (n=95)*[b]	*CKG-L (n=60)*[b]	*Ranges for French kitchen garden soils (n=104)*[a]	*Agronomically optimal ranges*[a]
pH$_{water}$	6.6 – 7.0	6.2 – 7.8	8.1 – 8.3	6.2 – 8.3	6.5 – 7.5
% Sand	23	Sandy loam to silty sand	34	-	-
% Silt	53		50	-	-
% Clay	24		16	-	-
OM (g kg^{-1})	51	19 - 76	90 - 120	17 – 103	40 – 100
CEC (cmol+ kg^{-1})	-	-	14 - 17	-	-
P (g P_2O_5 kg^{-1})	0.2 – 0.8	-	0.3	-	-
$CaCO_3$ (g kg^{-1})	3 - 6	0 - 20	50 - 100	0 – 563	-
[N] (%)	1.8	-	2	-	-
[C] (%)	30	-	62	-	-
C/N	17	-	33	10– 24	8 – 10

OM: organic matter; CEC: cation exchange capacity; P: available phosphate; EC: electrical conductivity

[a] Joimel, 2015, [b] REPJAR data; [c] JASSUR data

Table 2-2. **Preliminary selected kitchen garden soil metal(loid) concentrations (data from REPJAR and JASSUR projects) and comparisons to French background values and regional analytical values**

	PKG (n=25)[b]	*CKG-N (n=95)[c]*	*CKG-L (n=60)[c]*	*Median geo-chemical background values in Nord-Pas-de-Calais topsoil (n=232)[d]*	*Median geo-chemical agricultural background values in France (n=815)[e]*	*Limit of "ordinary" metal(loid) concentrations in France (n=815)[e]*	*Proposed REFUGE limit indicating an urban agricultural soil posing reasonable health risks based upon such soils in Ile-de-France[f]*
[As] (mg kg^{-1})	-	29 - 92	13 - 17	8.3	-	25	20
[Cd] (mg kg^{-1})	4 - 6	0.1 - 20	1	0.40	0.16	0.45	1.0
[Pb] (mg kg^{-1})	250 - 350	100 - 600	300 - 1000	29.7	34.1	50	100
[Zn] (mg kg^{-1})	300 - 400	25 - 300	400 - 900	67.1	80	100	264

[a] Joimel, 2015, [b] REPJAR data; [c] JASSUR data; [d]Sterckeman et al., 2007; [e] Baize, 2000; [f] AgroParisTech, 2019

PKG – Private kitchen garden in Evin-Malmaison

One soil was collected from a private kitchen garden “PKG,” located in Evin-Malmaison (Hauts-de-France), in the former coal-mining area of Northern France where considerable emissions were generated by the former lead smelter Metaleurop Nord (Figure 2-2). More specifically, this 150 m^2 private garden is located in a household backyard that has been characterized over the course of 4 years during REPJAR project. This soil is a slightly acidic, predominately silty soil (53%) with 23% sand and 24% clay, 51 g kg^{-1} OM, a relatively low carbonate content of below 6 g kg^{-1}, and a C/N of 17 (Table 2-1). A study of 104 French kitchen garden soils found that their pH values range from 6.2 to 8.3, OM values from 17 to 103 g kg^{-1}, $CaCO_3$ from 0 to 563 g kg^{-1}, and C/N from 10 to 24, with agronomically optimal ranges being 6.5 to 7.5 for pH, 40 to 100 g kg^{-1} for OM, and 8-10 for C/N (Joimel, 2015). PKG thus has some agronomically beneficial qualities, but an elevated C/N. The soils in this region are impacted by high levels of atmospherically-deposited Cd, Pb, and Zn, with this site presenting on average 4 mg kg^{-1} Cd, 250 mg kg^{-1} Pb, and 300 mg kg^{-1} Zn (Table 2-2). This soil thus exceeds values for Nord-Pas-de-Calais, as well as background values for French agricultural soils, and and ordinary levels for Cd, Pb, and Zn, (Douay et al., 2009; Baize, 2000). Moreover, regarding REFUGE[3] limits (Table 2-2), PKG possesses potentially risky concentrations of Cd, Pb, and Zn exceeding 1.0, 100, and 264 mg kg^{-1} respectively in its soil (AgroParisTech, 2019).

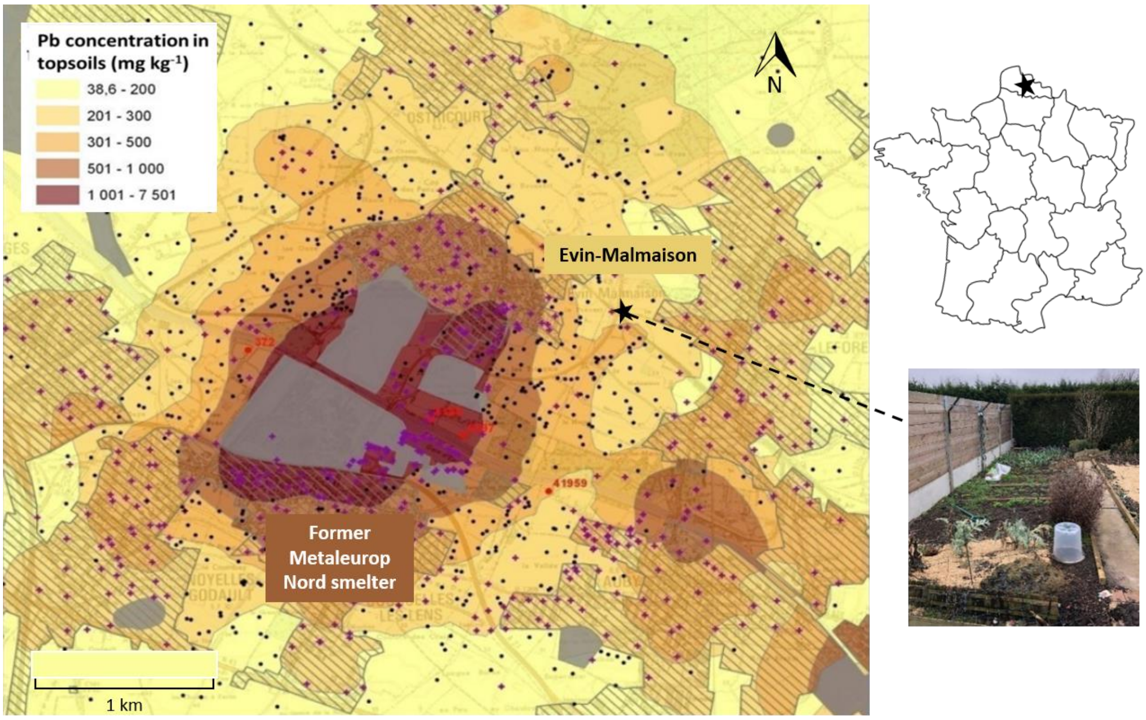

Figure 2-2: **Localization of PKG in Evin-Malmaison (France) and Pb contamination footprint due to Metaleurop Nord past activities (adapted from Douay et al., 2011)**

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[3] REFUGE: “**R**isques en **F**ermes **U**rbaines : **G**estion et **E**valuation”, Guide of recommended urban agriculture contamination limits based upon the characterization and health risk evaluation of urban market soils in the Ile-de-France region

Studies carried out on this garden showed that certain plants grown on the soil contained elevated levels of Cd and Pb exceeding regulatory values set by the European Commission regulation amendment 2021/1317 of 9 August 2021 to amendment 1881/2006 for sellable vegetables in their edible parts. These affected kitchen garden plants included carrots, celery, chicory, shallots, turnips, leeks, potatoes, radishes, lettuce, tomatoes, spring onion, thyme, rosemary, sage, and mint (Pelfrêne et al., 2015).

CKG-N – Community kitchen garden in Nantes

The second soil "CKG-N," was collected from an individual parcel of approximately 200 m^2, located in Nantes (Pays de la Loire) in the 230,000 m^2 community kitchen garden named Les Eglantiers (Figure 2-3). In this community garden, the soils have a sandy loam to silty sand texture, and present a pH between 6.2 and 7.8, and a OM content between 19 and 76 g kg^{-1} (Table 2-1). This garden is located in proximity to a highway, and is impacted by geogenic As and Pb linked to the region itself as well as the presence of shallow mineralized micaschist which runs through the community garden (Bechet et al., 2018; Jean-Soro et al., 2014; Le Guern et al., 2018). This site is divided into 100 parcels, for which the median As content is 29 mg kg^{-1} and the median Pb content in 84 mg kg^{-1} (Table 2-2). The CKG-N parcel itself is also associated with past agricultural and viticultural activity, and exceeds median values for As and Pb concentrations found in the entire garden to such an extent that this portion of the garden was closed. Additionally, previous studies have shown that this plot is associated with the production of some non-conform tomato and green bean plants, as compared to pre-2021 EU foodstuff regulations (Le Guern et al., 2018).

The first 25 cm of this garden contains levels of As that range between 29 and 92 mg kg^{-1}, between 0.1 and 20 mg kg^{-1} Cd, from 100 to 600 mg kg^{-1} Pb, and between 25 and 300 mg kg^{-1} Zn. The particular plot sampled, CKG-N, is confirmed to have levels of both As and Pb in its area of approximately 250 m^2 that represents some of the more contaminated plots in Les Eglantiers. Based upon the ranges of metal(loid)s found in the garden, this soil exceeds background values for French agricultural soils for Cd and Pb, and potentially levels of ordinary metal(loid) concentrations in French topsoils for As, Cd, Pb, and Zn (Baize, 2000). In terms of urban agricultural soil metal(loid) concentrations that could pose human health risks as set by REFUGE (Table 2-2), CKG-N has potentially risky amounts of As, Cd, Pb, and Zn.

2-4).

Figure 2-3: **CKG-N localization in Les Eglantiers community kitchen garden (Nantes, France) and mapping of anomalies in Pb and As concentrations in the first 25 cm of soil exceeding background values (adapted from Le Guern et al., 2018)**

CKG-L – Community kitchen garden in Lille

The third soil was collected from a recently closed Bazinghien community garden, located in Lille (Hauts-de-France) (Figure 2-4). This garden is located next to a highway, and associated with dumpsite activity and variable individual plot activity. It was also impacted by past industrial activities. This garden was characterized during the JASSUR project, which indicated variations in contamination, specifically in Pb. The soil is silty with a basic pH (8.1 – 8.3) and an OM content between 90 and 120 g kg^{-1}. This soil also has a CEC between 14 and 17 cmol^{+} kg^{-1}, an available P content of 0.3 g P_2O_5 kg^{-1}, a $CaCO_3$ content of more than 50 g kg^{-1}, and a C/N of 33 (Table 2-1). This soil thus possesses an elevated, non-optimal pH and levels of OM, $CaCO_3$, and C/N based upon typical ranges for kitchen garden (Joimel, 2015). Lettuce, radishes, zucchini, and mint grown in this area were found to be non-conform according to amendments to the European Commission regulation 1881/2006 for maximum levels of contaminants in foodstuffs. A square of the garden representing approximately 50 m^2 that presented moderate levels of Pb contamination likely between 301 – 600 mg kg^{-1} was sampled as "CKG-L" (Figure 2-4).

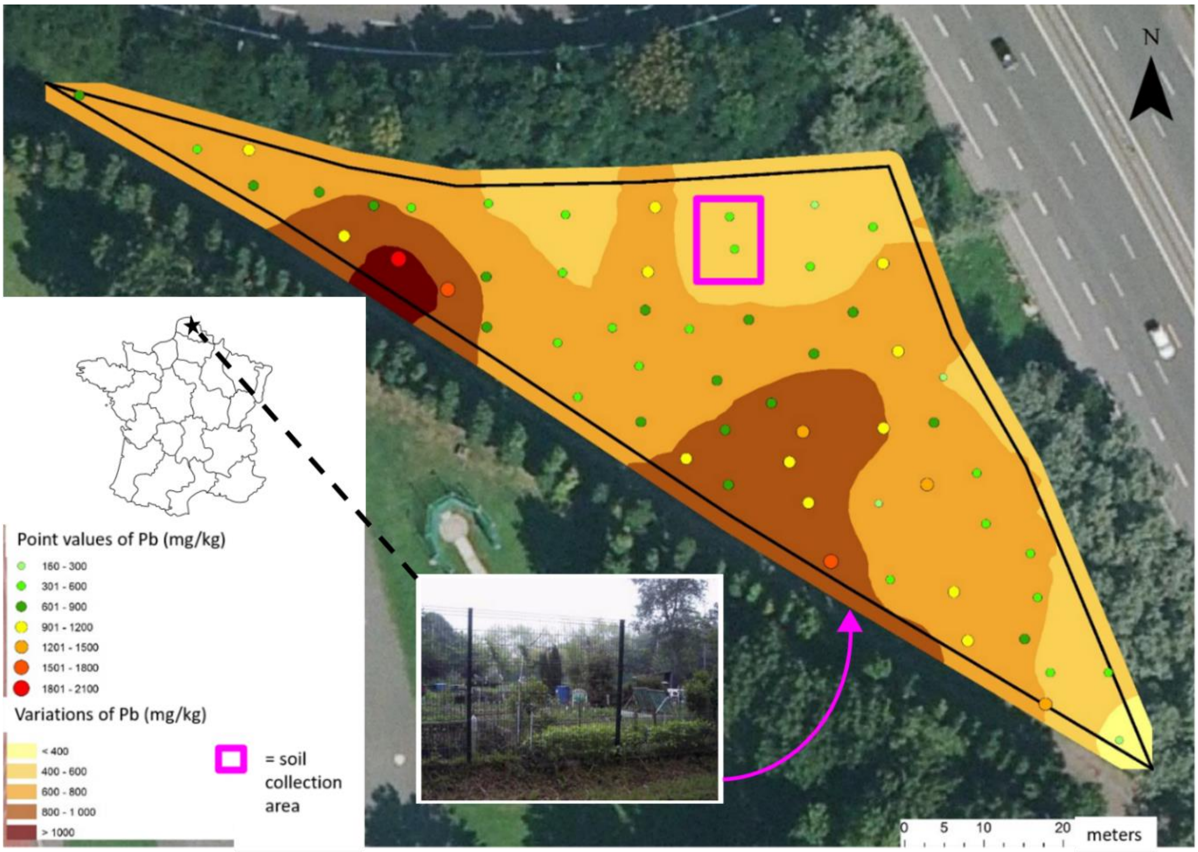


Figure 2-4: **Bazinghien kitchen garden Pb contamination footprint and CKG-L soil collection site**

Previous studies of the parcel have confirmed that portions of Bazinghien garden and presumably the selected parcel contains between 13 and 17 mg kg^{-1} As, 1 mg kg^{-1} Cd, from 300 to 1000 mg kg^{-1} Pb, and 400 to 900 mg kg^{-1} Zn (Table 2-2) . CKG-L thus likely exceeds geochemical background values for Nord-Pas-de-Calais for As, Cd, Pb, and Zn (Douay et al., 2009) as well as background values for French agricultural soils and ordinary values of metal concentrations in French topsoils for Cd, Pb, and Zn (Baize, 2000). According to REFUGE limit values, CKG-L has potentially risky amounts of Pb and Zn.

1.1.2 Collection and preparation of soil samples

Approximately 50 kilograms of soil was collected from each garden (PKG, CKG-N and CKG-L) using a shovel. A composite topsoil sample (between 5 and 10 samples) was constituted from the ploughed layer (0-25 cm) of each of the three sites separately. The three soil samples were first air-dried at a temperature below 40°C, homogenized, and crushed to pass through a 10-mm stainless steel sieve according to the ISO 11464 standard (AFNOR, 1995). The soils were then further sieved to 2 mm before initiating pot and greenhouse experimentations. Some soils were ground to 250 µm for characterization analyses depending on protocols.

1.2 Amendments

1.2.1 Selection

Amendment selection was based on a database developed from a review of 128 scientific articles during the PhytExPPo^4 project. This database contains data about metal(loid) concentrations (As, Cd, Cu, Cr, Ni, Pb, Zn) in soils and vegetables before and after the addition of amendments. Specifically, information about experiment types (pots or *in situ*), contamination origins (geogenic, artificial, anthropogenic), physico-chemical characteristics of soils before and after amendment (pH, clay content, organic C content, CEC, metal(loid) concentrations), amendments (type, dose), and the studied plants (variety, analyzed organs, cultivation time, metal(loid) content) are detailed. The database also included corresponding values of changes in environmentally available metal(loid)s in order to calculate an efficacy rate for amendments, based upon the percent by which the amendment changed phytoavailability in comparison to the control.

During the thesis, this database was revised to include soil type and an expanded amendment classification system based upon bibliographic research. It was also updated with more current research from 2017 to 2020. This culminated in a revised database comprised of a total of 225 articles, 547 different amendment conditions, and 54 different kitchen garden plants. This final database included 18 different data fields, and soil metal(loid) concentrations ranging from 0.11 to 4,772 mg kg^{-1} As, 0.1 to 296 mg kg^{-1} Cd, 41 to 42 mg kg^{-1} Cr, 2.4 to 3,524 mg kg^{-1} Cu, 2.5 to 160 mg kg^{-1} Ni, 25 to 19,129 mg kg^{-1} Pb, and 10 to 19,510 mg kg^{-1} Zn. To focus on amendments suitable for use in the three kitchen garden soils studied, queries were modified to pertain specifically to these soils as described in preliminary investigations (Table 2-2). A first screening was realized considering the physico-chemical characteristics of the CKG-N, CKG-L and PKG soils. Notably, studies examining soil pHs between 6 and 8 and organic matter contents between 40 and 100 g kg^{-1} were first considered.

A total of 67 amendments were cited as able to reduce the availability of As, Cd, Pb, and/or Zn. Secondly, the metal(loid) sources (*e.g.*, not artificially contaminated) and concentrations of the soils studied in the literature were also considered, in order to focus on similar qualities of soil as the CKG-N, CKG-L and PKG soils. The following ranges were considered in database queries: As from 5 to 100 mg kg^{-1}, Cd from 0.1 to 20 mg kg^{-1}, Pb from 100 to 1,000 mg kg^{-1}, and Zn from 50 to 1,000 mg kg^{-1}. According to the specific soil characteristics demanded, 17 different amendments listed in Table 2-3 were identified as possibly effective (*e.g.* green waste compost, manure, bone meal, triple superphosphate, hydroxyapatite, hydrated lime, magnesium lime, calcium silicate, sodium silicate, synthetic zeolites, vermiculite). The doses at which their application have an effect on metal availability were also considered and reported in this table.

Table 2-3. List of amendments (nature and dose) which have been studied in mixture with soils meeting the selection criteria for physicochemical soil characteristics and which had an effect on metal(loid) availability (↑ and green increase and ↓ and red decrease in environmental availability, "-" no effect or a variable effect , "x" non-tested metal(loid)).

Nature	Amendment	Dose	Cd	Pb	Zn	As	Source
OM-rich	Green waste compost	0.3%	↓	-	↓	x	He et al., 2019
		2.5%	↓	x	x	x	Al Mamun et al., 2016
		6%	↓	↓	↓	↓	Liénard et al., 2016
	Vermicompost	0.15%	x	x	x	↓	Das et al., 2016
	Manure	0.25 – 2 %	x	x	↓	x	Narwal et al., 1992
		3%	↓	↓	↓	x	Kim et al., 2012
		4.5%	x	x	x	↓	Das et al., 2016
	Peat	3%	↓	↓	x	x	Chen et al., 2016
		5 – 10%	x	x	↓	x	Angelova et al., 2010
Phosphate-rich	Bone meal	0.03%	x	↓	x	-	Paltseva et al., 2018
		2%	x	↓	x	x	Obrycki et al., 2016
		4%	x	↑	x	x	
	Triple superphosphate	2.5 – 5%	↓	↓	↓	x	Hettiarachi & Pierzynski, 2002
	Single superphosphate	5%	x	↓	x	x	Chen et al., 2006
	Rock phosphate	1%	↓	↓	↓	x	
		10%	↓	↓	↓	x	Baste et al., 2001
	Hydroxyapatite	1.5 – 3%	↓	↓	↓	x	Li et al., 2015
		5%	↓	↓	x	x	Wang et al., 2014
Calcareous	Hydrated lime	0.1%	↓	x	↓	x	Lu et al., 2014
		0.25%	↓	x	↓	x	Lombi et al., 2002
		0.27%	x	x	x	↓	Warren & Alloway, 2003
		0.68%	x	x	x	↓	
		1.36%	x	x	x	↓	
		0.45%	↓	x	↓	x	Lehoczky et al., 1998
		0.9%	↓	x	↓	x	
		1%	↓	↓	↓	x	Kim et al., 2012
		1%	x	x	↓	↓	Hartley & Lepp, 2008
	Dolomite (Mg lime)	3%	↓	↓	↓	x	various
Siliceous	Calcium silicate	0.095%	↓	x	↓	x	Lu et al., 2014
		1%	↓	x	x	x	Chang et al., 2016
		2%	↓	x	x	x	
		4%	↓	x	x	x	
	Sodium silicate	0.1%	↓	x	↓	x	Lu et al., 2014
	Natural zeolite	3%	↓	↓	↓	x	Kim et al., 2012
	Synthetic zeolite	1%	↓	↓	x	x	Cheng & Hseu, 2002
	Vermiculite	3%	↓	↓	x	x	Chen et al., 2016
Mixes	Potting soil	3%	↓	↓	x	x	
		33%	x	↓	x	↑	Paltseva et al., 2018

1.2.2 *Characteristics of amendments used in the experiments*

To choose appropriate amendments to test during experimentations carried out during the thesis, further consideration was then given to the qualifying 17 amendments from the database with specific natures listed in Table 2-3. These include amendments that were (i) commercially available or otherwise easily accessible in France, (ii) affordable, and (iii) easily applicable. Likewise, public acceptance in terms of environmental friendliness was also considered. Among them, seven amendments fitting these criteria that had successfully decreased the concentration of metal(loid)s in plants or available metal(loid)s in soils were chosen for application on the three soils. These are compost, manure-based organic fertilizer, bone meal, hydrated and magnesium limes, zeolite and potting soil.

Compost used in the experimentations was produced by a composting company (Agriopale, Cucq, France) from early summer green waste collected from landfills, door-to-door collection, enterprises, and local collectives working on green area maintenance. This product was sold for 0.05 € kg^{-1} . The compost was allowed to mature for 6 months, and then was collected and tested as **C6**. The remaining compost was let to mature for two additional months at the composting company, and tested as **C8**. The two different degrees of compost maturity were selected in order to study the effect of compost stability on metal behavior in (KG) soils studied.

Organic fertilizer (OF) in the form of a commercialized chicken manure (Plein Champ, France) for 2.50 € kg^{-1} and complying to the NF U 42-001 standard (1981) was chosen for experimentation. This product contains 4% organic N, 3% phosphoric anhydride, 2.5% potassium oxides, and 1% magnesium oxides.

The **bone meal (BM)** chosen for the experimentations is commercialized by Agro-Sens (Agout-Rousseau, France), sold for 6.50 € kg^{-1} , and contains non-homogenous granules made up of 7% N org, 15% phosphoric anhydride, 15% calcium oxides, and 54% organic matter. It also complies to the NF U 40-001 standard (1981) for soil amendments.

Two **limestones** were studied in this work: hydrated lime (**HL**) and magnesium lime (**ML**). HL was marketed as Terrecalco 70 and sold by Carmeuse (France) for 1.04 € kg^{-1} . This product contains 72% calcium oxides and 0.7% magnesium oxides. ML is produced by DCM® (Aire sur l’Adour, France) as “calcaire vert” (0.90 € kg^{-1}) and contains 30% calcium oxides and 15% magnesium oxides.

Natural **zeolite (Z)** containing 68.7% chabasite and 20.03% potassium feldspar sold by Chabasite France for 12 € kg^{-1} was also studied.

A seeding **potting soil (PS)** composed of peat moss, perlite, sand, and dolomite and containing 34% of dry matter by mass and 65% organic matter by mass made by Scotts (Ecully, France) and sold by Fertiligène for 4.95 € kg^{-1} was tested as an amendment in the following experiments.

Some of the 17 amendments identified as effective by the database are not available, or inappropriate for kitchen garden contexts despite their effectively immobilizing effect on metal(loid)s. A substitute with the same active compounds, or of the same nature or with a close composition as identified amendments was thus chosen. Their cost, ease of application, and their likely social acceptance to implement them as an amendment were still considered.

Calcium and sodium silicates effectively immobilize certain metal(loid)s but the latter can be mildly toxic upon ingestion and caustic, and both are rarely marketed for garden. The commercially available garden amendment "**diatomaceous earth (DE)**" could have the same effect on metal(loid)s availability since is composed of an amorphous silica (SiO_2-nH_2O). This product contains minimal amounts of microcrystalline material: 80-90% silica and 10-20% Fe, Al, Mg and/or Ca, which occur as clay minerals, quartz, gypsum, calcite, feldspar, micas and to a small extent salts, phosphates, pyrite and/or volcanic ash. This amendment often includes forms of calcium and oxides, such as $CaCO_3$, SiO_2, Al_2O_3, and Fe_2O_3 (Costa et al., 2018). DE can be marketed as either a non-calcinated, finely ground natural product and amendment, or a calcinated, crystallized, insecticide. Diatomaceous earth applied in the garden is typically composed of primarily amorphous silica and nutrients such as B, Ca, Fe, Mn, Cu, and Na, which can contribute to kitchen garden health. Furthermore, due to its very high water retention capacity, the addition of 15-25% (v/v) diatomaceous earth is recommended in the creation of potting soils or on landscaping soil (Brown, 2017). The product chosen for testing is a non-calcinated 100% silicon dioxide with a basic pH sold by Bio-Control Professionals (France) for 7.56 € kg^{-1}.

Phosphates were identified in the database as a metal(loid) immobilizer. Two of the most commonly used phosphorous compounds for metal(loid) remediation in scientific literature are superphosphate and insoluble apatite. However, the former is a fertilizer with a questionable production background, and the latter is not sold on the gardening market. Both are widely regarded as potentially toxic for wildlife. **Crushed horn (CH),** commercially available in gardening as a flour or as shavings, is a phosphate-rich and nitrogen-rich product composed of ground bovine horns and hooves and could be an environmentally friendly alternative. Moreover, this product contains calcium and (α)keratin (Zhang et al., 2013). The (α)keratin contains various functional groups, such as $-OH$, $-NH_3$, $-O_2$, and $-SH$ giving it immobilizing ability of metal(loid)s as reported for the treatment of industrial water (Kar and Misra, 2004; Nikiforova et al., 2019; Cao et al., 2002, Saoag et al., 2009, Chen et al., 2019). According to our knowledge, at the time of amendment selection no experiment had yet studied the effect of **CH** on metal(loid) behavior in soil. The commercialized amendment chosen for the experiment complies to NF U 42-001 (1981) for fertilizers, is produced by Solabio (Ecully, France) for 6.60 € kg^{-1} and contains 13% organic N.

In total, ten amendments which had, according to the literature, successfully decreased the concentration of metal(loid)s in plants or available metal(loid)s in soils, or contained products that did so, were retained for pot experimentations. These amendments represent five amendment types, including organic matter-rich amendments (two maturities of C6 and C8, OF), phosphate-rich amendments (BM, CH), calcareous amendments (ML and HL), siliceous amendments (Z, DE), and amendment mixes (PS). Depending on amendment type and when applicable, all amendments adhere to either NF U 42-001 (1981) standards for fertilizers, NF U44-051 standards (2006) for organic amendments for agricultural use, the 1998 limit for sewage sludge agricultural use, or NF U44-551 standards (2002) for culture supports (AFNOR, 2018; JORF, 1998; SATEGE, 2019). The characteristics of amendments selected for experimentation are presented in Table 2-4.

Table 2-4. **Physico-chemical characteristics and metal(loid) concentrations of amendments selected for experimentations**

	pH_{H2O}	CEC cmol+ kg^{-1}	P_2O_5 g kg^{-1}	$CaCO_3$ g kg^{-1}	EC µS cm^{-1}	N %	C %	Cd mg kg^{-1}	Pb mg kg^{-1}	Zn mg kg^{-1}	As mg kg^{-1}
C6	8.6	35.85	4.82	60	1,620	1.5	18.4	0.30	20.5	229	2.94
C8	8.3	36.94	7.10	57	2,100	1.6	18.4	0.32	22.7	338	2.79
OF	5.9	24.72	20.51	74	12,270	4.9	33.9	0.91	19.9	171	1.24
BM	6.0	26.67	39.56	31	3,180	7.0	33.2	<0.1	<2	138	<0.15
ML	8.5	3.46	0.08	279	980	<0.2	11.9	0.47	155	64	2.23
HL	12.2	44.31	0	91	8,240	<0.2	4.9	0.25	3.5	34	0.65
Z	8.1	9.99	0.19	2	114.5	0.1	<1	0.10	47.7	54.5	26.0
PS	7.4	37.89	0.39	24	953	0.9	25.1	0.11	5.4	26	3.84
DE	8.9	9.29	0.05	417	837	0.04	0.28	0.055	<2	11	<1
CH	6.6	14.82	14.40	18	1,819	13.6	40.3	<0.1	<2	96	<0.15

CEC: cation exchange capacity; P_2O_5: assimilable phosphorus; EC: electric conductivity; N: total nitrogen; C: organic carbon; C6: young compost (6 months); C8: mature compost (8 months); Z: zeolite; OF: organic fertilizer; ML: magnesium lime; HL: hydrated lime; DE: diatomaceous earth; PS: potting soil; BM: bone meal; CH: crushed horn

1.2.3 Preparation of amendments

Before their addition to the soils, the selected ten amendments were prepared in order to facilitate their addition to the soil. HL and DE remained unaltered, as they were already finely ground. The C (C6 and C8) and PS, sold at a size of about 10 mm, were sieved to a 2 mm size in order to be in the same condition as the soils and to promote homogeneity to facilitate analyses. OF, ML, Z, BM and CH were crushed to 250 µm before proceeding with experimentation because of their size and hardness which would not allow for sieving.

2. Experimental design

2.1 Experiment 1

Experiment 1 was divided in two experiments, named 1a and 1b (Figure 2-5).

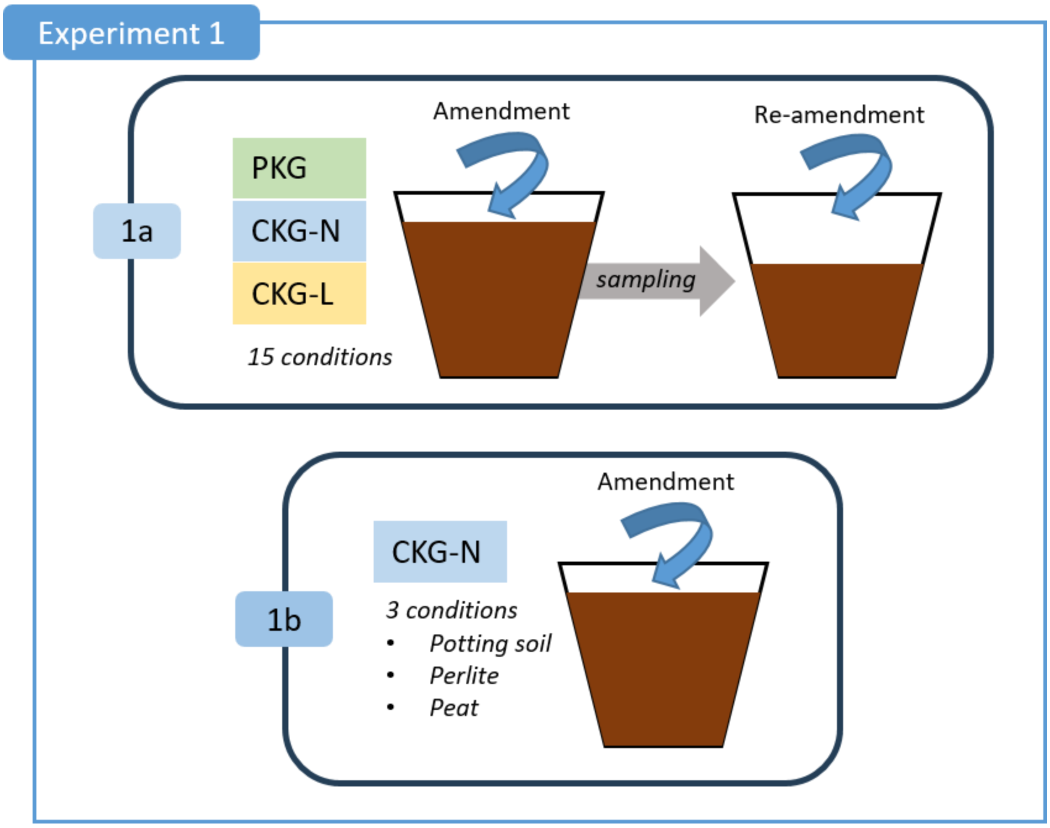


Figure 2-5. **Experiment 1 design where PKG: private kitchen garden; CKG-N: community kitchen garden in Nantes; and CKG-L: community kitchen garden in Lille**

2.1.1 Experiment 1a

This experiment aimed to assess the effect of the ten selected amendments on the metal(loid) behavior in the three kitchen garden soils (PKG, CKG-N and CKG-L). More specifically, 15 conditions, including a control (*i.e.*, U1 without amendment), were applied where the amendments selected were considered alone or in mixture. Moreover, to simulate two crop years, soils received a second dose of amendments. So for each amended conditions, “D1” represented the first dose and “D2” the final dose of amendments after their re-application (Table 2-5). For each condition, three pots were prepared. Amendment rates were chosen to mimic cultural seeding practices that a gardener would typically use.

Table 2-5. **Amendment rates used in the Experiment 1a in comparison to cultural seeding practices**

Amendments	*Name*	*D1*	*D2*	*Cultural uses*
Compost				0.6%
6 months (young)	**C6-20**	0.6%	1.2%	-
	C6-40	1.2%	2.4%	-
8 months (mature)	**C8-20**	0.6%	1.2%	-
	C8-40	1.2%	2.4%	-
Compost + zeolite				10:1
Young compost + zeolite	**C6+Z**	0.6% + 0.06%	1.2% + 0.12%	-
Mature compost + zeolite	**C8+Z**	0.6% + 0.06%	1.2% + 0.12%	-
Chabasite natural zeolite	**Z**	2%	4%	1.8%
Organic fertilizer (chicken manure)	**OF**	0.5%	1%	0.1%
Magnesium lime	**ML**	0.1%	0.2%	0.036%
Hydrated lime	**HL**	0.05%	0.1%	0.03%
Diatomaceous earth	**DE**	0.1%	0.2%	1%
Potting soil (for seeding)	**PS**	3%	6%	33%
Bone meal	**BM**	0.05%	0.1%	0.03%
Crushed horn	**CH**	0.05%	0.1%	0.024%
Unamended control	**U1**	-	-	-

Calculations based upon dry weights, a soil density of 1.3 g cm^{-3}, and an application depth of 0.25 meters. D2 represents the final dose and corresponds to a double dose of D1.

Dried 2 mm-sieved soil (500 g) and amendments were thoroughly mixed, humidified to 60% with osmosed and tap water (*v:v*, 4:1; pH of 7.0), and placed into pots. These pots were humidified to maintain weekly water holding capacity (WHC) at 60% and kept in a cool, dark place at a constant temperature (Figure 2-6).

Figure 2-6: **Experiment 1 amended soil pot setup maintained in controlled conditions**

After six weeks of maturation, soil-amendment mixes were removed from their pots and left to dry at ambient temperature. One hundred and fifty grams were then removed, one part was sieved to 2 mm and the other ground to 250 µm for further analysis. These samples were analyzed as “D1” soil. Three hundred grams of the remaining soil was then amended again with the same D1 dose of amendment in order to simulate cultural practices of gardeners over two years, humidified at 60% of WHC, repotted to continue maturing for eight additional weeks in the same conditions. At the end of the maturation period, soils were dried and ground in a similar manner. These samples were analyzed as “D2” soils.

2.1.2 Experiment 1b

This experiment was carried out to study more specifically potting soil (PS), and identify which active components in this product could act on metal(loid) behavior. The potting soil used is composed of peat moss (40%), perlite (40%), sand (15-20%), and dolomite (2.5%). Dolomite, peat and perlite are cited in the literature as metal(loid) immobilizers, unlike sand, which is an inert material (Kelley et al., 2007; Abbar et al., 2017; Chen et al., 2016). Dolomite is an anhydrous carbonate mineral composed of calcium magnesium carbonate ($CaMg(CO_3)_2$), as magnesium lime (ML). This amendment was already studied and applied at a superior rate in the part 1a of the experiment. Consequently, dolomite and sand were not tested in experiment 1b. Thus, regarding the results obtained in the experiment 1a, specifically on As, this supplementary experiment consisted in testing the effect of peat (PEAT) and perlite (PERL) in comparison to PS on the availability of As in the CKG-N soil, and in the unamended control soil (U1). Potting soil was applied with the same application rate (D1) as in Experiment 1a (Table 2-5). Peat sieved to 2 mm and perlite ground to 250 µm were separately added to the soil by respecting the composition of potting soil (*i.e.*, 40% each) with a rate of 1.2%. This experiment was carried out in triplicates in pots of 300 g, mixed, humidified, matured, dried, and prepared as in Experiment 1a.

2.2 Experiment 2

Experiment 2 was conceived in order to assess the effect of the most pertinent amendments (composts, bone meal, hydrated lime, zeolite, crushed horn, potting soil) and doses tested during Experiment 1 on the phytoavailability of metal(loid)s for lettuce grown on the same three soils (PKG, CKG-N and CKG-L). For each soil, selected amendments were added to 1.5 kg of soil in the same manner as the previous experiment. A control condition without amendment (U2) was also included in the experimental design (Figure 2-7).

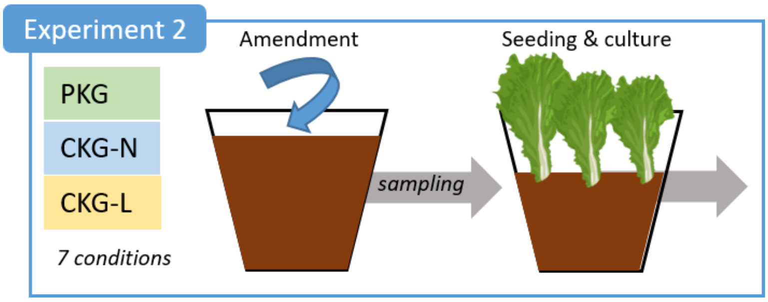


Figure 2-7. Experiment 2 design where PKG: private kitchen garden; CKG-N: community kitchen garden in Nantes; and CKG-L: community kitchen garden in Lille

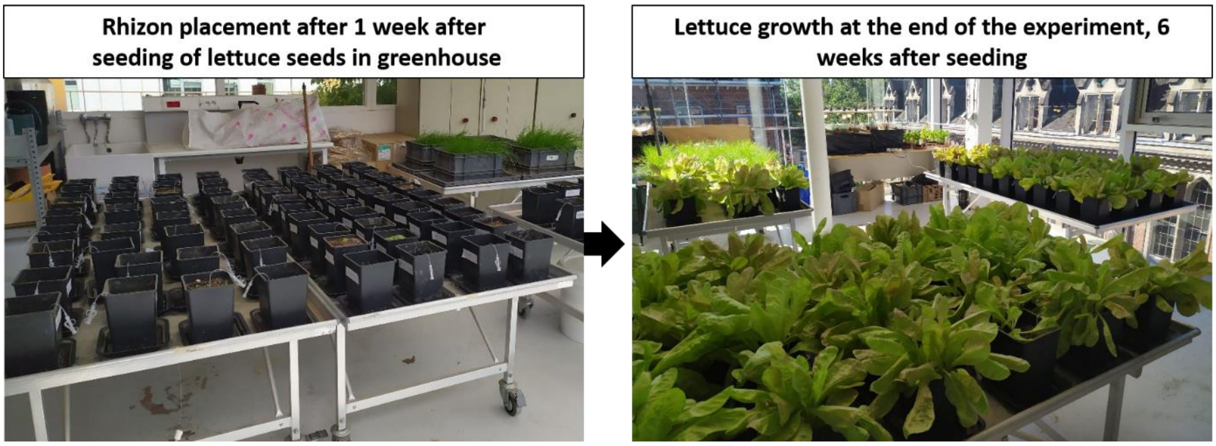
Table 2-6 lists the amendments and doses at which they were applied to the tested soils. D1 and D2 both refer to the doses tested in Experiment 1, with D2 being added at once instead as the culmination of two doses of D1.

Table 2-6. Amendments and doses from Experiment 1 chosen to be followed Experiment 2

PKG		CKG-N		CKG-L	
Condition	*Dose*	*Condition*	*Dose*	*Condition*	*Dose*
CH	*D1*	PS	*D1*	PS	*D1*
C6+Z	*D1*	C6+Z	*D1*	C8+Z	*D2*
C6-20	*D1*	C6-20	*D1*	C8-40	*D1*
C6-40	*D1*	C6-40	*D1*	C6-40	*D1*
Z	*D1*	Z	*D1*	BM	*D1*
HL	*D2*	HL	*D2*	HL	*D1*

PS: potting soil; C6-20: young compost (6 months) at 20 t ha−1; C6-40: young compost (6 months) at 40 t ha−1; C8-20: mature compost (8 months) at 20 t ha−1; C8-40: mature compost (8 months) at 40 t ha−1; C6+Z: mixture of young compost and zeolite; C8+Z: mixture of mature compost and zeolite; Z: zeolite; HL: hydrated lime; BM: bone meal; CH: crushed horn.

After six weeks of maturation in a temperate and dark place, amended soils were placed in the greenhouse and seeded with less than ten lettuce seeds (*Lactuca sativa* L., var. Merveille des 4 saisons). Germination was followed and after 2 weeks, seedlings were thinned to select three of the healthiest plants per pot, for each of the three pots tested per condition and soil. One week later, porous needles (Rhizons®) capable of sampling the soil solution were placed in these pots. This soil pore water (SPW) was collected 3 weeks and 6 weeks after seeding (Figure 2-8).



Rhizon placement after 1 week after seeding of lettuce seeds in greenhouse

Lettuce growth at the end of the experiment, 6 weeks after seeding

Figure 2-8. Experiment 2 greenhouse setup and lettuce growth over time

After 6 weeks of growth lettuce leaves were harvested, double-washed with tap water, and dried at 40°C before being ground to 250 µm for analysis. Pots were watered as needed. Soils were removed, dried at 40°C, and sieved to 2 mm and/or ground to 250 µm for further analysis.

2.3 Experiment 3

The third experiment aimed to study a self-produced compost hailing from a contaminated context's release of metals (Cd, Pb and Zn) in soils, and the immobilizing effect of zeolite on these pollutants. The experiment was carried out in two phases (Figure 2-9). In the first phase, the objective was to study the metal(loid) immobilizing effect of different doses of chabazite zeolite (Z) combined with a self-produced compost (C). The objective of the second phase was to study the environmental and toxicological interest of the co-application of this compost and Z to manage kitchen garden soils, in particular a non-contaminated (NCS) soil and a contaminated soil (CS) corresponding to the CKG-L soil.

2.3.1 Experiment 3 - Phase 1

Five doses of chabazite zeolite were tested 0, 10, 15, 20, and 25% by mass. The zeolite was the same as that used in the first two experiments. The compost used in this experiment was auto-produced from garden scraps and grass grown on the PKG soil located near the former smelter Metaleurop Nord. The material, which was dark brown and visibly mature, was sieved to 2 mm. This phase was carried out in triplicates, in pots in which 100 g of contaminated compost were mixed with 0, 10, 15, 20, and 25% by mass of zeolite and named respectively Z0, Z10, Z15, Z20 and Z25. Mixtures were then matured in the same manner as the other amendments in the prior experiments. After maturation, they were removed, dried at 40°C, and sieved to 2 mm and/or ground to 250 µm for analysis.

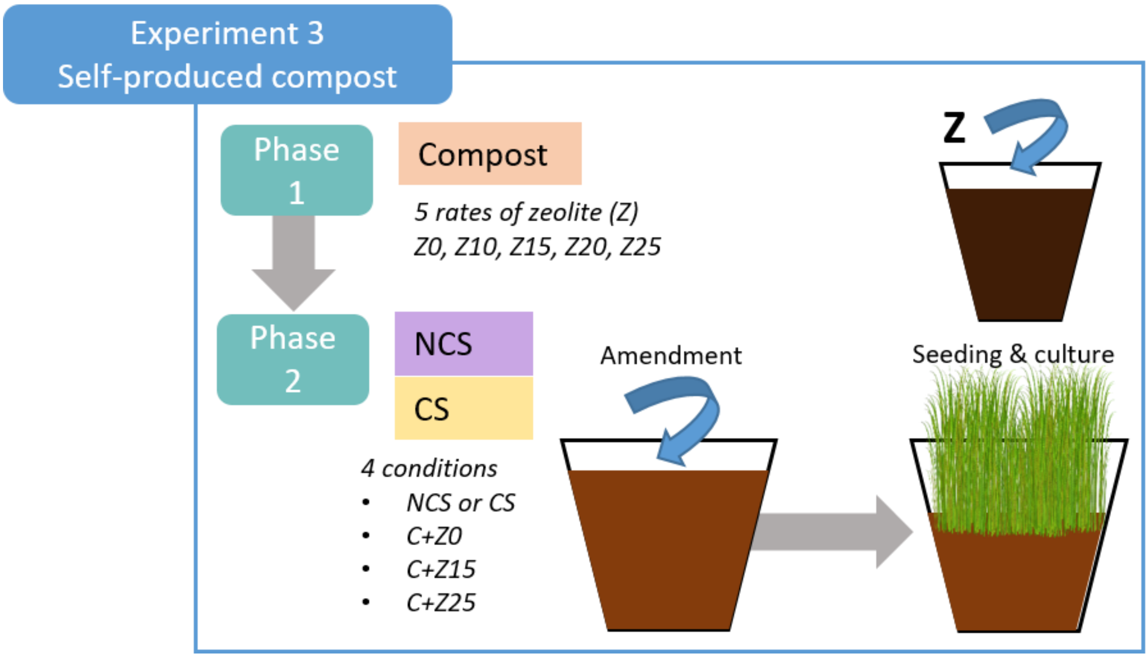


Figure 2-9. Experiment 3 design with NCS: non-contaminated soil; CS: contaminated soil (*i.e.,* CKG-L); C+Z0, C+Z10,C+Z15, C+Z20 and C+Z25: contaminated compost applied at 0.6% without zeolite, and mixed with 10%, 15%, 20% or 25% its dry weight in zeolite, respectively.

2.3.2 Experiment 3 - Phase 2

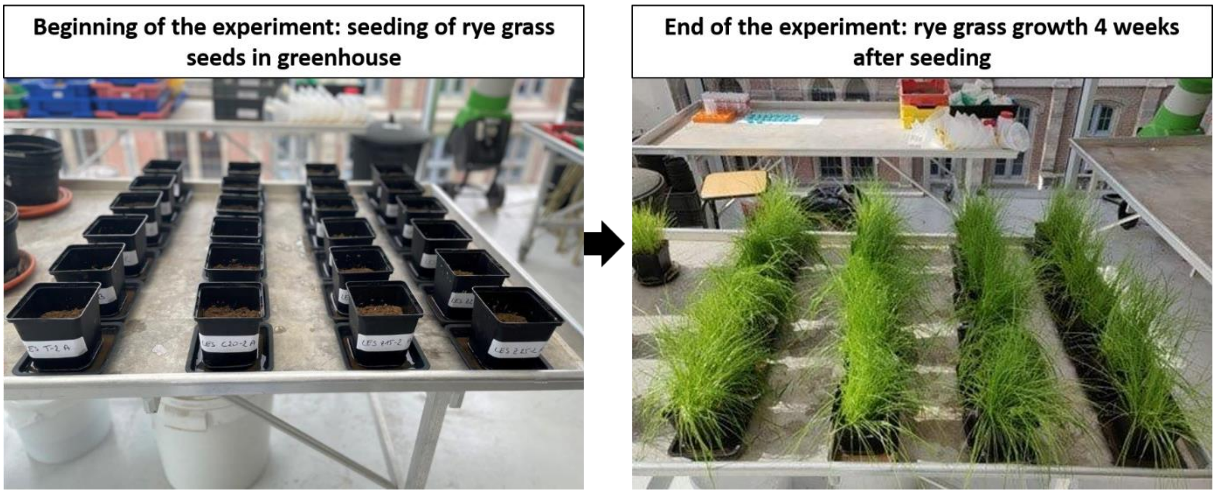
In the second phase, the most pertinent compost-zeolite mixes tested in phase 1 were added to a non-contaminated soil (NCS), and a contaminated soil (CS) (called CKG-L in Experiment 1 and 2). The experiment was composed by four experimental conditions for each soil studied, namely the unamended soil as the control (NCS or CS), soils amended with compost without zeolite (C + Z0), with 15% (C + Z15) and 25% (C + Z25) of zeolite (Figure 2-9).

The non-contaminated soil (NCS) was collected from the ploughed layer (0-25 cm) of an agricultural field located in the Nord of France (Lesquin) through a composite sampling (between 5 and 10 samples). The soil was prepared similarly to the three other soils studied. The different mixes of compost and zeolite were added to 500 g of dried 2 mm-sieved soils. The mixes were then humidified in the same manner as the other experiments, and placed into several pots in order to have replicates for each condition. The compost rate was chosen in concurrence with the recommended compost rate (*i.e.*, 0.6%, or 20 t ha^{-1}) and the one tested in Experiments 1 and 2. The zeolite amount was defined according to the compost mass (Table 2-7).

Table 2-7. **Amendment doses chosen for phase 2 of Experiment 3**

Condition	Code	Dose
Unamended control	NCS or CS	-
Contaminated compost + 0% zeolite	C+Z0	0.6% (20 t/ha)
Contaminated compost + 15% zeolite	C+Z15	0.6% + 0.09%
Contaminated compost + 25% zeolite	C+Z25	0.6% + 0.15%

During six weeks, WHC was maintained to 60% and kept in a temperate and dark place. After this maturation step, half of the 6 pots corresponding to each condition were dried, sieved and ground for analysis while the remaining three were placed in a semi-controlled greenhouse and seeded with 0.75 g of rye grass (Figure 2-10). Pots were regularly watered.



Beginning of the experiment: seeding of rye grass seeds in greenhouse

End of the experiment: rye grass growth 4 weeks after seeding

Figure 2-10: **Experiment 3 greenhouse setup and rye grass growth after 4 weeks**

After 4 weeks, aerial parts of the grass were harvested, double-washed, and dried at 40°C before being ground to 250 µm for analysis. Corresponding soils were removed, dried at 40°C, and sieved to 2 mm and/or ground to 250 µm for further analysis.

3. Analytical methods

3.1 Physico-chemical analysis

Soil and amendment **pH** was measured in a 1:5 volume ratio of 2 mm sieved soil to osmosis water suspension, according to NF ISO 10390 (AFNOR, 1994). **Total carbonate contents** ($CaCO_3$) were measured according to NF ISO 10693, through a change-in-volume calculation using CO_2 released following a HCl reaction with soil ground to 250 µm, a 1:5 tap water to reverse osmosis (RO) water mix, and 4 mol L^{-1} HCl (AFNOR, 1994). **Electrical conductivity** (EC) was measured using 1:5 ratio of soil sieved to 2 mm and double-distilled water, rotated for 2 hours and then centrifuged at 1000 RPM for 10 minutes before being measured in the filtrate using a conductimeter device with automatic temperature compensation (Cond330i/SET–2C20-0011, Metrohm, Switzerland). **Assimilated phosphorus**, expressed as P_2O_5, was extracted according to the method of Joret-Hébert (NF X 31-161) by using 25 mL of 0.1 M ammonium oxalate (pH = 7), agitated for 2 hours with 1 g of soil sifted to 2 mm, and then centrifuged at 1200 RPM for 15 minutes before filtration of the supernatant (0.45 µm cellulose acetate Whatmann filter). Then 1 mL of this filtrate, 450 mg L^{-1} phosphorous orthophosphate solution, or 0.1 mol L^{-1} ammonium oxalate extractant were mixed with 9 mL of a sulfomolybdic coloration reactive. After 30 minutes, each tube was heated to 75°C for 30 minutes using a water bath. Assimilated P was calculated after dosage of the blue phosphomolybdic complexes with an ultraviolet-visible spectrophotometer set to an optical density of 825 nm as according to NF X 31-161 (AFNOR, 1993). **Exchangeable bases** (EB) and **cation exchange capacity** (CEC) were analyzed according to NF EN ISO 11260. Exchangeable bases were extracted from amendments and soils (250µm-sieve fraction) by three successive extractions with barium chloride ($BaCl_2$; 0.1 M). A mass of 1.25 g of sample was agitated for 1 hour and then centrifuged at 3500 G for 10 minutes. This was repeated twice and then the volume was completed to 50 mL with 0.1 mol L^{-1} $BaCl_2$. After washing the sample remained with 0.0025 M of $BaCl_2$ over the night, $MgSO_4$ (0.020 M) was added to the sample, agitated for 16 hours, centrifuged, and then stored for CEC analysis. CEC and EB (Ca^{2+}, Mg^{2+}, K^+ and Na^+) were quantified using an atomic absorption spectrometer (AAS) (AA-6800, Shimadzu, Japan) with a calibration curve prepared in lanthanum for the former two elements. **Soluble organic carbon** content was determined by sulfochromic digestion according to NF X 31-109, for which purpose the organic matter present in 1 g of soil or compost ground to 250 µm was extracted with 40 mL of NaOH 0.1 mol L^{-1} mixed for 4 hours (Tavares et al., 2021).

3.2 Biological analysis

The determination of biological activities consisted of studying the overall bacterial activity as well as fungal biomass. Overall **soil bacterial activity** was analyzed following hydrolysis of fluorescein diacetate (FDA), which allows for the visualization of organic soil substrate degradation potential by certain enzymes (proteases, lipases and esterases). As according to Green et al., 2006, 500 mg of dried matrix sieved to 2 mm was incubated with a sodium phosphate buffer (0.06 M, pH 7.6) and FDA (4.9 mM) for 3 h at 37°C. The reaction was then stopped with 1 mL of acetone, centrifuged for 10 min at 1000 RPM and using a 0.45 µm cellulose acetate filter. Activity in the supernatant was dosed by assaying the light absorption (*i.e.,* fluorescein release) at 490 nm using a UV-visible spectrophotometer.

3.3 Degree of contamination

For each soil triplicate (amended or control), an acid digestion was performed using 300 mg of soil ground to 250 µm mixed with 1.5 mL of 70% HNO_3 and 4.5 mL of 37% HCl (*aqua regia*) and heated at 95°C in a HOTBLOCK DigiPREP MS (Environmental Express® SC100, Charleston, SC, USA) for 90 min for carbonate-poor soils (method adapted from Waterlot et al., 2012). For carbonate-rich soils, this protocol was preceded by an addition of 3 mL of 70% HNO_3, which was allowed to react for 90 min, and then by the addition of 3 mL of H_2O_2 (30%), which was allowed to sit for 16 hours before being heated at 95°C for 2 hours.

For the lettuce and ray grass, 300 mg was digested with 5 mL of nitric acid (70%) at 90 °C for 90 min and then with 5 mL of H_2O_2 (30%) at 95 °C. The resulting solutions was filled until 25 mL and filtered using a 0.45 µm cellulose acetate filter. All extractions and digestions were run with reference soils for quality control of the experimentations.

3.4 Extractability of metal(loid)s in studied matrices

3.4.1 Sequential extractions

Sequential extractions use reagents corresponding to different properties which allow for the successively stronger removal of metal(loid)s. Sequential extractions were performed according to the 4-step BCR protocol described by Rauret et al. (1999) and adapted by Waterlot et al. (2012), as presented in Table 2-8. According to this protocol, metal(loid)s are progressively removed and can thus be characterized by residing in either (i) the exchangeable, acid-soluble, carbonate-linked fraction, (ii) the reducible fraction, (iii) the oxidizable fraction, or (iv) the residual fraction. The exchangeable fraction represents the mobile and available metal(loid)s present in the soil (Gleyzes et al., 2002). These elements are easily mobilized via ionic exchanges, and thus represents the most mobile and therefore toxic soil fraction. In this fraction also resides the carbonate-linked metal(loid)s, which are sensitive to pH changes and thus extracted at a pH of 5 (Forstner *et al*., 1981). The reducible fraction determined by sequential extractions is linked to iron, aluminum, and manganese oxides, which are dissolved by a reducing agent. The oxidizable fraction is that which is mainly complexed to organic matter and sulfurs. When oxidized, bound metal(loid)s are liberated. The residual soil fraction is that which resides in primary or secondary minerals that remain after the other extraction steps. Only digestion by strong acids can dissolve the mineral matrix and free some of these trapped metal(loid)s, which are not considered as environmentally available in natural conditions (Singh et al., 1996; Basta & Gradwohl, 2000).

Concretely, to perform these extractions, one gram of soil ground to 250 µm was agitated with 40 mL of 0.11 M acetic acid for 16 hours before being centrifuged at 3000 RPM for 20 minutes and filtered with 0.45 µm cellulose acetate filter. This fraction represents the exchangeable and most mobile fraction of metal(loid)s (Fraction A). The soil residue was then rinsed by agitation with 20 mL of bidistilled water for 20 minutes before centrifugation and removal of the supernatant. Then, 40 mL of 0.5 M hydroxylamine hydrochloride ($HONH_2$ HCl) were added to the rinsed soil and agitated for 16 hours before centrifugation, filtration, and rinsing as done in the first step. This collected fraction represents Fraction B, or the reducible fraction of metal(loid)s linked to Fe and Mn (oxy)hydroxides. For the third step, 10 mL of H_2O_2 (30%) was added to the soil residue, and manually agitated periodically during an hour, caps loose. The tubes were then heated in a water bath heated to 85°C while being agitated for the first 30 minutes. After an hour, the caps were completely removed and the H_2O_2 was left to evaporate to a volume of 3 mL before 10 mL was again added and heated in the same manner. Once the tubes reached a volume of 1 mL of H_2O_2, 50 mL of 1 M of ammonium acetate, NH_4OAc (pH = 2), was added and agitated for 16 hours. The supernatant was collected as Fraction D, or the oxidizable fraction. All the fractions (A, B, D) were acidified and stored at 4°C until analysis. The final residual soil fraction (Fraction R) was determined according to the previously described mineralization protocol after having dried (40°C) and crushed the soil residue.

Table 2-8. Summary of the sequential extraction procedure and extractants used for each fraction

Step	Fraction	Extractant	Condition
A	Exchangeable (F1)	40 mL 0.11 M CH_3COOH	16h of agitation
B	Reducible (F2)	40 mL 0.5 M $HONH_2$ HCl	16h of agitation
D	Oxidizable (F3)	10 mL 8.8 M H_2O_2 + 10 mL 8.8 M H_2O_2 + 50 mL 1 M NH_4OAc (pH 2)	Evaporation at 85°C + 16h of agitation
R	Residual (F4)	4.5 mL HCl (37%) + 1.5 mL HNO_3 (70%)	90 min at 95 °C

3.4.2 Single extractions

Calcium chloride ($CaCl_2$)-extractions serve as a way to measure easily soluble, exchangeable, and/or environmentally available metal(loid)sand estimate bioavailability in plants and insects. These metal(loid)s were quantified using 3 g of matrix ground to 250 µm agitated with 30 mL of 0.01 M $CaCl_2$

for 2 hours before centrifugation at 4500 RPM for 20 minutes and filtration and acidification before storage (Houba et al., 1996). **Ammonium nitrate (**NH_4NO_3) extractions are typically used to indicate metal(loid) reactivity mimicking short-term environmental bioavailability. Extractable metal(loid)s were quantified after 10 g of soil or compost sieved to 2 mm has been mixed with 25 mL of a 1 M NH_4NO_3 solution for 80 minutes (NF ISO 19730). Samples were centrifuged (Rotanta 460, Hettich, Germany) at 1500 RPM for 10 minutes, and then filtered with a 0.45 µm cellulose acetate filter, acidified, and kept at 4°C until analysis. Both of these extractations are unbuffered and thus can allow for interactions to happen at soil conditions (Lebourg et al., 1998, Houba et al., 2000). **EDTA-extractable metal(loid)s** representing a less extractable, organic matter-, (hydr-)oxide-, or carbonate-bound, and potentially toxicologically bioavailable pool accessible over time, were quantified using 4 g of soil or compost sieved to 2 mm agitated with 40 mL of a 0.05 M EDTA solution (pH = 7) for 1 hour according to the BCR protocol (Quevauviller, 1998). Samples were then centrifuged at 4500 RPM for 20 minutes, and then filtered through 0.45 µm cellulose acetate filter, acidified, and stored at 4°C until analysis.

3.4.3 Soil pore water (SPW) extractions

Soil solutions in planted pots were collected using microporous needles called Rhizons® (SDEC, France). At collection time, these semi-permanent fixtures were attached to 10 mL syringes. Soil Pore Water (SPW) was collected by creating a vacuum depression in these syringes by use of a wooden prop used over the course of no more than an hour. The collected solution was filtered with a 0.45 µm cellulose acetate filter, acidified (HNO_3 70%), and stored at 4°C until SPW metal(loid) analysis.

3.5 Toxicological availability of metal(loid)s in amended/unamended soils

Toxicological availability was assessed through the orally bioaccessible metal(loid) fraction measured using the *in vitro* UBM (Unified Bioaccessibility Method; ISO 17924:2019). This method was validated *in vivo* (piglets) for As, Cd, and Pb (Denys et al., 2012). Digestive solutions used were made to mimic the composition of human digestive fluids, and were composed of inorganic, organic, and enzymatic components (Table 2-9).

Table 2-9: Composition of various digestive fluids used in the in vitro UBM bioaccessibility test

Saliva **pH = 6.5 ± 0.5**	**Gastric juice** **pH = 1.1 ± 0.1**	**Duodenal juice** **pH = 7.4 ± 0.2**	**Bile** **8.0 ± 0.2**
Inorganic constituents			
896 mg KCl 888 mg NaH_2PO_4 200 mg KSCN 570 mg $NaSO_4$ 298 mg NaCl 1.8 mL NaOH (1 mol/L)	824 mg KCl 266 mg NaH_2PO_4 400 mg $CaCl_2$ 306 mg NH_4Cl 2752 mg NaCl 8.3 mL HCl (37%)	564 mg KCl 5607 $NaHCO_3$ 50 mg $MgCl_2$ 80 mg KH_2PO_4 7012 mg NaCl 180 µL HCl (37%)	376 mg KCl 5785 $NaHCO_3$ 5259 mg NaCl 180 µL HCl (37%)
Organic constituents			
200 mg urea	85 mg urea 650 mg glucose 20 mg glucuronic acid 330 mg glucosamine chlorohydrate	100 mg urea	250 mg urea
Additional constituents			
145 mg alpha amylase 50 mg mucin 15 mg uric acid 800 mL bidistilled water	1000 mg bovine albumin 3000 mg mucin 1000 mg pepsin 1000 mL bidistilled water	1000 mg bovine albumin 200 mg $CaCl_2$ 3000 mg pancreatine 500 mg lipase 1000 mL bidistilled water	1800 bovine albumin 222 mg $CaCl_2$ 6000 mg bile 400 mL bidistilled water

Bioaccessibility was analyzed in two phases on two sets of triplicates of soil (amended or control) (Figure 2-11). All 600 mg of 250 µm sieved soil were mixed with 9 mL of a simulated saliva solution and 13.5 mL of a simulated gastric solution, controlled and adjusted with HCl (37%) to be at a pH of 1.2 ± 0.05, and shaken at 37°C for 1 hour before being centrifuged. This represents gastric phase G. Phase GI gastrointestinal extractions were continued on the second triplicate, to which 27 mL of simulated duodenal fluid and 9 mL of simulated bile were added, controlled and adjusted with NaOH (10 M) for a pH of 6.3 ± 0.5, and shaken at 37°C for 4 hours before being centrifuged. Solutions were made the day before starting the experiment and controlled for pH just prior to the starting the experiment. Extracted solutions were stored at 4°C until analysis within the next week.

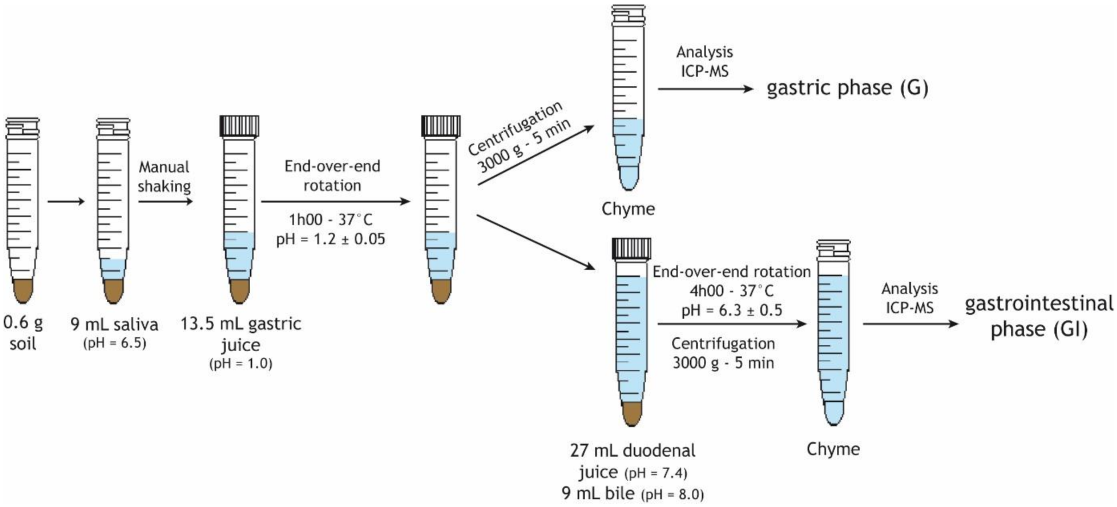


Figure 2-11. UBM test schema (adapted from Pelfrêne, 2016)

3.6 Synthesis of analytical methods

The analytical methods used in each of the three experiments outlined in this section 3 can be seen in Table 2-10, which synthetizes all the analyses realized for each experimentation and matrix.

Table 2-10: Summary of measured parameters organized by experiment and matrix

Experiment		Matrix	Parameters analyzed
1	a	Control PKG, CKG-N, CKG-N	Physico-chemical, pseudo-total metal(loid)s, NH_4NO_3 and EDTA extractable metal(loid)s, sequential extraction of metal(loid)s in soil, bioaccessibility (G, GI)
		C6, C8, Z, OF, ML, HL, DE, PS, BM, CH	Physico-chemical, pseudo-total metal(loid)s
		Amended PKG, CKG-N, CKG-L	Physico-chemical, pseudo-total metal(loid)s, NH_4NO_3 and EDTA extractable metal(loid)s
	b	CKG-N amended with (PS, PERL, PEAT)	Physico-chemical, pseudo-total metal(loid)s, NH_4NO_3 and EDTA extractable metal(loid)s
2		Control (U2) and amended PKG, CKG-N, CKG-L	Physico-chemical, biological, pseudo-total metal(loid)s, sequential extraction, passive extraction, NH_4NO_3 and EDTA extractable metal(loid)s, bioaccessibility (G, GI)
		Aerial lettuce parts	Biomass, pseudo-total metal(loid)s
3	Phase 1	Self-produced compost	Physico-chemical, pseudo-total metal(loid)s
		C+Z0, C+Z10, C+Z15, C+Z20, C+Z25	Physico-chemical, pseudo-total metal(loid)s, $CaCl_2$, NH_4NO_3 and EDTA extractable metal(loid)s
	Phase 2	Control and amended NCS and CS (= CKG-L)	Physico-chemical, pseudo-total metal(loid)s, sequential extraction, NH_4NO_3 and EDTA extractable metal(loid)s, bioaccessibility (G, GI)
		Rye grass shoots	Biomass, pseudo-total metal(loid)s

4. Treatment of results

4.1 Measurement of metal(loid)s

Extractability was calculated in dry weight, in terms of percent of acid-digestible or pseudo-total Cd, Pb, Zn, and As in control matrices. Extracted metals above detection limits were quantified using atomic absorption spectrometry (AAS, AA-6800, Shimadzu) or ICP-MS (Serie X2, Thermo Scientific) for As according to ISO 17025 by the COFRAC-accredited INRAe Soil Analysis Laboratory (Arras, France). All extractions and digestions were run with in-house and/or standardized reference soils and plants (in-house standard for soil digestions, sequential extractions, $CaCl_2$, and NH_4NO_3 extractions, in-house standard for plant digestion, BCR-483 for EDTA extractions, NIST 2710a for bioaccessibility) for quality control.

4.2 Amendment efficiency calculation

The influence of amendments on metal(loid) extractability (using NH_4NO_3 and EDTA) or oral bioaccessibility was evaluated by calculation of an efficiency factor (EF), which corresponds to the ratio of metal(loid) extractability with amendment to its concentration without amendment. Amendments were ranked as efficient if the EF values were less than 1 and inefficient when the EF values were greater than 1.

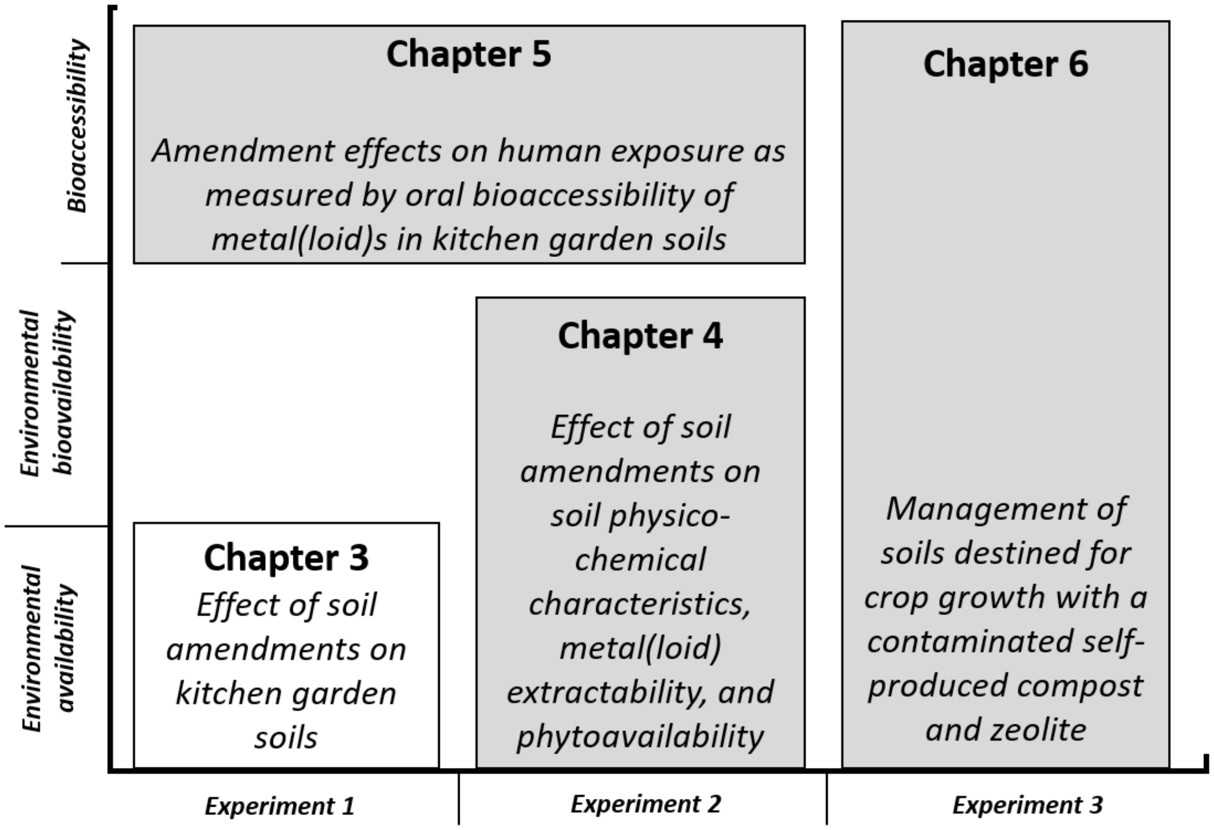
4.3 Bio-concentration factor calculation

The influence of amendments on metal(loid) uptake into plant was evaluated by calculation of a bio-concentration factor (BCF), which corresponds to the ratio of metal(loid) measured in the plant in dry weight to the pseudo-total metal(loid) content in soil corresponding to the same condition at the beginning of the experiment.

4.4 Statistical analysis

All data was analyzed using three replicates of soil or compost amended in constant conditions. Differences were assessed using a Fisher test and if present, calculated using a one-way ANOVA and a post-hoc HSD Tukey Test for comparison among data collected at the same time, a one-way ANOVA and a Bonferroni test for data collected before and after the re-application of amendments or before and after the growth of plants, and either a Student T-test or Wilcoxon test for comparisons between data collected at the same time. Correlations between parameters were assessed using a Pearsons correlation matrix. Analyses were done using XLSTAT 2019.3.2 and Microsoft Excel 2016.0.4966.

Chapter 3: Effect of soil amendments on kitchen garden soils



Chapter 3: Effect of soil amendments on kitchen garden soils

Among the techniques that can influence the behavior of metal(loid)s in soils, the addition of natural or synthetic products (organic or/and mineral) constitutes a promising alternative to the replacement of contaminated soils and other damaging methods of soil remediation such like vitrification or washing (Hanauer et al., 2011; Franca et al., 2017, Ferreira et al., 2018, Hallenbach et al., 2019). Amendment addition to contaminated soils can be environmentally friendly, suitable for relatively small areas, easy to implement, and socially accepted because of the long-standing practice and understanding of amendments' abilities to increase or maintain soil fertility. This practice is therefore particularly suitable for the remediation of kitchen garden soils contaminated by metal(loid)s. Amendment addition aims to reduce the mobility, bioavailability, and in particular phytoavailability of metal(loid)s by acting upon the physicochemical parameters of soils and influencing their biological activities as well as immobilizing pollutants by adsorption, complexation or precipitation.

The objective of this chapter is to study the interest of amendments, in particular both organic and mineral amendments, for the management of urban kitchen garden soils presenting moderate geogenous and/or anthropogenic contamination. The soil amendments were selected as detailed in Chapter 2, according to their environmental suitability, cost, applicability, and public acceptance, and then evaluated for their potential to sustainably manage the environmental availability of metal(loid)s in three different soils. Specifically, an *ex situ* experiment (Experiment 1a) was conducted in order to test 14 different amendments (single or in mixes) on the three KG soils described in previous chapter (PKG, CKG-N and CKG-L). These amendments (nature and doses) were evaluated by their efficiency to modify physico-chemical soil parameters and reduce the extractability of As, Cd, Pb, and Zn using both chemical extractants (EDTA and ammonium nitrate).

The steps taken to meet these objectives and the results obtained were the subject of an article accepted in 2022 and published in Advances in Environmental and Engineering Research, cited as follows:

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Original Research

Effects of Inorganic and Organic Amendments on the Predicted Bioavailability of As, Cd, Pb and Zn in Kitchen Garden Soils

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Abstract

Moderately contaminated garden soils can benefit from gentle remediation options such as soil amendments, which improve soil functions and agronomic potentialities while decreasing environmental and human risk. This study aimed to analyze the effects of doses of various common soil amendments generally applied by gardeners on the predicted bioavailability (i.e., extractability) of metal(loid)s (i.e., As, Cd, Pb, and Zn) in contaminated kitchen garden soils. Fourteen different amendment mixes (i.e., a green waste compost with two degrees of maturity used alone and in combination with zeolite, three organic fertilizers, two calcareous amendments, two natural siliceous or alumino-silicate amendments, and one potting soil) were tested on three different garden soils with diverse sources of contamination and physico-chemical characteristics. Chemically extractable metal(loid)s were analyzed using 0.05 M EDTA extraction and 1 M NH_4NO_3 extraction. In one soil sample, potting soil showed significant potential to reduce the availability of As, as analyzed by both extractants. This amendment also effectively reduced the Pb extractability in the geogenic-contaminated soil, as did other high-organic matter amendments such as various application rates of composts. Zeolite and zeolite-compost mixes demonstrated success on various metal(loid)s and therefore could be a promising emerging amendment mix. Other efficient amendments include crushed horn, which effectively reduced available Zn in all soils, as well as available Pb. The application of bone meal similarly reduced the extractable As, Pb, and Zn in various soils. The two applications of limes were effective against Cd, As, Pb, and Zn in the different soils studied. This study provided evidence that it is possible to reduce the extractability and thus the environmental availability of the metal(loid)s applied with available and affordable amendments. The results depended on the physico-chemical soil parameters and metal(loid)s considered. There is no single solution, which implies that tests must be carried out before any implementation activities on the kitchen gardens.

Keywords

Kitchen garden soils; metal(loid)s; amendments; extractability; immobilization

1. Introduction

Urban gardening is a growing trend in several cities in the world. The need for nature in the city, the growing movement towards healthy eating, and difficult economic and societal contexts have led to a re-emergence of gardening activities. This applies to both private gardens—most commonly adjoining homes—as well as community gardens. Several cities and urban communities are required to install and support community gardens, a term that includes allotments, shared, or integration gardens. It is common to see these gardens on urban wastelands, along roads or railways, near previously or currently active industrial sites, or even on former industrial or urban wastelands. In comparison with agricultural or forest soils, urban soils are more complex, often very heterogeneous, and which, depending on their history and/or their environment, may have poor agronomic qualities [1, 2]. These contexts also suggest the presence of inorganic contaminants (such as As, Cd, Pb, and Zn) of various origins and in variable concentrations [3, 4]. In addition to a geogenic origin (linked to the geochemical background) of the contaminants, soil contamination may result from past and/or present discharges from industrial or urban activities (e.g., combustion of fossil fuels, automobile traffic, incineration of household waste) [5-8], or from improper gardening practices (e.g., use of phytosanitary products, mineral fertilizers, contaminated irrigation water) [9-11].

Human exposure to metal(loid)s in soils can present risks that vary by the element, exposure pathway, vector, and receptor [12]. Considering kitchen gardens, humans may be exposed via ingestion/inhalation of soil particles and consumption of contaminated vegetables. Ingestion may be considered the main exposure route associated with the cultural practices of gardening [13]. Commercially sold vegetables are regulated by the European Union (European Directive of 25 June modifying the European Directive no. 1881/2006), which defines the maximum authorized concentrations of metals such as Cd and Pb in marketable food. These regulations do not apply to kitchen garden vegetables cultivated by individuals [14]. The accumulation of metal(loid)s in crops could vary as per the physico-chemical parameters of the soils, the metal(loid) speciation, the cultural practices (amendments, irrigation), the vegetable species, and the cultivar. The behavior of metal(loid)s in the soil relies on certain soil parameters, including but not limited to pH, cation exchange capacity, organic matter, nitrogen, phosphorous, carbonates, clay content, and biological activities [15-17]. According to these parameters and their temporal evolution, only a fraction of the metals is available for the soil biota. In general, reducing the availability of pollutants can play a key role in limiting their phytoavailability and potential toxicity via ingestion (and to a lesser extent, inhalation) of dust/soil particles and via consumption of vegetables [18-21].

There are various potential remediation strategies to limit the availability of metal(loid)s in soils. Regardless of the strategy utilized to manage kitchen garden soils, soil functions must be restored and maintained, and their agronomic potentialities improved. A feasible way to do this is via gentle remediation options [22]. One such method is using cost-effective, accessible, and easily applicable soil amendments [23-27]. Inorganic and organic soil amendments can act as *in-situ* metal(loid)-immobilizers and stabilizers [28]. Five types of products can be identified, namely, organic amendments (e.g., manure, compost, peat), natural organic fertilizers (e.g., crushed horn, bone powder), calcareous amendments (e.g., lime flower, magnesian lime), natural siliceous or alumino-silicate amendments (e.g., diatomaceous earth, natural zeolites), and expanded alumino-siliceous amendments (e.g., perlite, vermiculite).

Compost is the most commonly used among the organic amendments used by gardeners [29]. It is rich in nutrients, contributes to the carbon supply, increases the water holding capacity of the soil, improves biological functioning, and is an alternative to chemical fertilizers [30-32]. Its production is relatively simple to set up, and it is most often self-produced using green waste from the garden or cities. In addition to improving the agronomic potential of soils, compost can favorably influence the behavior of metal(loid)s present in the soil [33-35] by reducing their mobility and thereby toxicity to the biosphere. These pollutants can be immobilized via sorption, complexation, precipitation, and redox reactions, especially using amendments containing humic substances and inorganic compounds. However, research on the effects of compost on the transfer of pollutants from soil to vegetable production is still limited [29, 36-40]. Results are occasionally contradictory, although most often, the addition of composts to garden soils reduces the concentration of metal(loid) in vegetable production. However, these effects depend on the stage of maturity of the composts, their nature, their application rate, their soluble organic matter content, and the physico-chemical parameters of soil [29, 34].

Inorganic amendments have various origins and natures [41, 42]. They can be natural products, byproducts, or industrial wastes that can sometimes be combined with organic amendments. The physico-chemical processes involved in amended soils are a result of interactions between metal(loid)s, the soil constituents, and amendments. The referent mechanisms are those of chemical reactions such as adsorption or surface complexation (physisorption and chemisorption), precipitation, or coprecipitation. These reactions depend on the physical and/or chemical parameters of the soils, the biogeochemical cycles of the metal(loid)s, and biological activities. Phosphate/hydroxyapatite products are among the most studied mineral amendments [43, 44]. Their effects are dependent on not only the physico-chemical properties of the soils but also on the speciation of the phosphate ions and their respective counter ions. Carbonate and lime-based amendments are exploited for their alkaline character and are used to increase the pH of acid soils. The effective reduction of phytoavailability has been demonstrated for several metal(loid)s [45-53]. Aluminosilicates such as natural zeolites are efficient when employed alone for Cd and Pb [54, 55] and in a mixture with organic amendments in the case of Cd and Pb as well as Zn [56, 57].

The overall aim of the study was to examine a range of amendments, in particular either self-produced or cost-effective, commercially accessible and easily applicable composts and mineral amendments, to manage urban kitchen garden soils with moderate geogenic and/or nature of anthropogenic contamination. The effects of these amendments were evaluated on (i) the physico-chemical characteristics of soils, (ii) the extractability of As, Cd, Pb, and Zn using both chemical extractants (EDTA and ammonium nitrate), and (iii) their efficiency to reduce the metal(loid)s' extractability. An *ex-situ* experiment was carried out to compare the effects induced by a collection of 10 organic and mineral amendments, used alone or in combination, on three contaminated garden soils with different physical and chemical characteristics. One organic amendment (a green waste compost with two degrees of maturity), three organic fertilizers (crushed horn, bone powder, and organic complete fertilizer made from poultry manure), two calcareous amendments (lime flower and magnesian lime), two natural siliceous or alumino-silicate amendments (diatomaceous earth and natural zeolite), and potting soil (a mixture of peat, sand, perlite, and dolomite) were selected for the study. These are well-known products, commonly used by gardeners. Particular attention was paid to the rate of application of the amendments. The doses typically reported in studies are often very high and do not always reflect the cultivation practices. A specific objective of this study was to use appropriate application rates for each amendment tested, i.e., as close to cultural seeding practices as possible. The aim was to assess the potential of the amendments to sustainably manage the availability of metal(loid)s to limit human exposure.

2. Material and Methods

2.1 Experimental Kitchen Garden Soils

Experimental *ex-situ* assays were conducted using soils from three metal(loid)-contaminated kitchen gardens in France, representing a range of physico-chemical parameters, as well as origins and levels of moderate contamination.

One soil sample was collected from a private kitchen garden "PKG" (50° 26' 4 N and 3° 2' 18 E), in Evin Malmaison in the former coal-mining area of northern France. Here, considerable atmospheric dust emissions of Cd, Pb, and Zn were recorded, generated by the former lead smelter Metaleurop Nord. The second soil sample was collected from a community kitchen garden "CKG-N" (47° 16' 1 N and 1° 34' 30 W) in Nantes (in western France), in the vicinity of a highway. This area is associated with past agricultural activities. The arsenic and lead contamination in this soil is primarily of geogenic origin due to the presence of a mineralized vein of micaschist rich in As-and Pb-bearing minerals. The third soil sample was collected from a community garden "CKG-L" (50° 37' 14 N and 3° 1' 39 E) in Lille (in northern France). The soil of this garden is derived from backfill and is influenced by atmospheric fallout from former industrial activities and proximity to a highway. This soil is primarily contaminated with Pb.

For each site, bulk soil was sampled from the topsoil horizon tilled by the gardeners (0–25 cm deep).

2.2 Treatment and Experimental Design

The three soils samples (PKG, CKG-N, and CKG-L) were first air-dried at a temperature below 40°C, homogenized, and gently crushed to pass through a 2-mm stainless steel sieve as per the ISO 11464 standard (AFNOR, 1995). For each soil sample, 15 modalities, one of which is a control, and three repetitions of each were considered. In total, 126 amended soil samples and 9 control soil samples (i.e., unamended soils) were tested in polypropylene pots of 500 ml. 500 g of dry soil sieved to 2 mm were amended using the appropriate application rate with each of the amendments. The amendments involved using unaltered hydrated lime or diatomaceous earth, 2 mm sized compost and potting soil, and the 250 µm sized organic fertilizer, magnesium lime, zeolite, bone meal, and crushed horn. For the composts, two different degrees of maturation (i.e., 6 and 8 months qualified as young and mature, respectively) and two amendment rates (i.e., 20 and 40 t ha^{-1}) were tested. The compost was also tested as a mix with 10% of zeolite by mass. Amendment rates were selected to mimic cultural seeding practices that a gardener typically applies. The details are presented in Table 1. The physico-chemical parameters and concentrations of the metal(loid)s studied (As, Cd, Pb, and Zn), covering all the amendments, are presented in Table S1 in the Supplementary Material. All the amendments selected are commercialized and conform to European regulations.

Table 1 Amendment rates (mixed with soil) with applications A1 and A2 used in the experiment chosen according to the cultural seeding and gardening practices and compared to the scientific literature (where doses are based upon maximum doses of a given amendment tested for metal(loid) immobilization).

	Name	*A1*	*A2*	*Gardening practices*	*Literature*
Young compost (6 months)				0.6%/2 year	33%[a]
Single dose	C6–20	0.6%	1.2%	-	-
Double dose	C6–40	1.2%	2.4%	-	-
Mature compost (8 months)				0.6%/2 year	33%[a]
Single dose	C8–20	0.6%	1.2%	-	-
Double dose	C8–40	1.2%	2.4%	-	-
Composts + zeolite				10:1	-
Young compost + zeolite	C6+Z	0.6% + 0.06%	1.2% + 0.12%	-	-
Mature compost + zeolite	C8+Z	0.6% + 0.06%	1.2% + 0.12%	-	-
Other amendments					
Natural zeolite	Z	2%	4%	1.8%	3%[b]
Organic fertilizer (chicken manure)	OF	0.5%	1%	0.1%	4.5%[c]

Magnesium lime	ML	0.1%	0.2%	0.036%	3%[b]
Hydrated lime	HL	0.05%	0.1%	0.03%	1%[b,d]
Diatomaceous earth	DE	0.1%	0.2%	1%	4%[e]
Potting soil (for seeding)	PS	3%	6%	33%	33%[f]
Bone meal	BM	0.05%	0.1%	0.03%	4%[g]
Crushed horn	CH	0.05%	0.1%	0.024%	-
Unamended control	U	-	-	-	-

Calculations are based on dry weights. Gardening practice rates are based on suggested rates of application on commercialized amendment packaging. [a] [58]; [b] [59]; [c] [60]; [d] [61]; [e] [30]; [f] [62]; [g] [63].

Dried soil-amendment mixes were thoroughly mixed, humidified to 60% (pH of tap water at 7.0), and placed into pots. The pots were kept in the dark area at a constant temperature (18°C). The humidity was maintained at 60% of the field water capacity during the experiment. After six weeks of incubation with the first application A1 (Table 1), the soil-amendment mixes were removed from the pots and left to dry at ambient temperature. 150 g was then removed and sieved to 2 mm and ground to 250 µm for further analysis. The samples (n = 135) were analyzed as “A1” soils. 300 g of the remaining soil was further re-amended with the same application rate of the amendment (i.e., A2; Table 1), rehumidified to 60% humidity, repotted to continue incubation for eight additional weeks in the same conditions, and dried and ground similarly. These samples (n = 135) were analyzed as “A2” soils. The experimental design is presented in Figure S1 in Supplementary Material.

2.3 Amended and Unamended Soil Analysis

2.3.1 Physicochemical Characteristics

The soil pH was measured using a 1:5 volume ratio of 2 mm sieved soil and osmosis water, according to NF ISO 10390. The total carbonate content was obtained by measuring the volume of CO_2 released after a reaction with HCl (NF ISO 10693). The conductivity was measured using a 1:5 ratio of soil sieved to 2 mm and double-distilled water, rotated for 2 h, and then centrifuged at 1000 RPM for 10 min before being measured in the filtrate using a conductivity meter (Cond 330i/SET-2C20–0011) with automatic temperature compensation. The available P (expressed in g P_2O_5 kg^{-1} of soil) was measured after extraction with an ammonium oxalate solution and spectrocolorimetric determination (NF X31–161). The cation exchange capacity (CEC) was analyzed according to NF EN ISO 11260 and was then quantified using an AA-6800 Shimadzu atomic absorption spectrometer (AAS).

2.3.2 Degree of Contamination

The pseudo-total metal(loid) concentrations (As, Cd, Pb, and Zn) in the 270 soil subsamples (i.e., unamended and amended with A1 and A2) were obtained using the Hot Block system-assisted digestion (Environmental Express® SC100, Charleston, SC, USA) and determined by AAS for Cd, Pb, and Zn. For As, the analyses were performed using inductively coupled plasma mass spectrometry (ICP-MS, Serie X2, Thermo Scientific) by the INRAE Soil Analysis Laboratory (Arras, France) accredited by COFRAC according to the ISO 17025 standard. More specifically, 300 mg of each ground sample was digested in a mixture of 1.5 mL HNO_3 (70%) and 4.5 mL HCl (37%) at 95°C for 90 min [64]. For the carbonate-rich CKG-L soil, this step was followed by the addition of 3 mL of 70% HNO_3, which was allowed to react for 1.5 h. This was followed by the addition of 3 mL of hydrogen peroxide, which was allowed to sit for 12 h before being heated at 95°C for 2 h. After mineralization, the digestion products were completed to 25 mL with distilled water (resistivity 10 MΩ cm^{-1}), filtered using a 0.45 µm cellulose acetate filter, and stored at 4°C before analysis. The quality control was based on the use of internal reference material, which demonstrated good recoveries for As, Cd, Pb, and Zn (96.4–100.5%, 99.8–101.3%, 97.8–100.3%, and 88.1–90.2%, respectively).

2.3.3 Predicted Bioavailability of Metal(loid)s

For each of the 270 soil samples (i.e., unamended and amended with A1 and A2), the ammonium nitrate (NH_4NO_3)-extractable metal(loid)s were analyzed using 10 g of soil sieved to 2 mm and agitated with 25 mL of a 1 mol L^{-1} NH_4NO_3 solution for 2 h. The samples were centrifuged at 1500 *g* for 10 min and then filtered with a 0.45 µm cellulose acetate filter (NF ISO 19730). The EDTA-extractable metal(loid)s were quantified using 4 g of soil sieved to 2 mm and agitated with 40 mL of a 0.05 mol L^{-1} EDTA solution with a pH of 7 for 1 h [65]. Samples were then centrifuged at 4500 *g* for 20 min and filtered with a syringe and 0.45 µm cellulose acetate filter. The metal(loid) concentrations in the extracts were measured using AAS for Cd, Pb, and Zn, using ICP-MS for As. The use of EDTA as a strong extractant (able to chelate ions and dissolve amorphous oxyhydroxides) allows the estimation of the potential influence of these amendments in the long term. It is, however, to be noted that NH_4NO_3-extractable metal(loid)s are more relevant in terms of environmental availability of metallic elements in soils in the short term (as NH_4NO_3 displaces ions from exchange sites).

To compare their origin of contamination more specifically, only the Pb in the soil samples was fractionated using the modified sequential extraction procedure from the SM&T program [66], described by Waterlot et al. [64]. Each fraction was noted as fraction F1, F2, F3, or F4 and defined, respectively as (i) exchangeable, water-and acid-soluble (40 mL of 0.11 mol L^{-1} acetic acid was added to 1 g of soil sample, and the mixture was shaken at room temperature for 16 h); (ii) reducible (40 mL of 0.5 mol L^{-1} hydroxylammonium chloride was added to the residue from the previous step and the mixture was shaken for 16 h); (iii) oxidizable (8.8 mol L^{-1} H_2O_2, followed by 50 mL of 1.0 mol L^{-1} ammonium acetate at pH 2 and mixing for 16 h); and (iv) residual (*aqua regia*). The Pb concentrations in each fraction were measured using AAS.

2.4 Calculation of Amendment Efficiency

The influence of amendments on metal(loid) extractability (using EDTA and NH_4NO_3) was evaluated by calculating an efficiency factor (EF), which corresponds to the ratio of metal(loid) extractability with an amendment to its extractability without amendment (i.e., control). The amendments were ranked as efficient if the EF values were less than 1 and inefficient if the EF values were greater than 1.

2.5 Statistical Analysis

All the data were analyzed using three replicates of unamended or amended soil. The differences between amended and unamended soils were calculated using Student's t-test or Wilcoxon's test depending upon the parametricity of the data. A one-way ANOVA and a Bonferroni test were utilized to analyze the differences in data between A1 and A2 collected over time. The analyses were performed using XLSTAT 2019.3.2 and Microsoft Excel 2016.0.4966.

3. Results

3.1 Characteristics of the Three Soils Studied

On average, all three soils studied were found to have soil texture ranging from silt loam to loam according to the USDA textural soil classification (Table 2). According to the soils' physico-chemical parameters, the total carbonate and organic matter contents were higher in CKG-L than in PKG and CKG-N, while the available phosphorus content and cationic exchange capacity (CEC) were higher in PKG (Table 2). The pH values were slightly acidic in the PKG and CKG-N soils and slightly alkaline in CKG-L. Regarding the metal(loid)s present in the soils studied, (i) the PKG soil was found to be associated with moderately elevated anthropogenic levels of Cd, Pb, and Zn; (ii) the CKG-N soil detected high geogenic levels of As and Pb; and (iii) the CKG-L soil was associated with elevated point levels of Pb and Zn (Table 2). The median geochemical background values in the topsoil in northern France were found to be 0.4 mg kg^{-1}, 29.7 mg kg^{-1}, and 67.1 mg kg^{-1}, respectively for Cd, Pb, and Zn [67], while the median geochemical values in a sampling of the local site in the topsoil in western France was 29 mg kg^{-1} and 84 mg kg^{-1}, respectively for As and Pb [68].

Table 2 Physicochemical parameters and degree of contamination of the topsoil in the three sites (PKG, CKG-N, and CKG-L; n = 1).

		PKG	CKG-N	CKG-L
Clay	%	25	4	16
Silt	%	50	60	50
Sand	%	25	36	34
pH_{water}		6.0	6.8	7.7
$CaCO_3$ tot	g kg^{-1}	3	2	119
OM	g kg^{-1}	51.1	49.6	94.2
C/N		21.3	12.3	32.7
Available P	g kg^{-1}	1.3	0.7	0.4
CEC	$cmol^+$ kg^{-1}	32.5	12.6	15.5
As	mg kg^{-1}	16	32	12
Cd	mg kg^{-1}	6.3	0.24	0.73
Pb	mg kg^{-1}	264	238	384
Zn	mg kg^{-1}	337	77	399

$CaCO_3$ tot: total carbonates; OM: organic matter; C/N: ratio of organic carbon on total nitrogen; Available P: available phosphorus expressed in g of P_2O_5 per kg of soil; CEC: cationic exchange capacity.

Overall, the three soils presented a similar degree of contamination in terms of Pb (from 238 to 384 mg kg^{-1}). To specifically compare the origin of contamination, sequential extractions were used to evaluate the metal distribution within soils and to provide information on the affinity of Pb to the soil components and the strength with which it is bound to the matrix. The distribution of Pb in fractions F1, F2, F3, and F4 are presented in Figure S2 in the Supplementary Material. Overall, the PKG and CKG-L soils were found to be associated with anthropogenic contamination, and the distribution of metallic elements in the different soil fractions was found to be identical, suggesting similar behavior. Logically, for the PKG and CKG-L soils, for which pseudo-total concentrations of Pb were 264 and 384 mg kg^{-1}, respectively, Pb was primarily found in the reducible fraction (respectively, 77.6% and 78.5%). Negligible amounts of Pb were found in the exchangeable fraction (respectively, 2.6 and 2.3%), in the oxidizable fraction (respectively, 10.3 and 4.0%), and the residual fraction (respectively, 9.5 and 15.0%). For the CKG-N soil (238 mg of Pb kg^{-1}), 21.6% of Pb was linked to Fe/Mn oxides, and the remainder was found in the residual fraction (i.e., 78.4%). This high percentage of Pb in the latter fraction explains the geogenic origin of this contamination.

3.2 Effects of Amendments and Application Rates on Physicochemical Characteristics of Soils

Table 3 presents the effects of the amendments and application rates (A1 and A2) on the physico-chemical characteristics of soils (i.e., pH, electric conductivity, contents of total carbonates, and available phosphorus) for the three soils studied (PKG, CKG-N, and CKG-L).

Table 3 Effects of amendments on the physico-chemical soil characteristics with applications A1 and A2 for the three soils studied (PKG, CKG-N and CKG-L) CKG-L).

	pH		$CaCO_3$ (g kg^{-1} DW)		EC (µS cm^{-1})		P_2O_5 (g kg^{-1} DW)	
	A1	*A2*	*A1*	*A2*	*A1*	*A2*	*A1*	*A2*
PKG								
U	5.87	6.08*	2.27	1.24	1,769	1,716	0.66	0.69
OF	5.86	5.87 §	1.00	2.04 §	1,780	2,208 §	0.71	0.83 §
PS	5.90	6.12*	2.42	1.58	1,750	1,858	0.68	0.71
C6–20	5.85	6.11*	2.04	0.81*	1,781	1,709	0.66	0.77 §
C6–40	5.87	6.11*	2.81	1.74*	1,636	1,686	0.71	0.80 §
C8–20	5.93	6.07*	2.23	1.13	2,285	1,824	0.68	0.75
C8–40	5.84	6.08	2.88	1.95 §	1,783	1,620	0.74	0.78
C6+Z	5.80	6.03*	2.03	1.39	1,562	2,018	0.69	0.75 §
C8+Z	5.86	5.98	1.51 §	1.99 §	1,691	1,871	0.63	0.78*
Z	5.80	6.03*	1.68 §	1.96	2,083	1,597*	0.68	0.72
HL	5.77	6.09*	1.63	1.65 §	2,016	1,618	0.66	0.77
ML	5.87	6.23*	2.11	1.69	1,646	1,681	0.62	0.72
DE	5.96	6.06	2.36	1.62	1,694	1,762	0.63	0.77
BM	5.99	6.11	1.82	1.00	1,605	1,788	0.61	0.74
CH	5.84	6.00*	1.88	1.58	1,629	1,714	0.63	0.69
CKG-N								
U	7.12	7.28*	1.10	1.44	96	98	0.34	0.31
OF	7.30 §	7.40*	1.91 §	1.85	152 §	234 §*	0.44 §	0.60 §*

PS	6.80 §	7.12*	1.10	1.13	192 §	207 §	0.35	0.34
C6–20	7.34 §	7.28	1.17	2.44*	113	109 §	0.36	0.40
C6–40	7.31 §	7.33 §	1.47	2.29	112	140 §*	0.42	0.46 §
C8–20	7.28 §	7.30	1.52	1.36	106	116 §	0.39	0.42 §
C8–40	7.21 §	7.36 §	1.16	1.50	106	152 §	0.42 §	0.53 §
C6+Z	7.29 §	7.31	0.92	1.50	101	120 §	0.38	0.44 §
C8+Z	7.24 §	7.48 §*	1.52	1.06	104	129 §	0.42 §	0.55 §*
Z	7.25 §	7.45 §*	1.47	0.89	89	105	0.39	0.43 §
HL	7.20	7.49 §	1.73 §	1.61	92	104	0.38	0.46 §
ML	7.45 §	7.69 §*	2.20 §	1.23	96	102	0.37	0.47 §
DE	7.30 §	7.44 §*	1.90 §	1.70	92	109 §	0.39	0.47 §
BM	7.13	7.21	1.54	1.39	96	98	0.39	0.42 §
CH	7.14	7.18 §	0.84	0.75	100	84	0.36	0.37 §
CKG-L								
U	7.86	7.91	68.9	75.4	231	149	0.42	0.48*
OF	7.66 §	7.71 §	69.5	71.8 §	433 §	340 §*	0.54 §	0.49
PS	7.78	7.60 §*	68.3	73.0	270	326 §	0.48	0.40 §*
C6–20	7.68 §	7.85*	51.6 §	72.7*	239	196 §	0.47 §	0.48
C6–40	7.70 §	7.89*	60.8	73.7*	272	255 §	0.49 §	0.51
C8–20	7.70 §	7.88*	67.2	76.4*	258	201 §	0.47 §	0.51
C8–40	7.70 §	7.86*	60.4 §	74.4*	337 §	271 §*	0.49 §	0.58 §*
C6+Z	7.73 §	8.00*	67.1	73.1	250	201 §	0.48 §	0.47
C8+Z	7.79	7.77 §	67.1	74.1	238	211 §	0.50 §	0.56*
Z	7.89	7.79	66.6	71.5 §	204	211 §	0.47 §	0.44
HL	7.79	7.79	68.6	74.0	235	177	0.49 §	0.42
ML	7.88	8.09 §	71.1	76.2	262	174	0.49 §	0.44*
DE	7.76	7.62 §*	67.7	77.1	258	190 §	0.48 §	0.43
BM	7.85	7.84	68.2	76.2	219	154	0.49 §	0.50
CH	7.78	7.78	72.9	77.8	266	172	0.44	0.52*

DW: dry wet; P_2O_5: available phosphorus; EC: electric conductivity; U: unamended soil; OF: organic fertilizer; PS: potting soil; C6–20: young compost (6 months) at 20 t ha^{-1}; C6–40: young compost (6 months) at 40 t ha^{-1}; C8–20: mature compost (8 months) at 20 t ha^{-1}; C8–40: mature compost (8 months) at 40 t ha^{-1}; C6+Z: a mixture of young compost and zeolite; C8+Z: a mixture of mature compost and zeolite; Z: zeolite; HL: hydrated lime; ML: magnesium lime; DE: diatomaceous earth; BM: bone meal; CH: crushed horn. § denotes significant differences between the unamended control soil and a given amended soil, with A1 and A2, and * denotes a significant change between A1 and A2 ($p < 0.05$).

For each experiment conducted with A1 and A2, the pH values in the unamended control soils (U) were on average 6.0 for PKG, 7.2 for CKG-N, and 7.9 for CKG-L. Compared to U, the results for the PKG soil showed: (i) no significant change in pH associated with amendment addition with A1 and (ii) the addition of organic fertilizer (OF) was associated with a significant decrease in pH with A2 (0.2 pH units). For the CKG-N soil, the results highlighted: (i) with A1, a significant decrease (0.3 pH units) in pH with the addition of potting soil (PS). In contrast, OF, C6, and C8 composts (for both

20 and 40 t ha^{-1}) alone and with zeolite (Z), Z, magnesium lime (ML), and diatomaceous earth (DE) were associated with a significant increase in pH (between 0.1 and 0.2 pH units); and (ii) with A2, PS was associated with a significant decrease in pH (0.1 pH units), while a significant increase was observed with the addition of C8+Z, Z, HL, and ML (between 0.2 and 0.4 pH units). In terms of the CKG-L soil, the results showed (i) a significant decrease (about 0.2 pH units) in pH with the addition of C6 and C8 (for both 20 and 40 t ha^{-1}), C6+Z, and OF with A1, which corresponds to all amendments with high organic matter content and (ii) a significant decrease (between 0.2 and 0.3 pH units) in pH associated with the addition of OF, PS, C8+Z, and DE, and a significant increase (about 0.2 pH units) in pH was observed with the addition of ML with A2. Most of the changes in pH were observed in the soils, which were initially in the basic pH range. Moreover, composts tended to decrease the pH in the three soils with A1. Soil pH increased significantly between A1 and A2 with the addition of some amendments to the PKG soil (PS, C6–20, C6–40, C8–20, C6+Z, Z, HL, ML, and CH), CKG-N (OF, PS, C8+Z, Z, ML, and DE) and the CKG-L soil (PS, C6–20, C6–40, C8–20, C8–40, C6+Z, and DE). A slight increase in pH was observed in the control soils in the cases of PKG and CKG-N soils. This may be attributed to the water used to maintain the soil at a stable humidity over time. For CKG-L, the most alkaline soil, no change was associated with the irrigation process.

Regarding the electric conductivity (EC) in the control U soils, the values were approximately 1,700 µS cm^{-1}, 100 µS cm^{-1}, and 200 µS cm^{-1}, respectively for PKG, CKG-N, and CKG-L (Table 3). The addition of amendments to the PKG soil showed: (i) no significant change in the EC with A1; (ii) a significant increase in the EC associated with OF with A2; and (iii) a significant decrease in the EC between A1 and A2 of Z. For CKG-N, the results highlighted: (i) that the addition of OF and PS with A1 was associated with a significant increase in the EC in comparison to the control; (ii) a significant increase with A2 in the EC with the addition of OF, PS, and C6 and C8 composts alone and with Z, and DE and (iii) a significant increase in the EC between A1 and A2 with an increased dose of OF and C6–40. Regarding the CKG-L soil, the results showed (i) a significant increase in the EC associated with the addition of OF and C8–40 with A1; (ii) a significant increase with A2 in the EC associated with the addition of OF, PS, C6, and C8 alone and with Z, Z, and DE, and (iii) a significant decrease in the EC over the time associated with an increased dose of OF and C8–40. The most significant changes in the EC were observed in the soils having a lower EC (i.e., CKG-N and CKG-L). More specifically, the increases in EC may be linked to the organic matter content, specifically with the addition of compost, chicken manure, and potting soil.

In the control U soils, the mean content of total carbonates was relatively low for PKG, with 1.8 g kg^{-1}, and for CKG-N, with 1.3 g kg^{-1}, while the values were higher for CKG-L, with 72 g kg^{-1}. When compared to U, the results for the PKG soil showed (i) a significant decrease in the $CaCO_3$ content associated with the addition of C8+Z and Z with A1 but a significant increase in terms of A2 with OF, C8–40, C8+Z, and HL; and (ii) a significant decrease in the $CaCO_3$ content with increased amendment doses of C6 (for both 20 and 40 t ha^{-1}). For the CKG-N soil, it was observed that (i) the addition of OF, HL, ML, and DE with A1 resulted in a significant increase in the $CaCO_3$ in comparison to the control; (ii) addition of amendments with A2 did not show any significant changes in the $CaCO_3$ content; and (iii) a significant increase in the $CaCO_3$ was observed overtime linked to an increased dose of C6–20. Regarding the CKG-L soil, the results showed (i) a significant decrease in the $CaCO_3$ content associated with the addition of C6–20 and C8–40 with A1 (ii) that the addition of OF and Z resulted in a significant decrease in the $CaCO_3$ content with A2 and (iii) a significant increase over time with an increased dose of C6 and C8 (for both 20 and 40 t ha^{-1}).

Regarding the content of available phosphorus in the control soils, the values were approximately 0.7 g kg^{-1}, 0.3 g kg^{-1}, and 0.4 g kg^{-1}, respectively, for PKG, CKG-N, and CKG-L (Table 3). More specifically, the addition of amendments to PKG showed (i) no significant changes in the P_2O_5 content with A1; (ii) a significant increase in the available phosphorus with the addition of OF, C6–20, C6–40, and C6+Z with A2; and (iii) a significant increase between A1 and A2 with increased C8+Z in P_2O_5 in comparison to the control. For CKG-N, the results highlighted that (i) the addition of OF, C8–40, and C8+Z with A1 resulted in a significant increase in the P_2O_5 content; (ii) the addition of all the amendments (except PS and C6–20) with A2 was associated with a significant increase in the available phosphorus and (iii) a significant increase in P_2O_5 was associated with an increased dose of OF and C8+Z. With CKG-L, the results showed (i) a significant increase with A1 in P_2O_5 with the addition of all the amendments (except PS and CH) (ii) a significant increase in P_2O_5 with A2 associated with an increased dose of C8–40 and C8+Z, but a significant decrease with PS and (iii) a significant increase associated with an increased dose of PS, C8–40, C8+Z, ML, and CH.

3.3 Effects of Amendments and Application Rates on Extractability of Metal(loid)s

3.3.1 EDTA-Extractable Metal(loid)s

Figure 1 presents the extractability of metal(loid)s by EDTA in the three unamended and amended soils studied (PKG, CKG-N, and CKG-L) considering the two applications of amendments (A1 and A2). The extractability of the metal(loid)s studied in the control soils (i.e., unamended soils U) were expressed as a percentage of the pseudo-total concentrations and were approximately (i) 70%, 66%, and 50%, respectively for Cd, Pb, and Zn in the PKG soil (ii) 7%, 14%, and 17%, respectively for As, Pb, and Zn in the CKG-N soil and (iii) 48% and 14% for Pb and Zn, respectively in the CKG-L soil. Overall, the results showed that the extractability of the geogenous Pb (in CKG-N) was lower (14%) compared to the anthropogenic Pb (in PKG and CKG-L), where the percentages were 66% and 48%, respectively. Compared to the control sample for the PKG soil, the results showed: (i) a significant increase in extractable Cd in the case of A1 and A2 with C6 (20% at both 20 and 40 t ha^{-1}), and only A1 with CH (16%), and DE (14%); (ii) no significant change with A1 in the Pb extractability associated with amendment addition, but a slight decrease with A2 accompanied with the addition of OF and PS (of 11% and 9%, respectively) and (iii) that the addition of C6–20 (with A1 and A2) and ML (only with A2) was associated with a significant increase in extractable Zn (20% and 9%, respectively), while PS was linked to a decrease of 6%. For the CKG-N soil, the addition of PS, C6+Z, Z, DE, and BM with A1 was associated with a significant decrease (between 13% and 68%) in extractable As, while no significant change in the Pb or Zn extractability with any other amendment. However, several changes were recorded in the case of A2 for this soil: (i) a significant increase of As extractability associated with the addition of OF, C6–40, C8–20, C6+Z, C8+Z, Z, ML, and CH (between 38% and 86%), but a decrease by 63% with the addition of PS; and (iii) an increase (between 22% and 42%) in Zn extractability associated with the addition of C6 and C8 at 40 t ha^{-1} and C8+Z. For the CKG-L soil, no significant change was observed in Pb extractability with the addition of amendments with A1 and A2. On the other hand, the addition of C6–20 and C6–40 with A1 and that of OF, C8–20, C8–40, HL, and ML with A2 demonstrated an increase between 12% and 25% in Zn extractability.

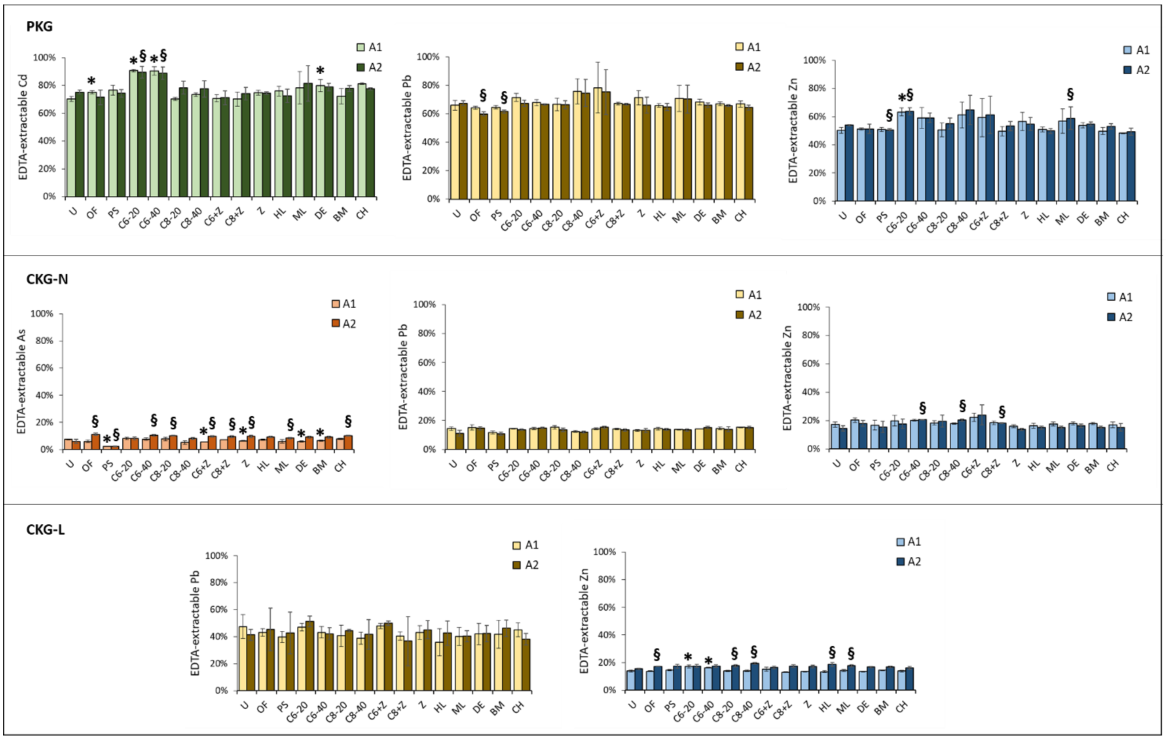

Figure 1 Comparison of metal(loid)s' extractability by EDTA for several amendments at application rates A1 and A2 for the three soils studied (PKG, CKG-N, and CKG-L). U: unamended soil; OF: organic fertilizer; PS: potting soil; C6–20: young compost (6 months) at 20 t ha^{-1}; C6–40: young compost (6 months) at 40 t ha^{-1}; C8–20: mature compost (8 months) at 20 t ha^{-1}; C8–40: mature compost (8 months) at 40 t ha^{-1}; C6+Z: a mixture of young compost and zeolite; C8+Z: a mixture of mature compost and zeolite; Z: zeolite; HL: hydrated lime; ML: magnesium lime; DE: diatomaceous earth; BM: bone meal; CH: crushed horn. * and § denote significant differences between a given amended soil and the unamended control soil, respectively with A1 and A2 ($p < 0.05$).

3.3.2 NH_4NO_3-Extractable Metal(loid)s

Figure 2 presents the extractability of metal(loid)s as evaluated by an NH_4NO_3-extraction performed on the three unamended and amended soils studied (PKG, CKG-N, and CKG-L) with the application of A1 and A2. Overall, in the control soils (i.e., unamended soils), the NH_4NO_3-extractable metal(loid) concentrations were very low. The extractability of As, Cd, Pb, and Zn is expressed as a percentage of the pseudo-total concentrations.

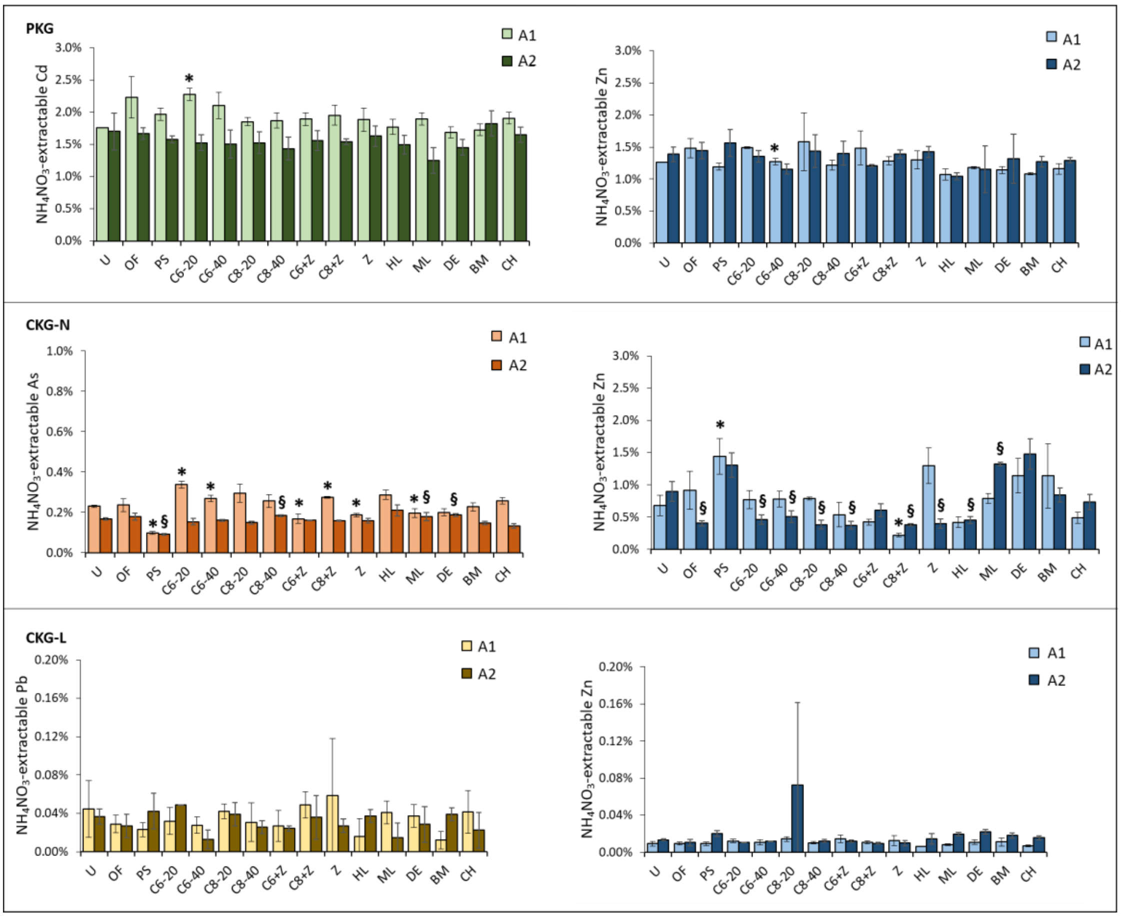

Figure 2 Comparison of metal(loid)s' extractability by ammonium nitrate for the amendments studied at applications A1 and A2 for the three soils studied (PKG, CKG-N, and CKG-L). U: unamended soil; OF: organic fertilizer; PS: potting soil; C6–20: young compost (6 months) at 20 t ha^{-1}; C6–40: young compost (6 months) at 40 t ha^{-1}; C8–20: mature compost (8 months) at 20 t ha^{-1}; C8–40: mature compost (8 months) at 40 t ha^{-1}; C6+Z: a mixture of young compost and zeolite; C8+Z: a mixture of mature compost and zeolite; Z: zeolite; HL: hydrated lime; ML: magnesium lime; DE: diatomaceous earth; BM: bone meal; CH: crushed horn. * and § denote significant differences between a given amended soil and the unamended control soil, respectively with A1 and A2 ($p < 0.05$).

The extractability of metal(loid)s were recorded as approximately: (i) 1.8% and 1.3%, respectively for Cd and Zn in the PKG soil (ii) 0.2% and 0.7%, respectively for As and Zn in the CKG-N soil and (iii) 0.04% and 0.009%, respectively for Pb and Zn in the CKG-L soil. The results of Pb extractability in the CKG-N and PKG soils are not presented because the extractable values by NH_4NO_3 were under the limit of detection.

Compared to the unamended PKG soil (control), the results showed no significant change in Cd or Zn extractability associated with the cases of both A1 and A2. However, there was an exception in the case of A1 with C6–20 for Cd and C6–40 for Zn. For CKG-N, the addition of amendments was associated with (i) a significant increase (between 6% and 46%) in extractable As with C6 (for both 20 and 40 t ha^{-1}), and C8+Z with A1 and with C8–40, ML and DE with A2. PS was associated with a significant decrease (of 50% on average) in the case of both applications; and (ii) a 100% increase in extractable Zn with PS and a significant decrease of 67% with C8+Z in the case of A1. In the case of

A2, ML was associated with a significant increase (47%) in extractable Zn, and OF, C6, C8 (for both 20 and 40 t ha^{-1}), C8+Z, Z, and HL were associated with a significant decrease (between 43% and 58%). For the CKG-L soil, no significant changes were observed in Pb or Zn extractability in the cases of both A1 and A2, whatever the type of amendment studied.

3.4 Efficiency of Amendments on Metal(loid) Extractability

The influence of the applied amendments was evaluated by the calculation of an efficiency factor (EF). An amendment was classified as efficient if it reduced the metal(loid) extractability in comparison to its given control soil, thereby being assigned an EF value of less than 1. Inefficient amendments are, on the other hand, associated with EF values greater than 1. Figure 3 presents both the efficiency and inefficiency of amendments with regards to the EDTA-and NH_4NO_3-extraction of metal(loid)s for the three soils. The focus was primarily on the efficiency of amendments at reducing EDTA-and NH_4NO_3-extractable metal(loid)s.

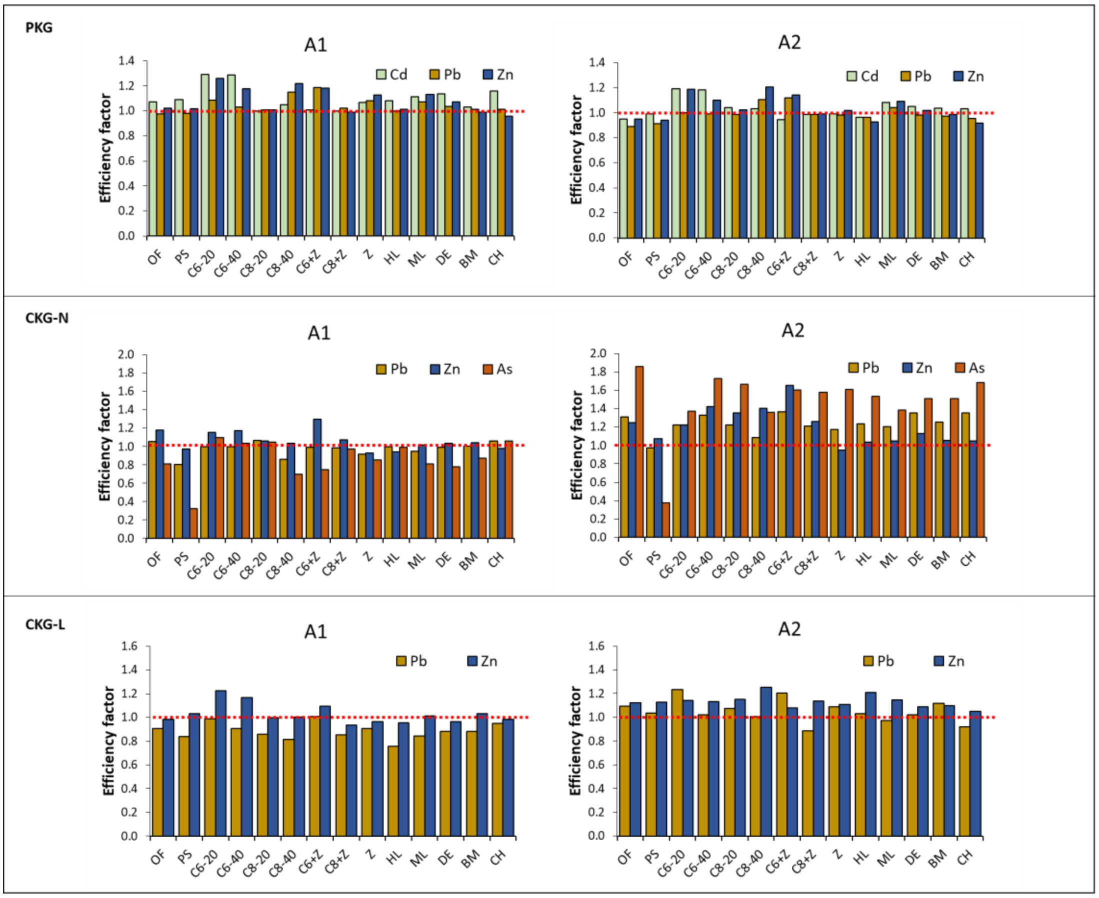

Figure 3 Immobilization efficiency of amendments on EDTA-extractable metal(loid)s for the three soils studied (PKG, CKG-N, and CKG-L); OF: organic fertilizer; PS: potting soil; C6–20: young compost (6 months) at 20 t ha^{-1}; C6–40: young compost (6 months) at 40 t ha^{-1}; C8–20: mature compost (8 months) at 20 t ha^{-1}; C8–40: mature compost (8 months) at 40 t ha^{-1}; C6+Z: a mixture of young compost and zeolite; C8+Z: a mixture of mature compost and zeolite; Z: zeolite; HL: hydrated lime; ML: magnesium lime; DE: diatomaceous earth; BM: bone meal; CH: crushed horn. Amendments were ranked as efficient if EF < 1 and inefficient if EF > 1.

Regarding the EDTA-extraction for the PKG soil (Figure 3), (i) none of the amendments resulted in a significant efficiency at reducing both Cd and Pb extractability in the case of A1 (EF between 1.0 and 1.3), while with A2, OF, C6+Z and HL were associated with relatively less extractable Cd (EF of 0.9 on average) and OF, PS, HL, DE, BM, and CH resulted in relatively less extractable Pb (EF of 0.9 on average) (ii) for Zn, in the case of A1, only the addition of CH allowed a reduction in its extractability (EF of 0.9), while in the case of A2, OF, PS, HL, BM, and CH resulted in less extractable Zn (EF of 0.9 on average). For the CKG-N soil, it was observed that PS, C8–40, Z, and ML with A1 were efficient (EF between 0.8 and 0.9), and their addition was associated with less extractable Pb, while with A2, none of the amendments resulted in significant efficiency at reducing Pb extractability (EF between 1.0 and 1.4). A1 with PS, Z, HL, and CH, resulted in decreased extractability (EF of 0.9 on average) in the case of Zn, while with A2, only Z was associated with relatively less extractable Zn (EF of 0.9). The amendments that efficiently reduced extractable As with A1 included OF (EF of 0.8), PS (EF of 0.3), C8–40 (EF of 0.7), C6+Z (EF of 0.9), Z (EF of 0.9), ML (EF of 0.8), DE (EF of 0.8), and BM (EF of 0.9), while only PS reduced extractable As in the case of A2 (with EF of 0.4). In the case of A1 in the CKG-L soil, the addition of all the amendments other than C6–20 and C6+Z was associated with efficiency at reducing the extractable Pb (EF between 0.7 and 0.9). A2 with only C8+Z and CH resulted in a similar reduction. In the case of Zn with A1, the addition of C8+Z, Z, HL, and DE resulted in less extractable Zn (EF of 0.9 on average). However, none of the amendments were efficient after the second application (EF between 1.0 and 1.3).

Regarding the efficiency factors for PKG from the NH_4NO_3-extraction (Figure 4), only DE and BM in the case of A1 are associated with relatively less extractable Cd (EF of 0.9), while with A2, the addition of all the amendments except BM reduced Cd extractability (EF between 0.7 and 0.9). For Zn, several amendments with both doses seemed efficient to reduce its extractability, more specifically PS, C6–40, C8–40, HL, ML, DE, BM, and CH with A1 (EF of 0.9 on average), and C6–20, C6–40, C6+Z, HL, ML, DE, BM, and CH with A2 (EF between 0.8 and 0.9). For the CKG-N soil (Figure 4), the addition of C8–40 (EF of 0.8), C6+Z (EF of 0.6), C8+Z (EF of 0.3), HL (EF of 0.6), and CH (EF of 0.7) with AI was associated with less extractable Zn. A2 with OF (EF of 0.4), composts with and without zeolite (EF of 0.5 on average), Z (EF of 0.4), HL (EF of 0.5), BM (EF of 0.9), and CH (EF of 0.8) also efficiently reduced extractable Zn. In the case of A1 with PS (EF of 0.4), C6+Z (EF of 0.7), and to a lesser extent Z, ML, and DE (with EF between 0.8 and 0.9), and the A2 of PS (EF of 0.5), and to lesser extent C6–20, C6–40, C8–20, C6+Z, C8+Z, Z, BM, and CH (EF between 0.8 and 0.9) reduced extractable As. For CKG-L (Figure 4), all amendments with A1 (excepted C8+Z and Z) were efficient at reducing Pb extractability (EF between 0.3 and 0.9). In the case of A2, several amendments were found to be efficient, more specifically OF, C6–40, C8–40, C6+Z, Z, ML, DE, and CH (EF between 0.4 and 0.9). For Zn, A1 with only HL, ML, and CH resulted in less metal extracted (EF of 0.8 on average), while A2 with OF, C6–20, C6–40, C8–40, C6+Z, C8+Z, and Z reduced extractable Zn (EF between 0.7 and 0.9).

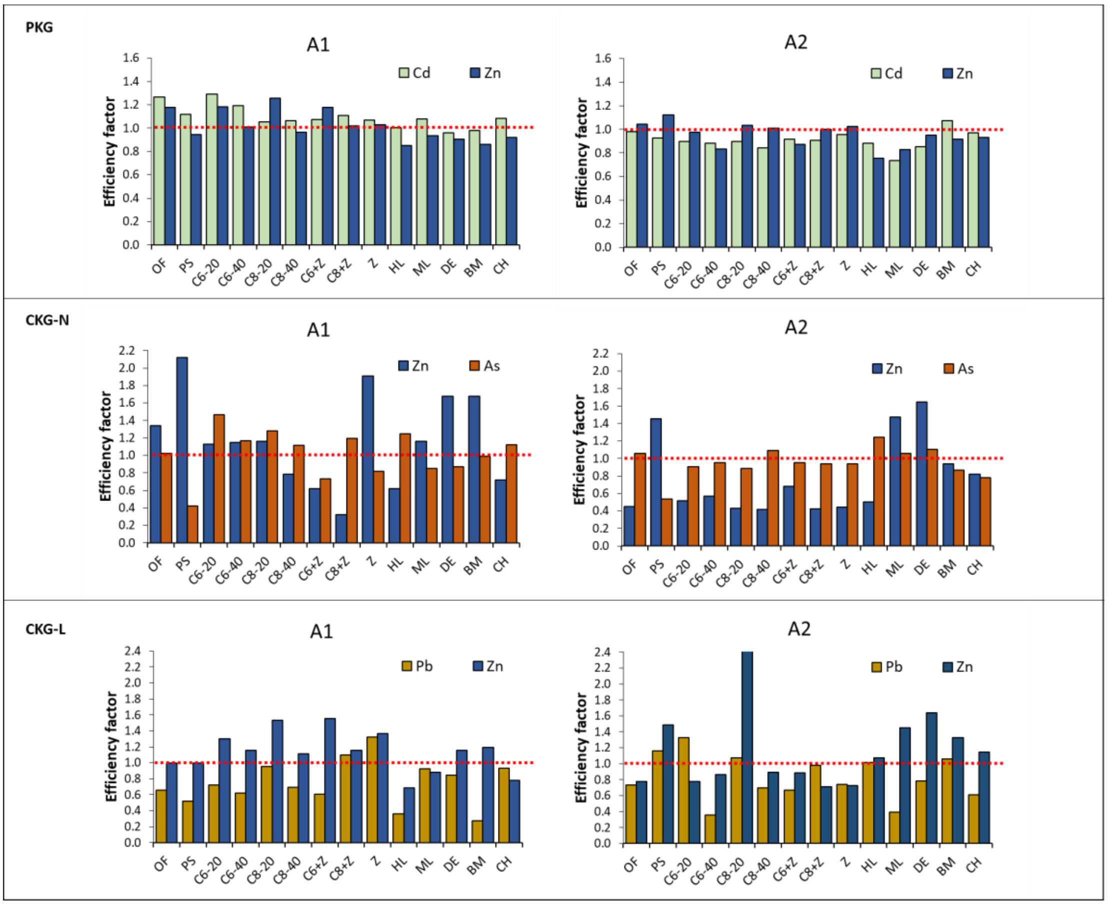

Figure 4 Immobilization efficiency of amendments on NH_4NO_3-extractable metal(loid)s for the three soils studied (PKG, CKG-N, and CKG-L); OF: organic fertilizer; PS: potting soil; C6–20: young compost (6 months) at 20 t ha^{-1}; C6–40: young compost (6 months) at 40 t ha^{-1}; C8–20: mature compost (8 months) at 20 t ha^{-1}; C8–40: mature compost (8 months) at 40 t ha^{-1}; C6+Z: a mixture of young compost and zeolite; C8+Z: a mixture of mature compost and zeolite; Z: zeolite; HL: hydrated lime; ML: magnesium lime; DE: diatomaceous earth; BM: bone meal; CH: crushed horn. Amendments were ranked as efficient if EF < 1 and inefficient if EF > 1.

4. Discussion

This study aimed to evaluate the effects of soil management practices based on the use of amendments on three contaminated kitchen garden soils under *ex-situ* conditions. Particular attention was paid to the influence and efficiency of organic and inorganic amendments with different application rates on metal(loid) extractability. The novelty of the study is based on (i) the comparison of a collection of amendments on soils with contrasting characteristics and sources of contamination and (ii) the use of doses commonly used by gardeners.

4.1 Organic Amendments

The organic amendment studied comprised of a commercialized green waste compost with two degrees of maturity. In terms of EDTA extractability of metal(loid)s for all three soils, A2 with composts is associated with a statistically significant decreased amendment efficiency in terms of metal(loid) reduction. These doses correspond to at least double that of what is recommended by gardening practices. This trend is echoed for extractable As in the CKG-N soil. Regarding the extractability of NH_4NO_3, it was observed that for all applications of composts, there was an increase in the available As in the CKG-N soil in comparison to the unamended soil. Though compost amendments are globally inefficient for this metalloid and soil, it was improved upon with the higher dose. Notably, the addition of compost amendments was also associated with a significant increase in pH in comparison to the control with A1 for the As-contaminated CKG-N soil and with A2 for C6–40 and C8–40. Though classified as an inefficient amendment for As immobilization in the CKG-N soil, the higher doses of some composts significantly decreased Cd availability in the PKG soil in comparison to A1. It has been shown that organic humidified materials can immobilize metals via adsorption or complexation, as the increase in soil organic matter content increases binding sites, thereby potentially reducing metal(loid) availability in soils [69]. OM increases Cd stability via adsorption and/or organic-metal complex processes, which can be improved with the addition of organic amendments, converting soluble and exchangeable fractions of metals to the less-available organic-bound fractions [70-72]. Additionally, the functional groups in organic materials show a high affinity for Cd ions [73-75]. For the CKG-L soil, many of the efficient, high-OM amendments with both A1 and A2 are associated with significant decreases in pH in comparison to the control soil, which had an alkaline pH of 7.9. However, the addition of C8–40 was associated with a decrease in NH_4NO_3-extractable Pb and Zn and significant increases in EC for this soil. A study by Alvarenga et al. [76] found that various soil amendments led to significant increases in the EC values, particularly for composts, which effectively reduced $CaCl_2$-extractable Cu, Pb, and Zn. $CaCl_2$ is an extractant that acts upon weaker bonds such as that of NH_4NO_3.

4.2 Natural Fertilizers

Three organic fertilizers were considered in this study—crushed horn (CH), bone meal (BM), and organic complete fertilizer made from poultry manure (OF).

CH is a bovine byproduct rich in keratin, N, P, K, and Mg, which decomposes slowly over time. The application of CH effectively reduced the extractable Pb and Zn from the soils in this study. This product, when hydrolyzed, has been associated with the reduction of available aqueous Cd up to 50% depending on its particle size [77]. This effect was attributed to the production of peptides, oligopeptides, and free amino acids with strong ion binding capacities upon hydrolysis. However, there is limited research and information on the effects of CH on soil metal(loid)s. However, the effect of the degradation of keratin complexed with the pollutants (i.e., the release of pollutant-bound keratin) in the medium term is also to be noted

BM has a composition close to CH and is a mixture of finely and coarsely ground animal bones and slaughterhouse waste products, rich in phosphorus and calcium. BM efficiently reduced the metal(loid)s (As, Pb, and Zn) with both applications when evaluated with the NH_4NO_3 extraction in this study. Similarly, a study by Sneddon et al. [78] found that the (relatively weak) $CaCl_2$ (0.01 M) extractions predicted a reduction in more metal availabilities than DTPA extractions conducted on the same BM-treated soils. Generally, DTPA extracts more metal from soils than $CaCl_2$, and this trend is the same for EDTA and NH_4NO_3 extractions, respectively. Thus, the results support the fact that BM can reduce the concentration of metal(loid) ions held on exchange sites, more so than on chelatable metals. BM demonstrated varied results for the different soils on reducing EDTA-extractable Pb, As, and Zn. The effective reduction of Pb in the CKG-L soil may be linked to sorption processes and a subsequent formation of metal phosphate, which retains Pb in the soil [79]. Other studies have suggested that bone char apatite, another source of phosphate, could remediate metal-contaminated soils, causing excessive P runoff [80, 81]. This amendment removes metals using adsorption and promotes ion-exchange reactions between ions in soil solution and calcium ions [82]. However, because of the low application rate of BM and the limited time of contact with the soils, the formation of a metal-phosphate phase is unlikely to be due to substitution, an ionic process that typically takes place slowly [79].

OF, another amendment rich in organic matter and N, P, K, resulted in a significant reduction of Cd in the case of A2 in the PKG soil, and Pb and Zn in the case of A1 in the CKG-L soil. Organic matter-rich amendments immobilize the metal(loid)s in the soil by increasing the pH, negatively charged surface sorption areas, and by forming hydroxyl forms of metal cations due to a subsequent increase in soil CEC [80, 81]. Specifically, organic fertilizer in the form of chicken manure is rich in humic substances, which reduces metal(loid) availability via adsorption or the formation of stable organic fractions [83, 84]. Chicken manure has been demonstrated to effectively reduce metals, especially Cd, alone and in composted manure [59, 72, 85, 86].

4.3 Calcareous Amendments

Two calcareous amendments (calcium-containing inorganic minerals composed primarily of oxides and hydroxides, usually calcium oxide and/or calcium hydroxide) were investigated, including lime flower (i.e., hydrated lime, HL) and magnesium lime (ML). Both applications (A1, A2) of the limes (HL, ML) were effective in immobilizing Cd, As, Pb, and Zn in the soils and were the most efficient among the amendments studied for the three soils tested. The addition of lime to soil can result in the precipitation of exchangeable soil Al, which can act as a cementing agent that binds soil particles, and improves soil structure. Liming can also significantly increase the concentration of exchangeable Ca and Mg in soils, a reaction that leads to an increase in CEC and the content of available soil phosphorous. Notably, lime can influence and increase soil pH, which is linked with the reduction of various bioavailable metal(loid)s, including Cd and Zn, via complexation and precipitation [87-92]. However, contrary to what was observed in this study, As is fairly available at the pH range in which other metals such as Cd and Pb may be immobilized [93].

4.4 Natural Siliceous and Alumino-Silicate Amendments

Two natural siliceous or alumino-silicate amendments were selected, including diatomaceous earth (DE) and natural zeolite (Z). DE demonstrated some success in reducing the extractability of As and Pb. A significant decrease in soil pH (from 7.9 to 7.6) was associated with the second application of DE in the CKG-L soil. This decrease may be due to the accumulation and retention of carbon dioxide (CO_2) and the creation of carbonic acids in the soil in the presence of moisture, which is retained by diatomite. A study by Prakash et al. [94] found that rates of application of diatomite as small as 0.3 t ha^{-1} result in a decrease in pH in alkaline soils and an increase in acidic soils at field water capacity. DE, a highly porous silicate, has a high specific surface area and is often used by gardeners as a pest deterrent and means of increasing soil water retention and improving soil quality. A study by Lu et al. [95] found that doses of calcium silicate, sodium silicate, and potassium silicate (1% by weight each) effectively reduced the amount of Cd accumulated in kale grown in garden soil (control) with a slightly acidic pH. This was similarly accurate for a 1.5% dose of silicate slag tested on cabbage for Cd uptake [96]. However, this was attributed to increased Cd adsorption by amended soil, leading to decreased Cd uptake by vegetables into the soil solution due to the increase in relative dissolved concentrations of cations competing with Cd^{2+}. In terms of soil Pb, studies have shown that active silicate materials can be useful in remediating Pb-polluted soils, as they can transform lead into oxidizable and residual soil fractions at neutral pH [97]. Little is known about the effects of silicates, particularly diatomaceous earth, on soil Pb and As.

Zeolites were successful on various metal(loid)s, at given applications and effectively reduced available As and Zn in the case of A1 and A2, respectively, in the CKG-N soil. Zeolites (Z) that contain calcium oxide and/or sodium hydroxide can also increase soil pH [98, 99]. Specifically, minerals added to the soil by zeolites can increase a soil's pH and CEC, and prevent the decrease in organic matter [100]. Similar studies have found that sepiolite (a magnesium hydro silicate clay mineral) significantly decreased HCl-extractable Cd due to an increase in soil pH, Cd complexation reactions, Cd diffusion into the clay lattice structure, and Cd substrate surface retention [101, 102]. At a pH value between 4 and 6, like in the PKG soil, zeolites are typically cited as immobilizing metals mainly through ion exchange [103]. Other studies cite sorption as the main mechanism that occurs at moderately alkaline pH's, like those seen in the CKG-L and CKG-N soils [98].

4.5 Mixtures Containing Organic Products

Two mixtures of products were tested—potting soil (PS) and a mixture of young or mature composts with zeolite (C6+Z and C8+Z). Among the amendments that were found to be efficient with both extractants, PS showed a statistically significant potential in reducing the availability of As and Pb with both applications, making it a potentially effective tool for risk reduction in As-and Pb-pollution kitchen garden soils (CKG-N). For the CKG-L soil, a significant decrease in soil pH was associated with the addition of the second application of PS. The addition of 6% PS by mass could result in the decrease of soil pH by way of dilution. Potting soils often consist of a mixture of peat, dolomite, vermiculite, or perlite, and are designed to hold water and nutrients in the soil. A typical mix contains 33–66% of peat rich in organic matter [104]. Peat and vermiculite are cited as heavy metal immobilizers [105, 106]. The addition of 3% vermiculite and peat separately to contaminated and slightly acidic soil can provoke a reduction in water-soluble and extractable soil Cd and Pb [106]. Vermiculite, particularly that which has been modified by cationic surfactants, has also been cited as an effective sorbent of As(V) and As(III) in aqueous solutions [107]. The addition of PS at 33% by mass resulted in the reduction of available Pb in garden soil with acidic pH, but an increase in available As [62]. The observed reduction in the available Pb could be due to mechanisms of complexation and adsorption but also due to dilution at the high application dose. In this study, PS very effectively reduced extractable As when applied at 3% (A1) and 6% (A2) by mass to alkaline soil. However, since the constituents of PS were not tested separately in this experiment, it is difficult to determine if it was the entire mixture or a single constituent that demonstrated the effects.

Young or mature composts mixed with zeolite were overall determined as efficient amendments as evaluated by both extractants. C6+Z with A1 significantly reduced available As in comparison to the control soil, and C6+Z and C8+Z with A2 reduced extractable Cd in the PKG soil. The application of C8+Z also reduced extractable Pb in the CKG-L soil. To reiterate, zeolites are natural or synthetic crystalline frameworks of alkaline-based aluminosilicates that can act as molecular sieves because of their adsorption capacity [98, 103]. They are linked to metal(loid) immobilization in conjunction with composts and have an immobilizing effect when applied to soil alone [57].

Table 4 presents a summary of the amendments applied on the three soils having the efficiency to reduce the extractability of metal(loid)s.

Table 4 Summary of the amendments for both applications A1 and A2 on the three soils studied (PKG, CKG-N, and CKG-L) having an efficiency (i.e., EF<1) to reduce the extractability of metal(loid)s.

Soil	Metal(loid)	Dose	Amendment
PKG	Cd	A1	DE, BM
		A2	OF, PS, C6–20, C6–40, C8–20, C8–40, C6+Z, C8+Z, Z, HL, ML, DE, CH
	Pb	A1	-
		A2	**OF**, **PS**, HL, ML*, DE, BM, CH
	Zn	A1	PS, C6–40*, C8–40, HL, ML, DE, BM, CH
		A2	OF, **PS**, C6–20, C6–40, C6+Z, HL, **ML**, DE, BM, CH
CKG-N	As	A1	OF, **PS***, C8–40, **C6+Z***, **Z***, ML*, **DE**, **BM**
		A2	**PS***, C6–20, C6–40, C8–20, C6+Z, C8+Z, Z, BM, CH
	Pb	A1	PS, C8–40, Z, ML
		A2	-
	Zn	A1	PS, C8–40, C6+Z, C8+Z*, Z, HL, CH
		A2	OF*, C6–20*, C6–40*, C8–20*, C8–40*, C6+Z, C8+Z*, Z*, HL*, BM, CH
CKG-L	Pb	A1	OF, PS, C6–20, C6–40, C8–20, C8–40, C6+Z, C8+Z, Z, HL, ML, DE, BM, CH
		A2	OF, C6–40, C8–40, C6+Z, C8+Z, Z, ML, DE, CH
	Zn	A1	C8+Z, Z, HL, ML, DE, CH
		A2	OF, C6–20*, C6–40*, C8–40, C6+Z, C8+Z*, Z

OF: organic fertilizer; PS: potting soil; C6–20: young compost (6 months) at 20 t ha^{-1}; C6–40: young compost (6 months) at 40 t ha^{-1}; C8–20: mature compost (8 months) at 20 t ha^{-1}; C8–40: mature compost (8 months) at 40 t ha^{-1}; C6+Z: a mixture of young compost and zeolite; C8+Z: a mixture of mature compost and zeolite; Z: zeolite; HL: hydrated lime; ML: magnesium lime; DE: diatomaceous earth; BM: bone meal; CH: crushed horn. An asterisk denotes a significant decrease in extractability in comparison to the given control soil for the NH_4NO_3 extraction. Amendments in bold denote a significant decrease in extractability in comparison to the given control soil as evaluated by the EDTA extraction.

5. Conclusion

Exposure to metal(loid)-contaminated kitchen garden soils can pose a great risk to human health. This study conducted an assessment of various amendments (at doses commonly used by gardeners), particularly composts and other organic and mineral amendments, used to manage urban kitchen garden soils with moderate geogenous and/or anthropogenic contamination. The impact of the amendments was evaluated via extractability of metal(loid)s by the use of two chemical extractants. An *ex-situ* experiment was performed, which provided evidence of the possibility of reducing the extractability of the metal(loid)s considered in the study. The results were, however, dependent on the physico-chemical soil parameters and the metal(loid) considered.

Overall, the efficiency of amendments at reducing the extractability of the selected metal(loid)s' was more marked for the ammonium nitrate extraction than for the EDTA extraction. It also varied greatly on the metal(loid) studied and the garden soil on which the amendment was applied to. Moreover, for the strong EDTA-extractant, several amendments (e.g., PS, OF, C8–40, C6+Z, Z, DE, BM) were efficient at reducing metal(loid)s' extractability with the first application in the cases of CKG-N and CKG-L. On the other hand, for PKG, the most acidic soil, reamendment (i.e., second application A2) was necessary to observe a significant efficiency for EDTA-extractable metal(loid)s. With the weakest NH_4NO_3-extractant, the behavior of the metal(loid)s varied with the soil: (i) while the effectiveness of certain amendments (e.g., DE, BM, C6–40) to the PKG soil was demonstrated in the case of A1, the positive effects were significantly more marked in the case of A2; (ii) in the CKG-N soil, A1 demonstrated some positive effects at reducing metal(loid)s' extractability. The effects were significantly more marked in the case A2 (e.g., PS, OF, C6, C8); and (iii) in the CKG-L soil, the effectiveness of certain amendments (e.g., OF, C6, C8, C6+Z, C8+Z) was demonstrated in both doses. For all the soils, the results also depended on the type of product studied. Considering the three soils are inherently different based on their agronomic characteristics, their origin, and the nature of their metallic contamination, there is no single optimal solution. Therefore, tests must be carried out before any implementation activities on the kitchen gardens. The durability of the effects obtained is also to be noted, specifically in the case of organic amendments.

In this study, the influence of amendments on the availability of metal(loid)s in soils was monitored using chemical extractions. The results should be validated by examining the phytoavailability of these pollutants through biological models (i.e., vegetables) in *ex-situ* conditions, followed by *in situ* tests. Further investigation is also required to assess the effects of amendments on agronomic parameters, including the cycle of elements and the evolution of organic matter in the medium term.

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Additional Materials

The following additional materials are uploaded at the page of this paper.

1. Table S1: Soil amendment parameters.
2. Figure S1: Experimental design - Description of the different steps and conditions of the experiment.
3. Figure S2: Fractionation of Pb in the three soils studied (PKG, CKG-N and CKG-L); F1: exchangeable, water- and acid-soluble fraction, F2: reducible fraction, F3: oxidizable fraction, F4: residual fraction.

Author Contributions

Ashley Schnackenberg: conceptualization, methodology, data acquisition and analysis, statistical analysis, writing original draft; **Géraldine Bidar:** conceptualization, methodology, supervision, writing review editing; **Laure Beaudet:** conceptualization, methodology, writing review editing; **Valérie Bert:** conceptualization, methodology, writing review editing; **Patrice Cannavo:** methodology, writing review editing; **Sébastien Détriché:** sampling and mapping, writing review editing; **Francis Douay:** conceptualization, supervision, methodology, writing review editing; **René Guenon:** conceptualization, methodology, writing review editing; **Liliane Jean-Soro:** conceptualization, methodology, writing review editing; **Alice Kohli:** methodology, writing review editing; **Thierry Lebeau:** conceptualization, methodology, writing review editing; **Karen Perronet:** conceptualization, methodology, writing review editing; **Christophe Waterlot:** methodology, writing review editing; **Aurélie Pelfrêne:** conceptualization (lead), supervision, methodology, data acquisition and analysis, writing original draft.

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Competing Interests

The authors have declared that no competing interests exist.

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The main results obtained in this study are:

- PS (D1=3% and D2=6%) showed a significant potential to reduce As availability from 50 to 70% in CKG-N; this amendment presents also an interest to reduce Pb extractability in this geogenically- contaminated soil, as did other high-organic matter amendments such as composts applied at two doses;
- Zeolite alone (Z) or in combination with compost (C+Z) had success with reducing extractable As, Cd, Pb, and Zn, and therefore could be an interesting amendment mix;
- Other efficient amendments include:
  (i) crushed horn (CH) on available Zn reduction in PKG, CKG-N, and CKG-L, and available Pb on PKG and CKG-L;
  (ii) bone meal (BM) to reduce extractable As in CKG-N, Pb on PKG and CKG-L, and Zn on PKG, CKG-N;
  (iii) limes (ML and HL), for which a dose of either or both effectively immobilized all metal(loid)s in each of the three soils studied.

Potting soil (PS) presents a significant potential to reduce As availability in soil with both application rates (3 and 6%); however PS itself has rarely been cited in the scientific literature as an As immobilizer. In fact, Paltseva et al. (2016) cited that this product mobilized As when applied to soil at 33% w/w. As detailed in Chapter 2, PS is mainly composed of peat, dolomite, vermiculite, and perlite. The question then arises as to which component of the mixture acts as effectively on the availability of As.

Potting soil is an amendment mix, and it was showed in the literature that some of PS's possible components (*i.e.,* peat, dolomite, vermiculite, perlite) used alone have been linked to reduced metal(loid) phytoavailability (Abbar et al., 2017; Chen et al., 2016, Tuchowska et al., 2019, Paltseva et al., 2018). A second experiment (Experiment 1b), described in Chapter 2, was therefore conducted specifically on some of the components of PS (*i.e.,* dolomite, peat, perlite) applied alone on CKG-N in order to identify which ones were responsible for reduction of As extractability. Dolomite's chemical composition ($CaMg(CO_3)_2$) closely resembles ML, which was tested on CKG-N soil in Experiment 1a. At D1 (0.1%), ML evoked no significant difference in As extractability whereas it mobilized As when its dose was raised to 0.2% (D2). As PS was applied at 3% to soils in Experiment 1a, and dolomite represents 2.5% of PS, this corresponds to a dolomite application rate of 0.075% on the CKG-N soil. This rate is inferior to the first tested rate of its analogous product ML. This amendment was thus determined not to be an immobilizing component of PS on As to test again separately. Therefore three amendments were tested: potting soil (PS, 3%), sphagnum peat (PEAT, 1.2%) and perlite (PERL, 1.2%) mixed with CKG-N soil. The determination of As extractability (NH_4NO_3 and EDTA) in amended soils were performed. The effects of PEAT and PERL were assessed in comparison with unamended soil U and PS applied to this soil (Figure 3-1). In the unamended control soil (Experiment 1a), 0.23% of As is extracted by NH_4NO_3, and 7.4% by EDTA (Schnackenberg et al., 2022). As's relatively low extractability by both NH_4NO_3 and EDTA can be explained by As's geogenic origins, as the Les Eglantiers garden is noted for the presence of a vein of micaschist that runs though it containing iron and sulphur-rich arsenopyrite, FeAsS (Le Guern et al., 2013; Baret, 1898). Indeed,metal extractions by NH_4NO_3, which simulate metal fraction in soil pore water, provide an estimate of the displacement of easily soluble metals (cation exchange process). This unbuffered extraction allows reactions and interactions that occur at the pH of the soil to take place (Lebourg et al., 1998; Houba et al., 2000; Amoakwah et al., 2013; Gryschko et al., 2004; Vincreanu et al., 2019). EDTA, conversely, is a strong chelator which can compete with more strong binding sites in soil (complexation processes), was used to assess the pool of metals absorbed both by organic matter, (hydr-)oxides (Fe, Al, Mn) and carbonates of soil with low carbonate contents (Sahuquillo et al., 2003; Quenea et al., 2009).

Concerning the addition of amendments to this As-contaminated CKG-N soil, it was noted in Figure 3-2 that PS, as also seen in Experiment 1a, and its components (PEAT and PERL) significantly reduce As extractabilities by 60% compared with unamended soil (U). Indeed, As dropped from 0.23%to between 0.11- 0.12% extractable by NH_4NO_3, and from 7.4% to between 2.5- 3% extractable by EDTA. However, there is no significant difference in extractability of As among the original amendment (PS) and its components (PERL and PEAT). Though PEAT is associated with slightly less As-extractable EDTA in CKG-N soil compared to PS and PERL (2.5 *vs* 2.8 and 3% respectively), the absence of a statistical trend suggests that no tested individual component of potting soil is responsible for the immobilization of As, and rather that both components play a part in As mobility reduction.

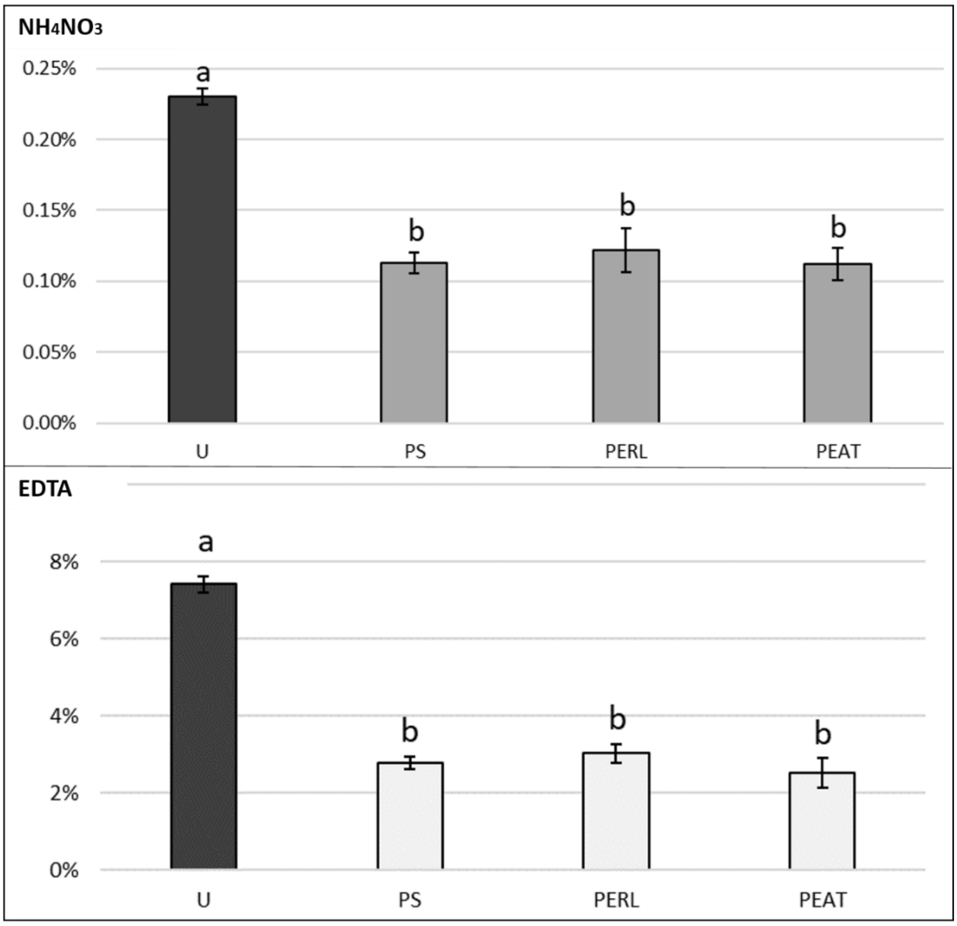


Figure 3-1: **NH_4NO_3- and EDTA -extractability of As (mean and standard deviation values expressed in % of pseudototal concentrations, *n* = 3) from CKG-N soil unamended (U) and amended with potting soil at 3% (PS) and its components (perlite for PERL and peat for PEAT). Values for U are taken from the above article (Schnackenberg et al., 2022). Different letters indicate significant differences ($p < 0.05$) between the different conditions.**

As reviewed in Chapter 1, peat is composed of organic matter and humic substances. Organic matter can immobilize metal(loid)s by aiding in the formation of metal(loid)-organic complexes (Singh & Oste, 2001). EDTA extractions are capable of giving an estimate of organic-matter complexed metal(loid)s associated with the oxidizable fraction of soil (Singh & Oste, 2001; Nwachukwu & Pulford, 2009; Sahuquillo et al., 2003; Quenea et al., 2009). The large decrease in EDTA-extractability of As occuring with the addition of PS and its components suggests that As shifts into a less available form. This is potentially a form linked to other organic matter, (hydr-)oxides (Fe, Al, Mn), and/or carbonates. This CKG-N has an OM content of 49.6 g kg^{-1}, a carbonate content of 2 g kg^{-1}, and a pH of 7.1 unamended and 6.8 amended with PS (Experiment 1a). This evidently favors As immobilization in organic matter complexes. Considering that the parent soil CKG-N contains arsenopyrite (FeAsS) that contributes to its contamination (Le Guern et al., 2013; Baret, 1898), there is a high probability that this soil also contains iron oxides, which could also contribute to As immobilization.

In soils, peat's immobilization of As can be improved in the presence of a soil rich in metal oxides (Wang et al., 2019; Eberle et al., 2020). Iron oxides can form some of the strongest As complexes (Boisson et al., 1999). This trend is echoed in extractability results. Indeed, the As found in soil pore water has been shown to significantly decrease as Fe oxide in the most available fraction of soil increases suggesting a decrease of available arsenate (AsO_4), a salt of arsenic acid (McBride *et al.,* 2013). Though alkaline pHs between 7.0 and 8.5 like that of CKG-N (U) tend to mobilize As, pH's below 7 like that seen in the presence of PS in Experiment 1a favor As immobilization (Eberle et al., 2020). This is aided if S is present in the soil or soil solution (Eberle et al., 2020). Indeed, other studies have linked the addition of peat to a soil contaminated by As to soil pH decreases, and the mobilization of S and Fe (Nawad et al., 2018; Gul et al., 2015, Brown et al., 2003). Thus the significant pH decrease seen in Experiment 1a may have mobilized soil S and Fe already present in the form of arsenopyrite in CKG-N, immobilizing As via complexation with iron oxides (Nwachukwu & Pulford, 2009; Eberle et al., 2020).

Potting soil also contains perlite, an expanded alumino-silicate that has the ability to immobilize metal(loid)s via ion exchange (Haidouti et al., 1997). As a siliceous amendment, it is often referred to as a molecular sieve because of its porous structure (Plummer & McGeary, 1993). Because of its large surface area and a high surface activity which provide space the attachment of various functional groups to their structure, siliceous amendments such as perlite favor reactions between metal(loid)s and other agents (Rodrigues-Salado et al., 2016, Marwa et al., 2011). Specifically, perlite is an expanded alumino-silicate composed of silica, alumina, iron oxide, lime oxide, magnesia, sodium oxide, and potassium oxide that has the ability to immobilize metal(loid)s via ion exchange (Haidouti et al., 1997; Ozdemir et al., 2020). Rodriguez-Salgado et al. (2016) studied the effects of a perlite applied on an acidic wine-growing soil, and found that it increased C_{total}, N_{total}, P_2O_5, and exchangeable K contents compared to the control soil. These properties can facilitate reactions among metal(loid)s and other agents present in kitchen garden soils (Lian et al., 2019). The iron oxide present in perlite has also been shown to be able to bind As (Wang et al., 2019; McBride *et al.,* 2013). This is potentially a form present in the less oxidizable soil fraction not highly extracted by EDTA, which could help explain Experiment 1a and 1b's result on concerning the reduction of extractable As with PS addition (Boisson et al., 1999).

As siliceous amendments share common properties such as framework lattice structures, high porosities, large surface areas and high CEC's, they can react similarly to one another under common conditions (Lian et al., 2019). Experiment 1a shows that another siliceous amendment, zeolite, applied at a 2% dose can also reduce the NH_4NO_3 and EDTA extractablity of As on CKG-N (by 10%) as perlite did (by 60%). The efficacy of these two amendments could be because of their ability to increase soil CEC and prevent organic matter deterioration. These effects on CEC and organic matter have been shown to help immobilize As (Li et al., 2009).

Thus it is important to consider potting soil not only as its individual components, as it was shown that no individual component was significantly more effective than another, but also as a whole. Studies suggest that organic and inorganic amendments mixtures can lead to increased amendment efficacy in comparison to their individual organic or inorganic components (Al Chami et al., 2013; Hamidpour et al., 2017, Schnackenberg et al., 2022). The mixture of an organic matter-rich amendment (such as peat) and a silicate-rich amendment (such as perlite) can invoke As immobilization because of a synergy between the two components. Organic matter is known to provoke metal immobilization and soil fertilization, but its decomposition over time can liberate metal(loid)s (Al Chami et al., 2013; Huang et al., 2016; Khan et al., 2017; Thi et al., 2013). However, the liberation of these metal(loid)s can be avoided or mitigated by the addition of mineral amendments which increases the immobilizing effectiveness and the durability of amendments due to their slow degradation speed (Golia et al., 2017, Hamidpour et al., 2017, Al Mamun et al., 2019; Liu et al., 2019; Singh & Kalamdhad, 2014; Zhang & Sun, 2015). For example, it has been found that compost mixed with i) limes, ii) phosphate-rich amendments, and iii) zeolites have effectively immobilized metal(loid)s (Golia et al., 2017; Hamidpour et al., 2017; Gadepalle et al., 2009; Najafi-Ghiri & Rahimi, 2016, Wong et al., 2006, Lu et al., 2014).

Experiment 1a suggests that organic matter and silicate-rich amendment mixes can immobilize metal(loid)s more effective in mix than separately. Mixes of composts and zeolite applied at 10% (C6+Z or C8+Z) were tested on three soils, one of which was CKG-N. The EDTA extraction saw that the addition of a compost mix immobilized As more than its individual components added alone (i.e., C6, C8, and Z) at the same dose as in the mix. Whereas EDTA extracted 7.4% of As present in CKG-N (U), C6+Z extracted 5.6%. By contrast, the compost present in C6+Z applied at the same rate (C6-20) extracted 8.2% of As, and zeolite alone added at the same dose (Z) extracted 6.4%. C8+Z extracted 7.2% of As, and the addition of the compost alone (C8-20) extracted 7.8%. It was hypothesized that the mixes were more effective than compost alone, because zeolite can modify mature compost parameters by buffering pH (Waqas et al., 2019). This parameter was seen to be lower on the soils amended with C6+Z (7.29) rather than C6-20 (7.34) alone (Waqas et al., 2019).

This first study conducted an assessment of various amendments (at doses commonly used by gardeners) used to manage urban KG soils with moderate geogenous and/or anthropogenic contamination. Among amendments tested for their ability to reduce metal(loid) availability in KG soils using chemical extractions, some were found to be more suitably applied on different soils and to immobilize different metal(loid)s than others. The purpose of the thesis being to propose amendments capable of limiting the transfer of metals to the edible parts of vegetables cultivated in moderately contaminated KG soils, it was necessary to confirm this effect in the presence of a plant model.

The amendments are selected on the basis of their positive effects (*i.e.,* reduction of metal(loid) extractability) but also with regard to negative or no effects in order to evaluate their evolution in the presence of a plant model. Notably, as compost is a commonly used amendment, this was selected as a pertinent amendment to test in Experiment 2. Zeolite (Z) alone and in combination will also continue to be studied in this experiment, because of its interest when co-applied with compost, and to serve as a comparison. The conditions chosen retains several amendments in common for each soil in order to be able to facilitate a comparison of their effects. Table 3-1 summarizes the effects of the most pertinent amendments tested in Experiment 1 chosen to test in Experiment 2, as well as the reason for their selection for further study.

Table 3-1: **Summary of most pertinent amendment effects on metal(loid) extractability in the three kitchen garden soils (PKG, CKG-N, CKG-L) chosen for study with a plant model in Experiment 2. Percentage represents the positive (↓ and green) or negative (↑ and red) efficiency of each amendment calculated from unamended conditions.**

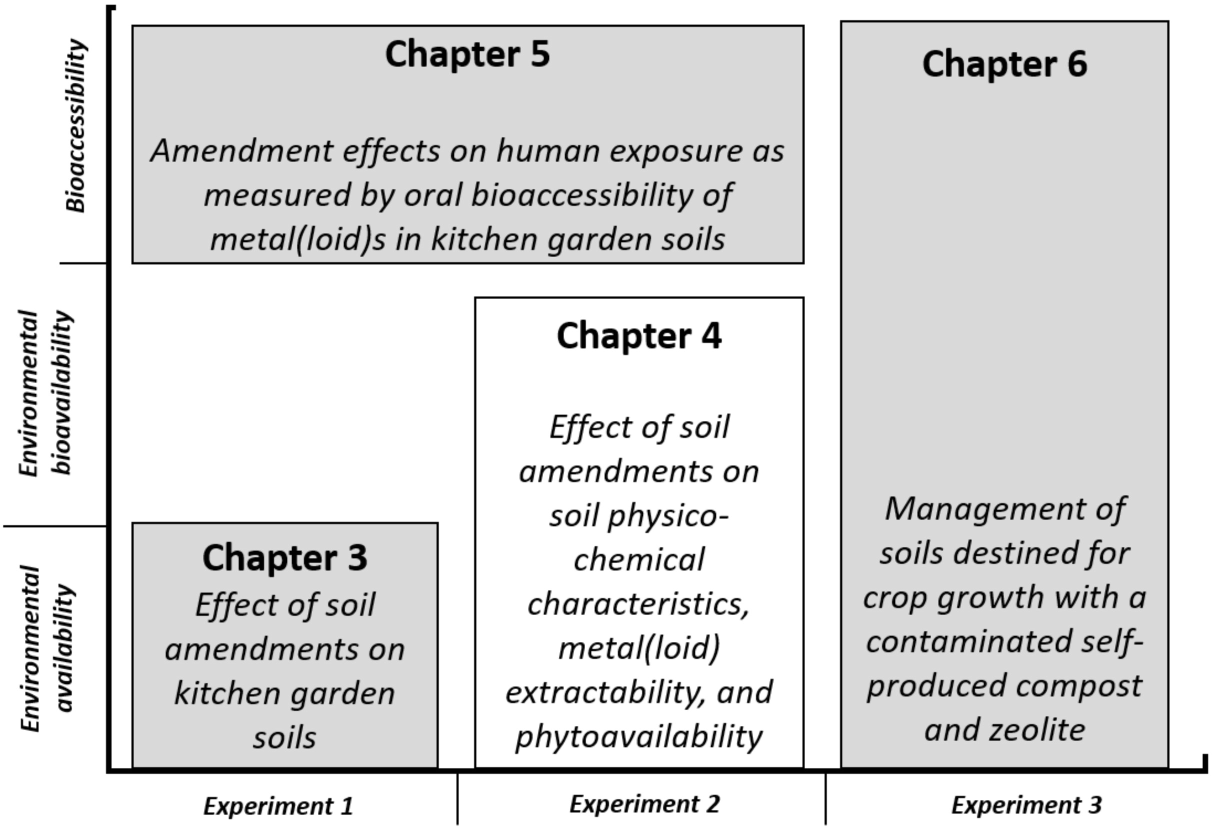
Soil	Amendment	Dose	Extractability
PKG	C6-20	D1	↑30% Cd ↑18% Zn
	C6-40	D1	↑16% Cd
	C6+Z	D1	no effect
	Z	D1	
	HL	D2	↓6% Cd
	CH	D1	↑9% Cd
CKG-N	C6-20	D1	no effect
	C6-40	D1	
	C6+Z	D1	↓27% As ↓38% Zn
	Z	D1	↓8% As
	PS	D1	↓68% As ↓68% Zn
	HL	D2	↓58% Zn
CKG-L	C6-40	D1	↓38% Pb
	C8-40	D1	↓31% Pb
	C8+Z	D2	↓2% Pb
	PS	D1	↓48% Pb
	HL	D1	↓64% Pb
	BM	D1	↓73% Pb

C6: young compost (6 months); C8: mature compost (8 months); Z: zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn.

Chapter takeaways

Chapter 3 showed that amendments applied a culturally-relevant doses can reduce metal(loid) extractability of three different unplanted soils. C+Z had success with reducing extractable As, Cd, Pb, and Zn on CKG-N. PS significantly reduced As extractability, and tended to reduce Pb extractability on this soil as well. Its active components peat and perlite where not seen to be significantly differently efficient when applied separately and evaluated on extractable As. CH reduced extractable Pb on PKG and CKG-L, whereas BM reduced extractable As in CKG-N and Pb on PKG and CKG-L. Limes (ML and HL) both effectively immobilized all metal(loid)s in each of the three soils studied.

Chapter 4: Effect of soil amendments on soil physico-chemical characteristics, metal(loid) extractability, and phytoavailability



Chapter 4: Effect of soil amendments on soil physico-chemical characteristics, metal(loid) extractability, and phytoavailability

The previous chapter studied the effects of a selection of 14 inorganic and organic amendments alone or in mixture on physico-chemical parameters and environmental availability of metal(loid)s (based on chemical extractions) in private and community urban kitchen garden soils (*i.e.*, PKG, CKG-N and CKG-L). The present chapter explores how the establishment of a crop in combination with amendments influence the environmental availability and phytoavailability of metal(loid)s. A second *ex-situ* greenhouse experiment (Experiment 2) was thus set up to study, for each soil, 6 of the most pertinent amendments identified in Chapter 3 in combination with lettuce. The relevance of amendments was assessed based on their positive (reduction), negative (increase), or insignificant effects on mobility. The effects of the amendments in a planted system were firstly assessed on (i) physico-chemical and biological soil characteristics, (ii) metal(loid)s extractability as analyzed by different extractions (sequential, passive, and single), and (iii) the plant model in terms of germination, biomass, and metal(loid) accumulation. Results were then discussed in order to assess the effects of plant on the amendment efficiency and finally highlight the combined effect of both lettuce and amendments on the metal(loid) behavior.

1. Effects of amendments on metal(loid) behavior in three metal(loid)-contaminated kitchen garden soils planted with lettuce

As described in detail in Chapter 2, seven conditions per soil were defined to test during Experiment 2, including:

- on PKG: unamended (U2) and amended with C6-20 at 0.6%, C6-40 at 1.2%, C6+Z at 0.6% containing 0.06% of Z, Z at 2%, HL at 0.1%, or CH at 0.05%;
- on CKG-N: unamended (U2), and amended with C6-20 at 0.6%, C6-40 at 1.2%, C6+Z at 0.6% containing 0.06% of Z, Z at 2%, PS at 3%, or HL at 0.1%;
- on CKG-L: unamended (U2) and amended with C6-40 at 1.2%, C8-40 at 1.2%, C8+Z at 1.2% containing 0.12% of Z, PS at 3%, HL at 0.05%, or BM at 0.05%.

This section describes the effect of amendments on soil physico-chemical and biological parameters, metal(loid) chemical distribution, metal(loid)s in soil pore water, environmentally available metal(loid)s, and the plant model.

1.1 Amendment impacts on soil physico-chemical and biological parameters in presence of lettuce

As described in Chapter 3 (*i.e.*, Schnackenberg et al., 2022), the three kitchen garden soils studied possess different physico-chemical characteristics in terms of texture, pH, electric conductivity (EC), cationic exchange capacity (CEC), contents of total carbonates, organic matter, available P, and metal(loid)s. Table 4-1 presents the effects of the chosen amendments in presence of lettuce on soil pH, EC, total carbonate ($CaCO_3$), available P (P_2O_5), NaOH-soluble organic carbon content, and global bacterial activity for PKG, CKG-N and CKG-L. Comparisons of the effects of amendments amongst each other can be found in Annexes 4-1, 4-2, and 4-3.

1.1.1 Physico-chemical parameters

PKG

In PKG, the pH in the unamended control (U2) was 6.3 (Table 4-1). Only the addition of C6-20 resulted in the significant further increase in pH to 6.4, probably explained by the alkaline pH of this compost (pH of 8.6). Double this dose of compost did not significantly change pH, but it did raise it to one of the highest pH's as compared to the other conditions. The addition of all amendments (*i.e.*, C6-20, C6-40, C6+Z, Z, HL, CH) to U2-PKG significantly increased $CaCO_3$ content from 1.12 to above 1.50 g kg^{-1}, with HL increasing this value the most to 3.62 g kg^{-1}. The high $CaCO_3$ contents of all amendments compared with this soil (*e.g.*, C6 = 60 g kg^{-1}, HL = 91 g kg^{-1}; *cf* Table 2-4) could be the main reason of these carbonate and therefore pH increases. Attanayake et al. (2015) found that during compost-soil maturation (compost pH of 7.9, and soil pH of 7.0), amended soils can have a higher pH than the control soil because of their higher soluble organic C content brought by OM. The electrical conductivity of the planted control PKG soil (U2) (887 µS cm^{-1}) significantly increased to 1,589 µS cm^{-1} after the addition of HL. This change can be attributed to HL's high EC of 8,240 µS cm^{-1} (*cf* Table 2-4). Though limes typically increase soil pH, the addition of HL to this soil did not do so. Despite zeolite's moderate EC of 114.5 µs cm^{-1}, this amendment also significantly increased EC. Zeolites tend to increase soil EC and Cl content (Hamidpour et al., 2017; Usman et al., 2005). As with EC, the addition of only Z and HL resulted in a significant change in available P. Despite the fact that these amendments had low available P contents of 0.19 and 0.00 g kg^{-1} (*cf* Table 2-4), respectively, their additions in U2 soil increased available P from 0.47 to 0.63 g kg^{-1} and 0.80 g kg^{-1}. This can be explained by these amendments' ability to promote ion exchange. Zeolite is indeed commonly cited as an absorbent because of its copious pore space, which can improve microorganism habitat and thus enhance the degradation of organic matter of soil (Ming & Allen, 2001; Phillips, 1998; Hamidpour et al., 2017). As siliceous amendments, Z can contribute to increases in available P, C_{total}, and N_{total} in acidic soils like the PKG control over time because of its capacity to promote ion exchange (Rodriguez-Salgado et al., 2016).

Table 4-1. Effects of amendments on the physico-chemical and biological soil characteristics of three kitchen garden soils PKG, CKG-N, and CKG-L

		pH	**$CaCO_3$** (g kg^{-1} DW)	**EC** (µS cm^{-1})	**P_2O_5** (g kg^{-1} DW)	**Soluble C_{org}** (mg g^{-1} DW)	**Bacterial activity** (nmol fluorescein g^{-1} soil min^{-1})
PKG	U2	6.27 ± 0.03	1.12 ± 0.07	887 ± 143	0.47 ± 0.02	6.16 ± 0.61	1.33 ± 0.09
	C6-20	6.42 ± 0.05*	1.51 ± 0.17	860 ± 38	0.47 ± 0.04	5.72 ± 0.13	1.46 ± 0.09
	C6-40	6.34 ± 0.11	2.03 ± 0.24*	1024 ± 169	0.53 ± 0.04	7.42 ± 0.39	1.60 ± 0.08*
	C6+Z	6.17 ± 0.10	2.11 ± 0.22*	1250 ± 387	0.57 ± 0.05	8.53 ± 1.18	1.32 ± 0.17
	Z	6.18 ± 0.06	2.62 ± 0.34*	1311 ± 184*	0.63 ± 0.05*	9.66 ± 0.24*	1.38 ± 0.20
	HL	6.29 ± 0.05	3.62 ± 0.49*	1589 ± 408*	0.80 ± 0.08*	10.95 ± 0.07*	1.63 ± 0.05*
	CH	6.29 ± 0.08	1.98 ± 0.14*	823 ± 56	0.45 ± 0.02	5.35 ± 0.18	1.43 ± 0.09
CKG-N	U2	7.13 ± 0.03	0.96 ± 0.08	107 ± 28	0.35 ± 0.02	4.76 ± 0.16	1.66 ± 0.13
	C6-20	7.09 ± 0.04	1.89 ± 0.22*	142 ± 15	0.47 ± 0.01*	5.64 ± 0.32*	2.02 ± 0.07
	C6-40	7.11 ± 0.04	2.09 ± 0.09*	151 ± 16	0.47 ± 0.03*	5.68 ± 0.33*	1.88 ± 0.23
	C6+Z	7.02 ± 0.03*	1.66 ± 0.09*	183 ± 13*	0.43 ± 0.03*	5.82 ± 0.46*	2.03 ± 0.08
	Z	7.05 ± 0.02*	1.23 ± 0.11*	155 ± 32	0.36 ± 0.02	5.29 ± 0.28	1.78 ± 0.08
	HL	7.34 ± 0.03*	1.67 ± 0.08*	172 ± 26	0.40 ± 0.03	5.23 ± 0.50	1.73 ± 0.19
	PS	7.18 ± 0.04	1.49 ± 0.09*	152 ± 14	0.37 ± 0.03	5.72 ± 0.55	1.87 ± 0.16
CKG-L	U2	7.77 ± 0.03	72 ± 2	187 ± 32	0.41 ± 0.01	2.88 ± 0.33	1.95 ± 0.10
	C6-40	7.84 ± 0.03*	83 ± 1*	181 ± 30	0.45 ± 0.03	2.97 ± 0.19	1.97 ± 0.10
	C8-40	8.10 ± 0.05*	77 ± 3	175 ± 4	0.48 ± 0.03*	2.64 ± 0.18	1.63 ± 0.05*
	C8+Z	7.89 ± 0.04*	78 ± 3	218 ± 45	0.48 ± 0.03*	2.97 ± 0.15	2.15 ± 0.22
	HL	8.02 ± 0.02*	76 ± 2*	154 ± 2	0.39 ± 0.00*	2.63 ± 0.09	1.74 ± 0.16
	PS	7.88 ± 0.03*	76 ± 0*	225 ± 43	0.41 ± 0.02	2.97 ± 0.21	1.63 ± 0.19
	BM	7.94 ± 0.04*	78 ± 1*	195 ± 53	0.42 ± 0.01	3.10 ± 0.34	1.76 ± 0.16

DW: dry weight; P_2O_5: available phosphorus; EC: electric conductivity; C_{org}: organic carbon; U2: unamended control; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn .* denotes a significant difference between the unamended control soil and the given amended soil ($p < 0.05$). as evaluated by a Student test

Lime is also often used to manage humic and acidic soils because of its ability to raise P availability by increasing pH and decreasing free Al^{3+} and Fe^{3+} ions and fixation to oxides (Mkhonza et al., 2020; USDA, 1995). Sodium hydroxide-extractable soluble organic carbon was also measured for the three soils, with U2 having an average of 6.16 mg g^{-1} of soil. As with EC and P_2O_5, this measure significantly increased to 9.66 and 10.95 mg g^{-1} with only the addition of Z and HL. Notably, at soil pH's between 5.5 and 7.5, organic matter degradation and soluble organic carbon have positive correlations as well as pH, and available P (USDA, 1995; Reichman, 2002; Mkhonza et al., 2020). Overall, Z and HL provoked the most physico-chemical responses; *i.e.,* increasing EC, available P, $CaCO_3$ and soluble C_{org}. Interesting, soil pH rarely changed with the addition of amendments, even those invoking changes in carbonate content. This could be because of the buffering effect of the lettuce rhizosphere.

CKG-N

CKG-N is an alkaline soil with an unamended pH of 7.1 in the presence of lettuce (U2; Table 4-1). The addition of both amendments containing Z, C6+Z and Z, resulted in a slight but statistically significant pH decrease to 7.02 and 7.05, respectively. In their study, Hamidpour et al. (2017) found that the application of an alkaline compost to a less alkaline soil resulted in a decrease in soil pH due to the production of acidic compounds during compost microbial oxidation. Additionally, Z has the ability to buffer pHs because of its affinity for cations (Usman et al., 2005). Because of this phenomenon, Z addition to soil can be associated with cation adsorption and subsequent pH maintenance and decrease. The addition of HL to CKG-N, conversely, resulted in a pH increase to 7.3, due to lime's ability to buffer and increase soil pH. As for PKG, all amendments (*i.e.,* C6-20, C6-40, C6+Z, Z, HL, PS) raised total carbonate content above 1 g kg^{-1}, with C6-20 raising it above 2 g kg^{-1} in comparison with U2 soil which contained 0.96 g kg^{-1} of $CaCO_3$. Since all amendments had higher $CaCO_3$ contents than this soil, their addition can easily explain the increase of this parameter. Despite the low conductivity of U2-CKG-N soil compared to amendments, their inputs were not associated with significant changes in EC on CKG-N soil (except C6+Z). In PKG, which had higher EC than CKG-N, an increase of the salinity had been however observed with Z and HL. Nevertheless, results showed that amendments tended to increase EC from 1.3 to 1.7 times. As conductivity is negatively related to pH in the form of a power function because of other soil characteristics (*e.g.*, soil minerals, porosity, soil texture, soil moisture content, soil temperature), and the amendments invoked little change in soil pH, this is likely a reason for little positive EC change (Provin et al., 2001; USDA, 2011). The addition of all compost mixes (*i.e.*, C6-20, C6-40, C6+Z) to U2-CKG-N soil resulted in an increase in available P from 0.35 g kg^{-1} by at least 0.8 g kg^{-1}. Available P increases during lettuce growth can be linked with the degradation of organic matter and influence of the rhizosphere, in particular the release of chelating root exudates (Reichman, 2002; Rengel, 2002). The addition of the mineral amendment HL, conversely, was associated in a significant decrease of available P to 0.39 g kg^{-1}. P availability can be reduced by OM and carbonates (Sample et al., 1980). Similarly, as with for phosphate content, all compost additions (*i.e.*, C6-20, C6-40, C6+Z) resulted in the significant increase in soluble carbon from 4.76 mg g^{-1} to 5.64, 5.68, and 5.82 mg g^{-1}, respectively. Again, the concept that available P content, organic matter content, and soluble organic carbon have links is supported. Globally, the compost amendments alone and in mix with zeolite had a tendency to increase available P, EC, and soluble C_{org}. The tested mineral amendments alone or in mix (*i.e.,* C6+Z, Z, HL, PS) correspond to the highest ECs measured for this soil. All amendments increase $CaCO_3$ contents since the U2-CKG-N has a low initial carbonate content. Concerning pH, only the lime (HL) significantly increased this value from 7.13 to 7.34.

CKG-L

In the presence of lettuce, the CKG-L soil had a pH of 7.8 (Table 4-1). All amendments resulted in a pH increase in comparison to U2 on the most alkaline, organic matter-rich, and carbonate-rich soil studied in this experiment. Both C8-40 and HL increased the pH to above 8.0. This was not the case with C6-40, the compost applied at the same rate of C8-40 but matured for 2 months fewer. More mature composts show less microbial oxidization, and thus a lower production of the acidic compounds which contribute to OM degradation and pH decreases (Hamidpour et al., 2017). The increase in soil pH with all amendment additions corresponded to a slight increase in total carbonate contents from 72 g kg^{-1} to up to 83 g kg^{-1}. These increases were larger than for the other two soils and statistically significant for C6-40, HL, PS, and BM. Soil carbonate content is linked to soil pH buffering abilities and could thus explain the pH increase (Ng et al., 2022). CKG-L's electrical conductivity of 187 µS cm^{-1} was not significantly altered by amendment. CKG-L could be resistant to amendment-led changes in EC because of its already high OM content (94.2 g kg^{-1}) (Schnackenberg et al., 2022). The addition of the larger quantities of compost of that which was matured for 8 months (*i.e.*, C8-40, C8+Z) to U2-CKG-L soil, resulted in a significant increase in available P from 0.41 to 0.48 g kg^{-1}. Indeed, C8 had a relatively high available P content of 7.10 g kg^{-1}, and high percentage of organic C at 18.4% (*cf* Table 2-4). The addition of HL, by contrast, was associated with a significant decrease in available P to 0.39 g kg^{-1}. The addition of HL raised the pH between 7.5 and 8.5, a range which is known to limit the availability of P for plants (USDA, 1995). Amendment addition to U2 did not however result in significant changes of soluble carbon content. Globally, for this soil, the tested amendments all were associated with an increase in soil pH and at least a slight increase of carbonates.

1.1.2 Biological soil activity

Bacterial activity was measured with a fluorescein diacetate (FDA) hydrolysis assay and displayed in Table 4-1. Fluorescein released is indicative of global enzymatic activity, notably that which is induced by lipases, esterases, and proteases (Green et al., 2006). This measure is not, however, necessarily an indicator of organic matter degradation, which requires the activity of laccases and lignin peroxidases secreted by fungi (Khatami et al., 2019). The more fluorescein released per gram of soil and per minute, the higher the bacterial enzyme activity, which suggests that a given soil can support the biochemical processes which are essential for maintaining soil fertility and soil health (Patle et al., 2018). The bacterial activity for the three planted, unamended and amended kitchen garden soils shows that the addition of C6-40 and HL to PKG-U2 slightly but significantly increased bacterial activity from 1.3 to 1.6 nmol g^{-1} min^{-1}. CKG-N's control had higher bacterial activity than PKG (1.7 *vs* 1.3 nmol g^{-1} min^{-1}), and no amendment resulted in a significant change in bacterial activity. The CKG-L had the highest relative bacterial activity of 2.0 nmol g^{-1} min^{-1}. In this study, soils with higher pH's were associated with the most bacterial activity. These finding was supported by Rousk et al. (2010) who reported that between pHs of 4 and 8, bacteria abundance and diversity increase with pH. For the most alkaline soil (CKG-L), the addition of C8-40 resulted in a significant decrease in bacterial activity (Table 4-1). This could be because the soil pH was increased above 8 with this addition, an alkalinity which is not suitable for neutrophilic bacteria. Globally, there was little effect of the amendments and rates tested on enzymatic activity in each soil.

1.2 Amendment impact on metal(loid) chemical distribution in lettuce-planted soils

As previously described, PKG was mostly contaminated by Cd, Pb, and Zn, whereas in CKG-N, As and Pb were the most concentrated metal(loid)s, and Pb and Zn in CKG-L. The chemical distribution of the four metal(loid)s studied in the three unamended soils (U2) was presented in Figure 4-1. The As present in CKG-N is of geogenous origins, with 79.1% residing in the residual Fraction R of the planted controls. Nevertheless, the 4.2%, 12.2%, and 4.4% residing in the first three fractions (*i.e.*, A, B and D) respectively are not negligible since they represented 1.3, 3.9, and 1.4 mg kg^{-1} As in soil. The Cd present in PKG hails from anthropogenic origins, and is most present in the first two soils fractions of the planted controls. The first fraction contains 36.1%, and the next 46.8%, 7.9%, and 9.3%, respectively. All three soils are contaminated by both Pb and Zn from anthropogenic or geogenous sources. However, Pb and Zn did not follow the same patterns of fractionation for a given soil.

For PKG and CKG-L, for all metal(loid)s, their majority is found in Fraction B. These soils are linked to primarily anthropogenic contamination events. PKG contained the most mobile Pb by both percentage of the pseudo-total pool and total concentration as compared to the other two soils. In this soil, 13.7 mg kg^{-1} (5.2%) was found in Fraction A, as compared to CKG-N for which Fraction A contained 4.5 mg kg^{-1} (1.9%) of its pseudo-total Pb content, and CKG-L for which contained 7.7 mg kg^{-1} (2.0%). This exchangeable fraction was the most easily altered. Zn was more mobile by percentage of the pseudo-total and total concentrations in PKG and CKG-L than in CKG-N, the geogenously polluted soil.

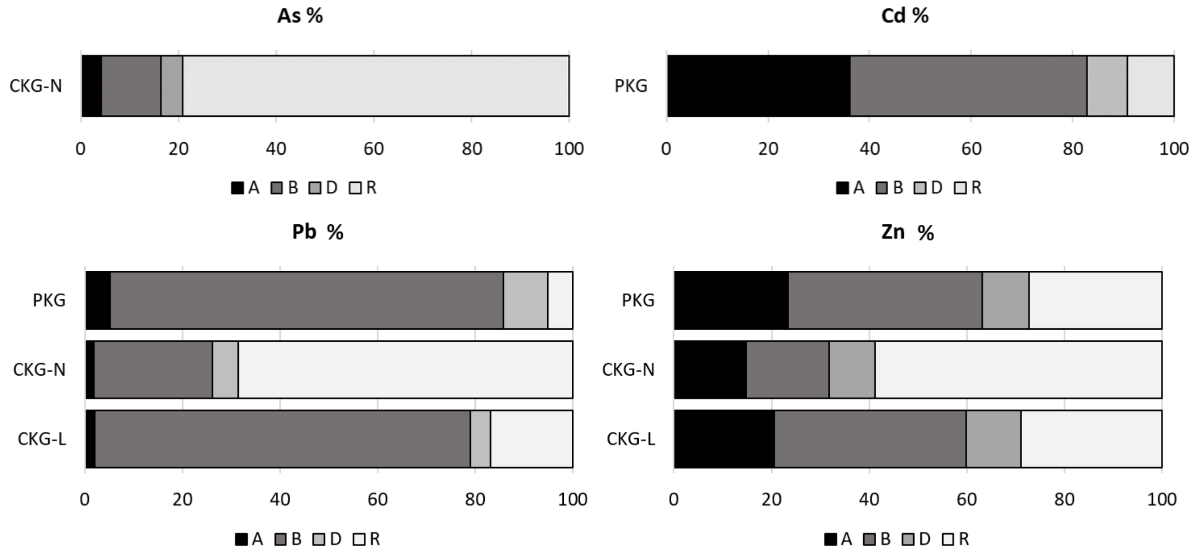


Figure 4-1. **Chemical distribution of metal(loid)s in three planted soils as shown by a sequential extraction of As, Cd, Pb and Zn carried out on all three planted kitchen garden soil controls (U2-PKG, -CKG-N, -CKG-L) and expressed in % of pseudo-total. A: the exchangeable and acid-soluble fraction; B: the reducible fraction; D: the oxidizable fraction; R: the residual fraction**

PKG contained 79 mg kg^{-1} (23.5%) Zn in Fraction A, whereas 11 mg kg^{-1} (14.8%) and 82 mg kg^{-1} (20.5%) were found in the Fraction A's of CKG-N and CKG-L, respectively. For CKG-N, a primarily geogenously contaminated soil, the majority of both metal(loid)s is found in Fraction R. The following paragraphs and tables show the effect of amendments on the fractionation of these metal(loid)s in PKG, CKG-N, and CKG-L.

PKG

Table 4-2 presents the chemical distribution of Cd, Pb and Zn as percentages of their pseudo-total concentrations of 6.3, 264 and 337 mg kg^{-1} respectively, in the control and amended planted PKG soil which was assessed by sequential extractions.

Table 4-2. Effect of amendments on the distribution of Cd, Pb, and Zn present in planted PKG soil assessed by sequential extraction (data expressed in % of pseudo-total concentrations)

		Cd				Pb				Zn			
		A%	B%	D%	R%	A%	B%	D%	R%	A%	B%	D%	R%
PKG	U2	36.1	46.8	7.9	9.3	5.2	80.7	9.1	5.1	23.5	39.8	9.6	27.2
	C6-20	38.2*	45.1	7.6	9.1	4.7	77.7*	11.9*	5.6	23.8	39.2	10.2	26.8
	C6-40	37.0	50.6*	7.2	5.2	4.7	76.4*	13.9*	5.1	24.4	40.7	10.2	24.7
	C6+Z	33.8*	54.5*	6.4*	5.3	3.9*	74.0*	14.0*	8.1	24.0	40.4	9.8	25.8
	Z	27.3*	59.6*	6.3*	6.8	3.6*	72.9*	16.5*	7.1	23.1	39.7	9.3	27.9
	HL	23.3*	65.3*	5.8*	5.6	2.9*	72.3*	17.2*	7.5	23.2	41.8	8.9	26.1
	CH	36.7	48.0	7.4	8.0	5.5*	79.7	9.4	5.4	23.7	39.9	9.7	26.7

U2: unamended planted control; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; Z: chabazite zeolite; HL: hydrated lime; CH crushed horn. A: the exchangeable, acid-soluble, carbonate-linked soil fraction; B: the reducible fraction linked to Fe, Al, and Mn oxides; D: the oxidizable fraction complexed to OM and sulphurs; R: the residual mineralized fraction of metal(loid)s. * denotes a significant difference ($p < 0.05$) between the unamended planted control (U2) and a given condition for a given soil fraction as evaluated by a Fisher test and ANOVA with a post-hoc Tukey test

The results showed that the addition of C6-20 to U2-PKG slightly but significantly increased the percentage of Cd in Fraction A from 36.1% to 38.2%, but decreases in other fractions were not significant. However, by doubling the dose of this amendment (C6-40), a slight increase of Cd was observed in Fraction B (from 46.8 to 50.6%). Similarly, the addition of C6+Z was associated with a significant increase to 54.5% in this fraction, and a decrease from 7.9 to 6.4% in Fraction D. Therefore, all compost amendments tested on this soil were associated with the migration of Cd into either fraction A or B of the soil. The addition of C6+Z, Z, and HL resulted in significantly less Cd in Fraction A, with 33.7, 27.3 and 23.3% respectively (*vs* 36.1% in U2), more Cd present in Fraction B at 54.5%, 59.6% and 65.3% (vs 46.8% in U2), and less Cd present in Fraction D for Z and HL at 6.3% and 5.8%, respectively (vs 7.9% in U2). The addition of C6-20 and C6-40 significantly decreased the Pb in Fraction B by -3 and -4.3% and increased the Pb in Fraction D by 2.8 and 4.8%, respectively. Similarly, C6-40 resulted in a decrease to 76.4% Pb in Fraction B and an increase in Fraction D to 13.9%. C6+Z, Z and HL showed the same effect on the chemical distribution of Pb. A significant decrease of Pb in Fraction A (by 1.3, 1.6, and 2.3% respectively) and Fraction B (by 6.7, 7.8, and 8.4% respectively), and a significant increase of Pb in Fractions D (by 4.9, 7.4, and 8.1 respectively) were observed. There were no significant differences in fractionation for Zn.

CKG-N

Table 4-3 shows the fractionation of Pb, Zn, and As in the control and amended lettuce-planted CKG-N soil, expressed in percentage of their pseudo-total concentrations of 238 mg kg^{-1}, 77 mg kg^{-1}, and 32 mg kg^{-1}, respectively, .

Table 4-3. **Effect of amendments on the distribution of Pb, Zn, and As present in planted CKG-N soil assessed by sequential extraction (data expressed in % of pseudo-total concentrations)**

		Pb				**Zn**				**As**			
		A%	**B%**	**D%**	**R%**	**A%**	**B%**	**D%**	**R%**	**A%**	**B%**	**D%**	**R%**
CKG-N	U2	1.9	24.2	5.4	68.5	14.8	17.0	9.5	58.7	4.2	12.2	4.4	79.1
	C6-20	1.4	25.6	5.4	67.5	16.5	13.8	11.9	57.7	4.3	11.5	4.3	79.9
	C6-40	1.9	23.3	5.1	69.6	14.1	12.8*	11.2	61.9	4.0	10.8	4.5	80.8
	C6+Z	1.9	23.8	4.7	69.6	15.7	12.6*	11.5	60.1	4.1	11.3	4.6	79.9
	Z	2.5	24.7	4.7	68.1	15.3	12.5	9.6	62.6	3.7	10.7*	4.4	81.3
	HL	1.9	23.4	4.2	70.4	14.0	15.0	11.2	59.8	3.4	11.2	3.9	81.5
	PS	2.3	23.9	4.3	69.5	13.9	14.3	11.3	60.4	4.0	12.4	4.4	79.2

U2: unamended planted control; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil. A: the exchangeable, acid-soluble, carbonate-linked soil fraction; B: the reducible fraction linked to Fe, Al, and Mn oxides; D: the oxidizable fraction complexed to OM and sulphurs; R: the residual mineralized fraction of metal(loid)s. * denotes a significant difference ($p < 0.05$) between the unamended planted control and a given condition for a given soil fraction as evaluated by a Fisher test and ANOVA with a post-hoc Tukey test

Due to the geogenous origin of Pb and As in this soil, their majority was found in Fraction R. This finding explained the absence of amendment effect on the chemical distribution of Pb and As, because metal(loid)s in this soil fraction are tightly bound in the soil mineral lattice of soil and extremely immobile. The addition of no amendment (U2) resulted in a significant difference in Pb fractionation for this planted kitchen garden soil as compared to the control soil. Globally, it seemed that Zn might decrease in Fraction B and increase in Fractions D and R in amended soils. However, this trend was significant only for C6-40 and C6+Z.

CKG-L

Table 4-4 shows the fractionation of Pb (present at 384 mg kg^{-1}) and Zn (present at 399 mg kg^{-1}) in the lettuce-planted CKG-L soil, expressed as percentages of their pseudo-total concentrations. The addition of C8-40 to U2 was associated with significantly less Pb found in Fraction D, from 4.2 to 3.1%. This did not correspond to significant differences in other fractions. The addition of HL, PS, and BM was associated with the presence of significantly less Pb in the least available fraction compared with U2 (16.9%), with less than 14% of Pb found. There were no significant changes in other fractions for these conditions, though there was a tendency for more Pb (4.6%) to be found in Fraction A of the PS-amended soil, in comparison to the other conditions. The addition of C6-40 was associated with significantly less (18.9%) Zn being found in Fraction A. This was not associated with other significant changes in fractionation. The addition of C6+Z to U2 was linked to less Zn in Fraction D (10.4 vs 11.2%)

and more (31.2 vs 28.9%) in Fraction R. The addition of HL was also associated with a decrease in Zn in Fraction D (10.3%). Though some of these results are significant, it is important to note that this corresponds to relatively small quantities of metal (1% of Pb and Zn corresponds to 3.8 mg kg^{-1}, and 4.0 mg kg^{-1}, respectively).

Table 4-4. **Effect of amendments on the distribution of Pb and Zn present in planted CKG-L soil assessed by sequential extraction (data expressed in % of pseudo-total concentrations)**

		Pb				Zn			
		A%	B%	D%	R%	A%	B%	D%	R%
CKG-L	U2	2.0	77.0	4.2	16.9	20.5	39.4	11.2	28.9
	C6-40	3.6	75.5	3.6	17.4	18.9*	39.5	13.0	28.6
	C8-40	3.5	75.8	3.1*	17.7	20.1	39.8	10.4	29.7
	C8+Z	2.8	75.9	3.6	17.7	19.8	38.6	10.4*	31.2*
	HL	3.4	79.6	3.5	13.5*	20.6	40.8	10.3*	28.3
	PS	4.6	78.0	4.1	13.4*	21.5	41.1	10.7	26.6
	BM	3.8	79.9	4.4	11.9*	21.9	39.5	11.2	27.4

U2: unamended planted control; C6-40: young compost (6 months) at 40 t ha^{-1}; C8-40: mature compost (8 months) at 40 t ha^{-1}; C8+Z: mixture of mature compost and 10% zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; A: the exchangeable, acid-soluble, carbonate-linked soil fraction; B: the reducible fraction linked to Fe, Al, and Mn oxides; D: the oxidizable fraction complexed to OM and sulphurs; R: the residual mineralized fraction of metal(loid)s. * denotes a significant difference ($p < 0.05$) between the unamended planted control and a given condition for a given soil fraction as evaluated by a Fisher test and ANOVA with a post-hoc Tukey test

1.3 Amendment effect on metal(loid)s in soil pore water (SPW)

For each kitchen garden, the metal(loid)s present in soil pore water (SPW) were sampled using a passive Rhizon® extraction. They represent the pool of labile, soluble metal(loid)s which can be absorbed by plant roots, and can correspond to the soluble part of the metal(loid)s in soil Fraction A, which also shows exchangeable metal(loid)s. Figure 4-2 presents the concentrations of metal(loid)s measured in the SPW of unamended (U2) and amended planted kitchen garden (KG) soils three weeks after seeding and during the lettuce germination period. The results showed that during germination, for the planted control PKG soil, 12 µg L^{-1} of Cd, 43 µg L^{-1} of Pb, and 455 µg L^{-1} of Zn were present in the soil solution. For CKG-N, 6.3 µg L^{-1} of Pb, 65 µg L^{-1} of Zn, and 53 µg L^{-1} of As were present. In CKG-L soil, 5.4 µg L^{-1} of Pb and 63.2 µg L^{-1} of Zn were present in SPW. Notably, PKG showed the highest concentrations of water-labile Pb and Zn in comparison to the other two kitchen garden soils. For each control soil (U2), Zn was the most labile metal(loid). For PKG, no amendment resulted in a significant difference as compared to the control for Cd, Pb, or Zn. The addition of Z, however, tended to make Pb more labile, increasing the mobility of the control soil Pb to 77.7 µg L^{-1} present in SPW. Though the addition of C6+Z and Z resulted in higher labile Zn contents, with Z reaching 725 µg L^{-1} Zn on average, these increases in availability were not significant. For CKG-N, the addition of no amendment resulted in a significant difference in comparison to the control soil for Pb and As. The addition of C6-40, however, significantly decreased labile Zn to 28.5 µg L^{-1}, and all amendments tended to do the same. Regarding CKG-L, no amendment resulted in a significant change in Pb or Zn lability, with results being highly variable among pots. Soil solution collected on the day the lettuce (Annex 4-4) was harvested showed that over time, (i) Cd, Pb, and Zn lability globally decreased, excepting for the amendment HL and (ii) Pb, Zn, and As lability in CKG-N globally decreased, excepting for HL. No trend was evident for CKG-L.

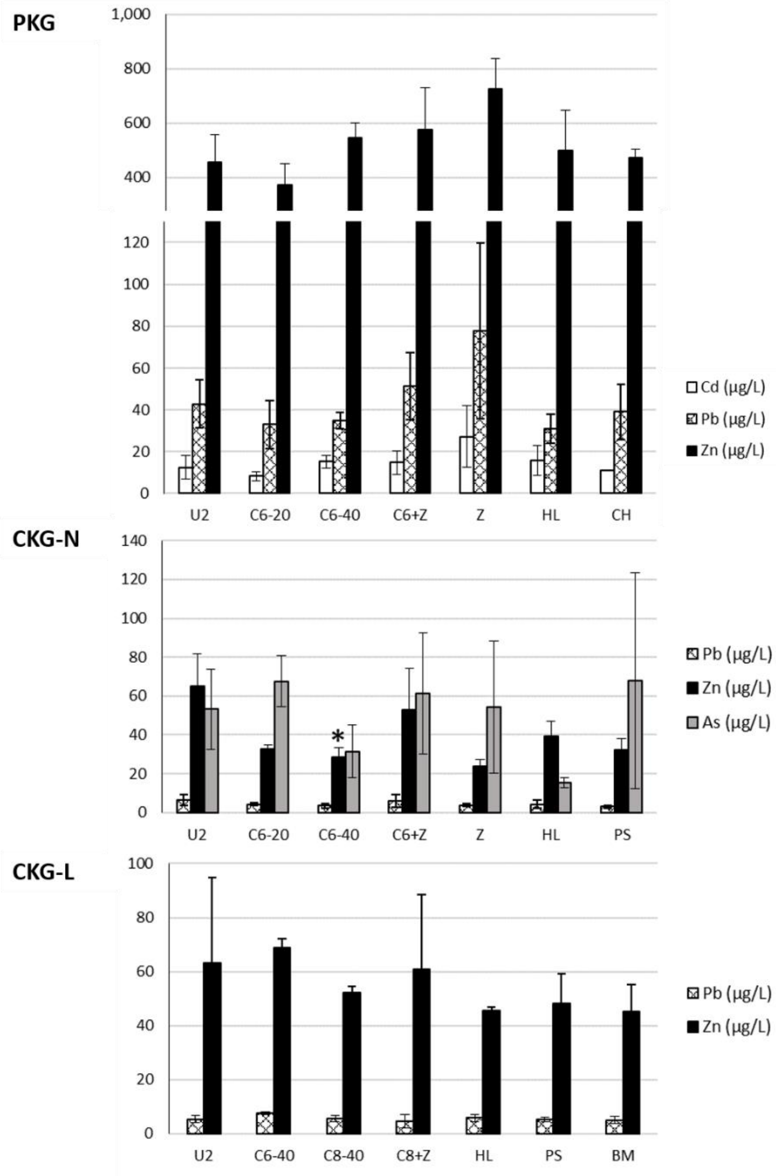


Figure 4-2. Concentrations of metal(loid)s in soil pore water (mean and standard deviation values expressed in µg L^{-1}) in the three kitchen garden soils (PKG, CKG-N, CKG-L) 3 weeks after lettuce seeding. U2: unamended planted control; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. * denotes a significant difference ($p < 0.05$) between the unamended planted control U2 and a given condition for a given soil as evaluated by a Student test

Overall, the PKG soil had the most available Zn. This element has been shown to lead to *Lactuca sativ*a toxicity and germination decreases at soil water high concentrations (*e.g.,* 32,700 µg L^{-1}), as well as cell damage, less root dry matter, and less leaf matter at concentrations of 150 mg to 300 mg Zn kg $^{-1}$ anthropogenically-contaminated soil (Barrameda-Medina et al., 2014; Cinto de Moraes et al., 2022). Whereas 346 µg L^{-1} of Zn were present in the PKG's soil solution, less than one seventh of that was present in CKG-N and CKG-L's soil solutions. Similarly, the sequential extraction on PKG showed that Zn was most available in this soil as compared to the others, with 23.5% being found in Fraction A. This trend in high Zn availability is seemingly linked to a significantly lower rate of biological activity seen on this soil as compared to the other two as well.

1.4 Amendment effect on the environmental availability of metal(loid)s

Figure 4-3 presents the extractability of Cd, Pb, Zn, and/or As in unamended and amended planted PKG, CKG-N, and CKG-L soils, as evaluated by two extractants, NH_4NO_3 and EDTA. Ammonium nitrate is used as an indication mimicking environmental availability of metal(loid)s in soils in the short term (as NH_4NO_3 displaces ions from exchange sites), whereas EDTA-extractable metal(loid)s is considered as a strong extractant able to chelate ions and dissolve amorphous oxyhydroxides linked to OM, and allows the estimation of the potential influence of the amendments in the long term (Gupta & Aten, 1993; Novozamsky et al., 1993; Zhang et al., 2019; Snape et al., 2004; Andrews & Sutherland, 2004).

PKG

For U2, 2%, 0.09%, and 0.23% of pseudo-total Cd, Pb, and Zn, respectively, were extracted by NH_4NO_3 (Figure 4-3). Extractable Cd was significantly decreased by at least 12% with the addition of all compost- and zeolite-containing conditions (*i.e.*, C6-20, C6-40, C6+Z, Z) as well as HL, which was associated with the largest decrease of 55%. The addition of amendments did not result in significant differences in Pb extractability. The addition of composts alone (C6-20, C6-40), as well as HL and CH resulted in weak significant decreases in extractable Zn from 0.23% to under 0.20%. The fact that amendments containing zeolite decreased Cd availability, but did not decrease these of Pb or Zn could be explained by the phenomenon of competitive sorption for zeolite binding sites between these two metals (Usman et al., 2005).

As expected, Cd, Pb, and Zn were more highly extracted from U2 soil by EDTA (47%, 46%, and 34% respectively) than NH_4NO_3 (Figure 4-3). Opposite effects of amendments on Cd and Zn availability were observed with this extractant compared with NH_4NO_3. The addition of C6-20, C6+Z, Z, and HL resulted in a significant increase in extractable Cd from 47% to more than 55%. For Zn, the addition of C6+Z, Z, and HL resulted in the significant increase in extractable Zn to 42%, 50%, and 49% respectively. The addition of C6-20, C6-40 and C6+Z also led to an increase in extractable Pb from 46% to more than 65%.

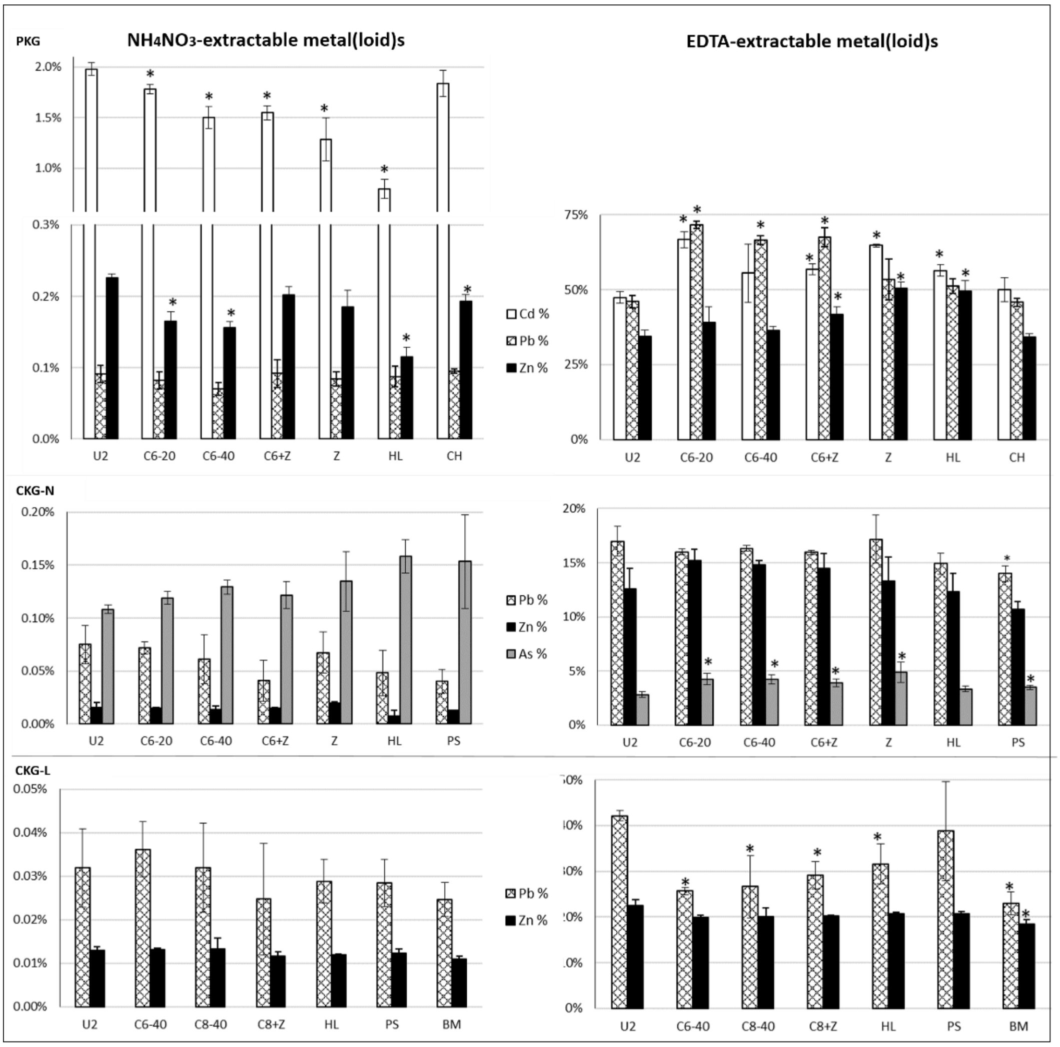


Figure 4-3. **NH$_4$NO$_3$- and EDTA- extractability of Cd Pb, Zn, and As from the three unamended (U2) and amended planted kitchen garden soils (PKG, CKG-N, CKG-L) in the presence of a lettuce model. C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. * denotes a significant difference ($p < 0.05$) between the unamended planted control U2 and a given condition as evaluated by a Fisher test and ANOVA with a post-hoc Tukey test**

CKG-N

The weaker extractant, NH$_4$NO$_3$, removed 0.07% of Pb, 0.015% of Zn, and 0.1% of As in U2 (Figure 4-3). The addition of no amendment resulted in a significant change in extractability. This could be due to the fact that this relatively weak extraction removed relatively little metal(loid) from this soil mainly because these metal(loid)s are mostly present in mineral lattice of soil. Nevertheless, As appeared to be more available than Pb and Zn and seems to become more extractable, with amendment addition unlike Pb.

Concerning EDTA, 17%, 13% and 3% of Pb, Zn, and As, respectively were extracted on the planted control soil (U2; Figure 4-3). Only the addition of PS resulted in a significant decrease in Pb extractability from 17% to 14%. Conversely, As extractability increased from 2.8% to at least 3.5% with the addition of all amendments (C6-20, C6-40, C6+Z, Z, PS) excepting HL, which was associated with the highest soil pH. However, amendment addition had no significant effect of Zn extractability. It is noteworthy that As is less extracted by EDTA than Pb, while the reverse was observed with NH_4NO_3.

CKG-L

Regarding CKG-L, NH_4NO_3 extracted only 0.03% of pseudo-total Pb and 0.01% of pseudo-total Zn (Figure 4-3). No amendment addition significantly changed the extractability of either metal because very little Pb and Zn could be extracted from this soil. EDTA extracted 42% and 22% of the pseudo-total Pb and Zn contents (Figure 4-3). The addition of all amendments (*i.e.*, C6-40, C8-40, C8+Z, HL, BM) except PS resulted in the significant decrease of Pb extractability by at least 20%. BM decreased both Zn and Pb extractability.

Among the three soils, similar percentages of Pb were extracted by NH_4NO_3, with all less than 0.1% of their pseudo-total suggesting the low short-term availability of this element regardless of the environmental context (*i.e.*, contamination origin). PKG was associated with a higher amount of extractable Zn than the other two soils. Regarding EDTA, similar percentages of Pb and Zn were extracted from anthropogenically-contaminated PKG and CKG-L, whereas these percentages were lower from the geogenically-contaminated CKG-N.

1.5 Amendment influence on the plant model

1.5.1 Lettuce germination, biomass, and essential nutrient uptake

Germination monitoring

Germination of the eight lettuce seeds present in each pot of soil was tracked until all possible seeds had germinated and each pot was controlled to have a uniform number of plants (n = 3). Table 4-5 shows the average number of seeds having germinated and present in the three pots destined for each modality and soil 4, 6, 12, 14, 15, 19, 21, and 42 days after seeding. Among soils, it is seen that PKG is associated with the slowest germination. On this soil, the addition of Z and HL were associated with a delay of 6 and 9 days in germination compared with the control soil (U2). On average, between 4 and 6 plants germinated on this soil at this time. For CKG-N, on average 2 plants per pot had germinated after 4 days from seeding (Table 4-5). Two days later, an addition of 2 plants had germinated, and between 2 and 3 more plants germinated over the course of the next 6 days of growth. The maximum amount of lettuce seeds had germinated after 14 days, with between a total of 7 and 8 seeds germinating in each pot. For CKG-L, on day 12, between 5 and 6 plants had germinated in total (Table 4-5). Two days later, after 14 days, the maximum number of seeds (between 6 and 7) had germinated. For these two soils, germination was more uniform among conditions. Overall, lettuce seeds germinated better in both CKG soils than in PKG, suggesting toxicity of unwanted soil properties on the private garden soil (PKG).

Table 4-5. Average number of germinated seeds sowed in pots. They were calculated from the three replicates per condition per soil over the course of a 42 day experiment. Green color gradient indicates the germination progress.

		Days								
		0	**4**	**6**	**12**	**14**	**15**	**19**	**21**	**42**
PKG	**U2**	0	1.0	3.0	4.7	5.7	*3*	*3*	*3*	*3*
	C6-20	0	1.0	3.0	4.0	5.0	*3*	*3*	*3*	*3*
	C6-40	0	1.0	3.0	4.0	5.0	*3*	*3*	*3*	*3*
	C6+Z	0	0.7	2.0	3.0	3.7	3.7	4.3	*3*	*3*
	Z	0	0.0	0.3	1.7	4.0	4.3	5.3	*3*	*3*
	HL	0	0.0	0.0	0.3	0.3	2.7	4.3	5.7	*3*
	CH	0	1.0	2.0	3.3	3.3	4.3	*3*	*3*	*3*
CKG-N	**U2**	0	2.0	4.0	6.7	7.7	*3*	*3*	*3*	*3*
	C6-20	0	2.0	4.0	6.0	7.0	*3*	*3*	*3*	*3*
	C6-40	0	2.0	4.0	6.3	7.3	*3*	*3*	*3*	*3*
	C6+Z	0	2.0	4.0	6.7	7.7	*3*	*3*	*3*	*3*
	Z	0	2.0	4.0	6.0	7.0	*3*	*3*	*3*	*3*
	HL	0	2.0	4.0	6.7	7.7	*3*	*3*	*3*	*3*
	PS	0	2.0	4.0	6.7	7.7	*3*	*3*	*3*	*3*
CKG-L	**U2**	0	2.0	4.0	6.0	7.0	*3*	*3*	*3*	*3*
	C6-40	0	2.0	4.0	6.0	7.0	*3*	*3*	*3*	*3*
	C8-40	0	2.0	4.0	5.3	6.3	*3*	*3*	*3*	*3*
	C8+Z	0	2.0	4.0	6.3	7.3	*3*	*3*	*3*	*3*
	HL	0	2.0	4.0	6.0	7.0	*3*	*3*	*3*	*3*
	PS	0	2.0	4.0	6.0	7.0	*3*	*3*	*3*	*3*
	BM	0	2.0	4.0	6.0	7.0	*3*	*3*	*3*	*3*

Whereas a white box with a 3 denotes that the final lettuce seeds had germinated and the final 3 plants were left to grow in each pot, and increasingly darker shades of green denote more germination. C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn.

Excess nitrogen can cause plant toxicity, Fe deficiency, and delayed maturity (Goyal & Huffayker, 1984). Plant growth and plant growth rate is typically governed by N, P, and S content, and to some extent by B, Fe, and Zn (Mahler, 2004). These elements were not seen to be significantly lower in the PKG soil, however. It is more probably that PKG's high relative salinity (887 µS cm^{-1} in the control) and/or labile and phytoavailable metallic contamination is responsible for the delay in germination. Metallic contamination can affect germination rates, plant growth, and plant health. Literature suggests that anthropogenic Cd can hinder seed germination because of its ability to induce oxidative stress, inhibit water uptake, and decreases sugar mobilization via the suppression of hydrolyzing enzymes such as amylases, proteases, and phosphatases (Huybrechts et al., 2019). This translates to a lower biological activity in Cd-contaminated soils such as PKG. Indeed, Bautista et al. (2013) found that lettuce seed germination was reduced by 64% at a concentration of 2.8 µg L^{-1} Cd, which also reduced the mature plants' fresh weight. On a cellular level, Cd is linked to plant DNA damage at various concentrations. Lettuce root tips can acquire DNA damage after 48 h of exposure to a solution containing 2.8 µg L^{-1} of Cd (Silveira et al., 2017). Tanee et al. (2016) showed that *Ipomoea aquatic* seedlings had DNA damage in the first 21 days of life when planted in soil contaminated by as little as 15 mg kg^{-1} Cd. In *Trifolium repens* roots, as little as 2.5 mg kg^{-1} of Cd present in the soil can alter plant DNA 3 days after being planted (Lanier et al., 2019). These DNA impacts, in turn, can impact cell and plant growth in all of the plant (Silveira et al., 2017; Lanier et al., 2019). This may apply to lettuce plants, as well.

Lettuce biomass

The aerial lettuce biomass collected after these 42 days (6 weeks) of growth is illustrated in Figure 4-4. For the three unamended soils, the average dried biomass followed the pattern PKG (4.81 g) > CKG-N (3.88 g) > CKG-L (2.72 g). Contrary to the observations seen with seed germination, PKG was the soil promoting the best lettuce biomass. This trend in aerial dried biomass (PKG > CKG-N > CKG-L) followed these soils' trends for soluble C_{org}, and inversely followed the pH trend. Higher soil organic carbon promotes soil structure by improving soil aeration, water drainage and retention, and reducing nutrient leaching. Soil organic carbon enhances garden fertility and nutrient holding capacity, and its increase typically results in increased agricultural productivity (Corning et al., 2016). Additionally, PKG's pH is ideal for promoting growth. Maynard & Hochmuth (1997) stated that a pH between 6 and 6.8 is the ideal soil pH for lettuce growth in mineral soils. It can be assumed that lettuce biomass differences among the control soils therefore are partially due to differences in C_{org} levels and pH.

The addition of HL on PKG, however, divided lettuce mass in two as compared with U2 (1.94 *vs* 4.81 g). This amendment was also associated with a significant increase in soil $CaCO_3$, EC, P_2O_5, and C_{org} in comparison to its planted control (U2). Additionally, HL was linked to the least amount of Fe present in lettuce for this soil (Table 4-6), which can delay maturity and decrease plant biomass (Goyal & Huffayker, 1984). Though the addition of lime to soils is typically linked with increased biomass and N content, this amendment does not necessary increase P and K presence in the plant (Brito et al., 2014). Excess nitrogen and incorrect nitrogen ratios can cause plant toxicity, Fe deficiency, and delayed maturity, which can engender decreased plant biomass (Goyal & Huffayker, 1984). This amendment also tended to decrease lettuce biomass in CKG-L whereas the reverse was observed in CKG-N. The addition of C6-40 to U2 increased plant uptake of P and tended to increase uptake of Al and Fe in lettuce grown on PKG (Table 4-6), but had little effect on biomass changed for this soil. This amendment, however, did tend to increase biomass on CKG-L and CKG-N. For these two soils, there was no significant difference in lettuce yield among all conditions, though the addition of Z on CKG-N was related to highly variable lettuce biomass (6.4 ± 6.0 g). Because of high variability in biomass, few significant differences between the control and other conditions were present for each soil.

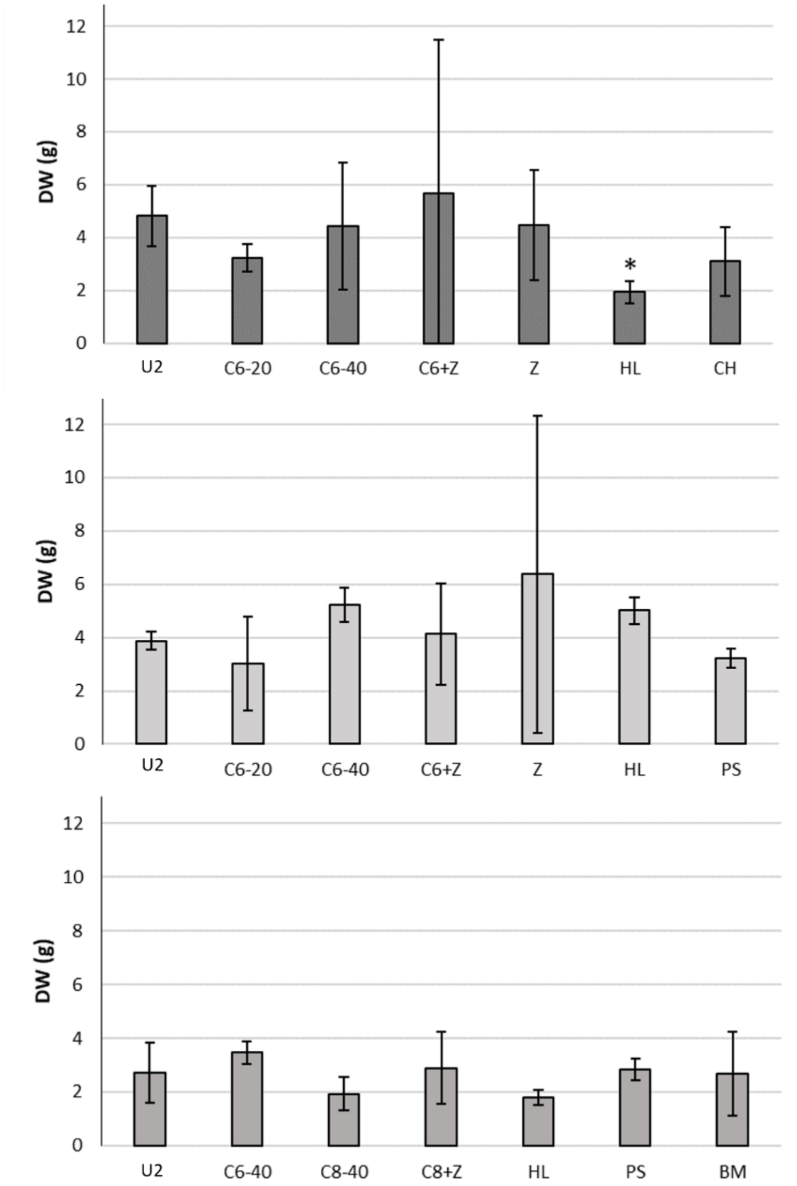


Figure 4-4. **Aerial lettuce biomass dry weight (DW) in g after 6 weeks of growth. U2: unamended planted control; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn.* denotes a significant difference ($p < 0.05$) between the unamended control U and a given condition as evaluated by a Student test.**

Accumulation of essential elements in aerial parts of lettuce

Plants typically require fourteen different essential soil-derived nutrients for growth, including N, P, K, S, Ca, Mg, B, Cl, Cu, Fe, Mn, Mo, Ni, and Zn. The most important macronutrients, which typically exceed 0.1% of a plant's weight, include N, P, K, S, Ca, and Mg. Micronutrients which can help plant growth at small concentrations as low as a few parts per million include B, Cl, Cu, Fe, Mn, Mo, Ni, and Zn (Mahler, 2004). Table 4-6 shows the concentrations of micro- and macro-nutrients found in the lettuce leaves grown on the three soils. The EAT2[1] study by ANSES[2] calculated average nutrient contents in French commercialized vegetables sold in metropolitan areas (ANSES, 2011) and was used for comparison purposes to the current study.

Globally, there were very few significant changes in nutrient contents between the control soil (U2) and a given amended soil. Some differences among soils exist, however. Notably, on PKG, and the addition of OM-rich compost amendments (*e.g.,* C6-20, C6-40, C6+Z) raised the amount of Al in lettuce from undetectable to 0.20 mg kg^{-1} and above, C6-40 and C6+Z had a tendency to increase nutrient contents in lettuce biomass in comparison to the control soil (U2), and HL is associated with less Na in the lettuce. For CKG-N, the addition of the highest rate of compost significantly increased the concentration of Na in lettuce. Though not significant, both C6+Z and HL decreased the amount of Al in lettuce to an undetectable amount, and Z had the tendency to increase Fe content from 4.76 to 6.98 mg kg^{-1}. For CKG-L, the addition of all compost amendments (C6-40, C8-40, C8+Z) significantly increased Na content in the lettuce grown on this soil. These amendments also had the tendency to increase P, Ca, and K On this soil, the doubled dose of compost (C6-40) and C6+Z had the tendency to increase P, Mg, Ca, K, Zn, Al, Cu, and Fe content. Other trends included the addition of C8+Z, which decreased Al concentration to be undetectable, and HL, which raised it 0.71 mg kg^{-1}. Overall, CKG-L is the least rich soil regarding each element studied excepting Al and Fe. Concerning Mg content, PKG soils tend to be slightly above the average of 19 mg kg^{-1}, whereas the addition of HL and CH decreased the average lettuce Mg content to below this concentration. CKG-N soils were all above the average for French vegetables, whereas CKG-L soils were all below. For Ca and K, present in commercialized vegetables at 0.31 mg kg^{-1} and 2.52 mg kg^{-1}, respectively, all soils contained more the national average. For Na, Al, and Cu all soils contained less than the average concentration of 1.20 mg kg^{-1}, 2.51 mg kg^{-1}, and 0.66 mg kg^{-1}. Finally, the PKG lettuces tended to contain more Fe than average, excepting for the HL-amended soil, associated with 3.24 mg kg^{-1} instead of 4.60 mg kg^{-1}. This condition was also associated with the highest EC for this soil, suggesting salts stayed in the soil and were not transferred

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[1] EAT 2 : " Etude de l'alimentation totale française 2 " studying the contamination of commercialized food products available in metropolitan France

[2] ANSES : " Agence nationale de sécurité sanitaire alimentation, environnement, travail" French agency of food, environment, and work sanitary safety

into the plant with this pH-increasing amendment. For CKG-N, U and C6-40 were associated with more Fe than average, whereas the rest of the conditions are associated with less. This was not linked with salinity results. For CKG-L, all soils contained less Fe than the average, and so significant differences in salinity were present.

Table 4-6. Concentration of selected micro- and macro-nutrients in aerial parts of lettuce grown for 6 weeks on unamended (U2) and amended planted PKG, CKG-N, and CKG-L soils

	P	Mg	Ca	K	Na	Al	Cu	Fe
	g kg^{-1} FW					*mg kg^{-1}* FW		
PKG								
U2	0.40	0.20	1.03	5.73	0.29	<LD	0.40	4.60
C6-20	0.49	0.20	1.11	5.82	0.39	0.20	0.44	5.53
C6-40	0.71	0.30	1.60	8.31	0.51	0.22	0.62	5.92
C6+Z	0.67	0.27	1.35	8.51	0.37	0.34	0.63	7.34
Z	0.53	0.21	1.05	6.53	0.31	<LD	0.45	4.95
HL	0.36	0.15	0.66	4.36	0.16	<LD	0.35	3.24
CH	0.40	0.17	0.98	4.69	0.27	<LD	0.37	4.30
CKG-N								
U2	0.56	0.28	1.42	5.84	0.27	0.76	0.48	4.76
C6-20	0.42	0.20	1.00	4.96	0.27	0.49	0.37	4.24
C6-40	0.54	0.25	1.20	6.18	0.34*	0.86	0.43	4.75
C6+Z	0.48	0.25	1.17	5.96	0.33	<LD	0.36	4.00
Z	0.60	0.27	1.22	6.99	0.30	1.53	0.50	6.98
HL	0.42	0.30	1.57	4.85	0.31	<LD	0.37	3.97
PS	0.44	0.24	1.06	4.63	0.28	0.59	0.37	4.92
CKG-L								
U2	0.20	0.11	0.82	4.93	0.08	0.14	0.33	2.37
C6-40	0.34	0.18	1.24	7.83	0.27*	0.34	0.52	3.89
C8-40	0.29	0.13	1.02	6.08	0.29*	0.41	0.37	3.05
C8+Z	0.27	0.15	1.01	6.15	0.24*	<LD	0.33	2.61
HL	0.25	0.15	0.87	4.89	0.11	0.71	0.34	3.33
PS	0.23	0.14	0.90	5.56	0.10	<LD	0.31	2.86
BM	0.25	0.14	0.96	5.82	0.12	0.32	0.34	3.20
Comparative values								
EAT 2[1]	-	0.19	0.31	2.52	1.20	2.51	0.66	4.60

U2: unamended and planted control; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn; FW: fresh weight. * denotes a significant difference between the unamended control and a given condition as evaluated by a student test. <LD means below the limit of detection for ICP-MS. EAT2 refers to the ANSES[2] study's average values in for commercialized vegetables bought in French metropolitan areas.

1.5.2 Accumulation of metal(loid)s in aerial parts of lettuce

The effects of amendments on studied metal(loid) accumulation in lettuce were assessed by analyzing their concentrations in the fresh weight (FW) (Figure 4-6). Concentrations of Cd and Pb in lettuce were then compared with the European Union permissible limits in commercialized foodstuffs. Council Regulation amendments 2021/1317 and 2021/1323 altering EC No 1881/2006 set the maximum permissible levels of metals in certain foods, including Cd and Pb in leafy vegetables such as lettuce, as 0.1 mg kg^{-1} FW and 0.3 mg kg^{-1} FW, respectively. However, there is no EC regulation for maximum permissible levels of As or Zn in foodstuffs or leafy vegetables. The People's Republic of China, however, sets standards for maximum levels of contaminants in foods (GB 2762-2017), including for total As in vegetable products as 500 µg kg^{-1} and Zn as 50 mg kg^{-1}. Metal(loid) concentrations in lettuce growth in this experiment were also compared with the EAT2 average contaminant concentrations in non-contaminated, commercialized foodstuffs found in metropolitan France, including for vegetables excluding potatoes for metal(loid)s (ANSES, 2011). These averages include (i) 11 µg kg^{-1} of As, 0.0122 mg kg^{-1} Cd, 0.008 mg kg^{-1} of Pb, and 2.34 mg kg^{-1} of Zn.

Metal(loid) accumulation in lettuce was also apprehended through bioconcentration factors in order to compare metal(loid) behavior between the different conditions and soils (Table 4-7). Since they correspond to the ratio of metal(loid) accumulation in dry weight of the plant to the pseudo-total metal(loid) content in the soil, these factors allow to break free of changes in lettuce biomass among conditions.

Arsenic

The As in lettuce grown on the unamended and planted CKG-N soil (U2) showed an average concentration of 42 µg kg^{-1} of the metal(loid) (Figure 4-5). No significant difference in accumulation arose with amendment, and there were no strong tendencies in the data. Though the EU does not govern As content in foodstuffs, the People's Republic of China's standards of 500 µg kg^{-1} of As is not reached. According to this standard, the lettuce grown on this soil accumulated less than one tenth of that which is acceptably safe for human consumption. The lettuce, however, contained more than three times the As than the average French vegetable (11 µg kg^{-1}), with the unamended planted control (U2) containing 39 µg kg^{-1} of As. Concerning As' bioconcentration in this plant, however, the planted control soil (U2) showed a ratio of 0.023 for As (Table 4-7). The literature reported BCF as low as 0.09 time up to 13.47 times in the aerial part of lettuce in anthropogenically contaminated soils for this element (Warren et al., 2003; Yanez et al., 2019). Lettuce's lower BCF in our experiment is likely due to its geogenous origin. No amendment additions resulted in significant changes in this BCF.

Cadmium

Results showed that on the unamended and planted PKG control soil (U2), 0.91 mg of Cd per kg of soil was concentrated in the plant (Figure 4-5). The addition of HL resulted in a significant decrease in accumulation to 0.33 mg kg^{-1}, or nearly one third of that of the control. Nevertheless, regardless of the condition, Cd accumulated in the plant exceeded both the EU limit of 0.1 mg kg^{-1} by more than three times, and up to 27 times and the average amount in French vegetables (0.0122 mg kg^{-1}) by 75 times.

Considering the BCF, Cd was the most highly concentrated metal, with a factor of 3.56 for lettuce grown on the control soil PKG (Table 4-7). Lettuce BCF's of Cd typically ranges from 0.03 - 2.39 in contaminated soils, which is typically lowered in the presence of Pb, however Chaney et al., 2009; Ergönül et al., 2019; Qianqian et al., 2022). In this soil, the addition of C6-40, Z, and HL resulted in the significant reduction in the BCF, to 2.45, 1.87, and 0.94, respectively. As its control BCF was above 1.0, this lettuce can be called a hyperaccumulator of Cd (Baker, 1981). Only HL reduced the absorption of Cd below 1.0.

Lead

On average, lettuce grown on the anthropogenically-contaminated PKG contained 0.07 mg kg^{-1} Pb in U2 (Figure 4-5). Most conditions exceeded the national EAT2 average value by at least 7 times, in the case of the control soil U2. The addition of HL significantly reduced the concentration of the metal in lettuce to 0.03 mg kg^{-1}. However, the effective amendment HL was associated with an elevated concentration 3 times the national average. For CKG-N, which presents a geogenous contamination by Pb, lettuce grown on the control soil accumulated on average nearly ten times less this element than in PKG, with 0.009 mg of Pb per kg of soil. No amendment significantly altered this uptake for this metal. For CKG-L, which presents an anthropogenic contamination by Pb, the control lettuces' uptake of 0.036 mg kg^{-1} was weakly but significantly increased to 0.041 mg kg^{-1} by the addition of C8+Z. Similarly, a study on a soil contaminated by Cu, Pb, Zn, and Cd supported that lettuce accumulates more Pb when amended with NPK rich substances (Smical et al., 2008). The Pb uptaken by lettuce on CKG-L represented approximately half of this of the lettuce grown on PKG, though both soils present an anthropogenic contamination. For all conditions of all soils, accumulated Pb was between the average concentrations in French vegetables of 0.008 mg kg^{-1} and the EU limit for permissible Pb in commercialized lettuce of 0.3 mg kg^{-1} of fresh weight. The magnitude of the three soils' BCF correspond to their accumulations of Pb in the plant. On average PKG, CKG-N, and CKG-L have weak control (U2) ratios of 0.004, 0.001, and 0.002 (Table 4-7). A weak significant decrease in the BCF in lettuce to 0.002 occurred with the addition of HL on PKG. This plant has the ability to accumulate 12 times more Pb in its leaves when in a contaminated environment, as compared to a non-contaminated one (Bidar et al., 2020). In contaminated soils, its BCF in lettuce ranges from 0.04 to 1.31 (Lee et al., 2011; Gunes et al., 2014; Liénard et al., 2016; Ergönül et al., 2019).

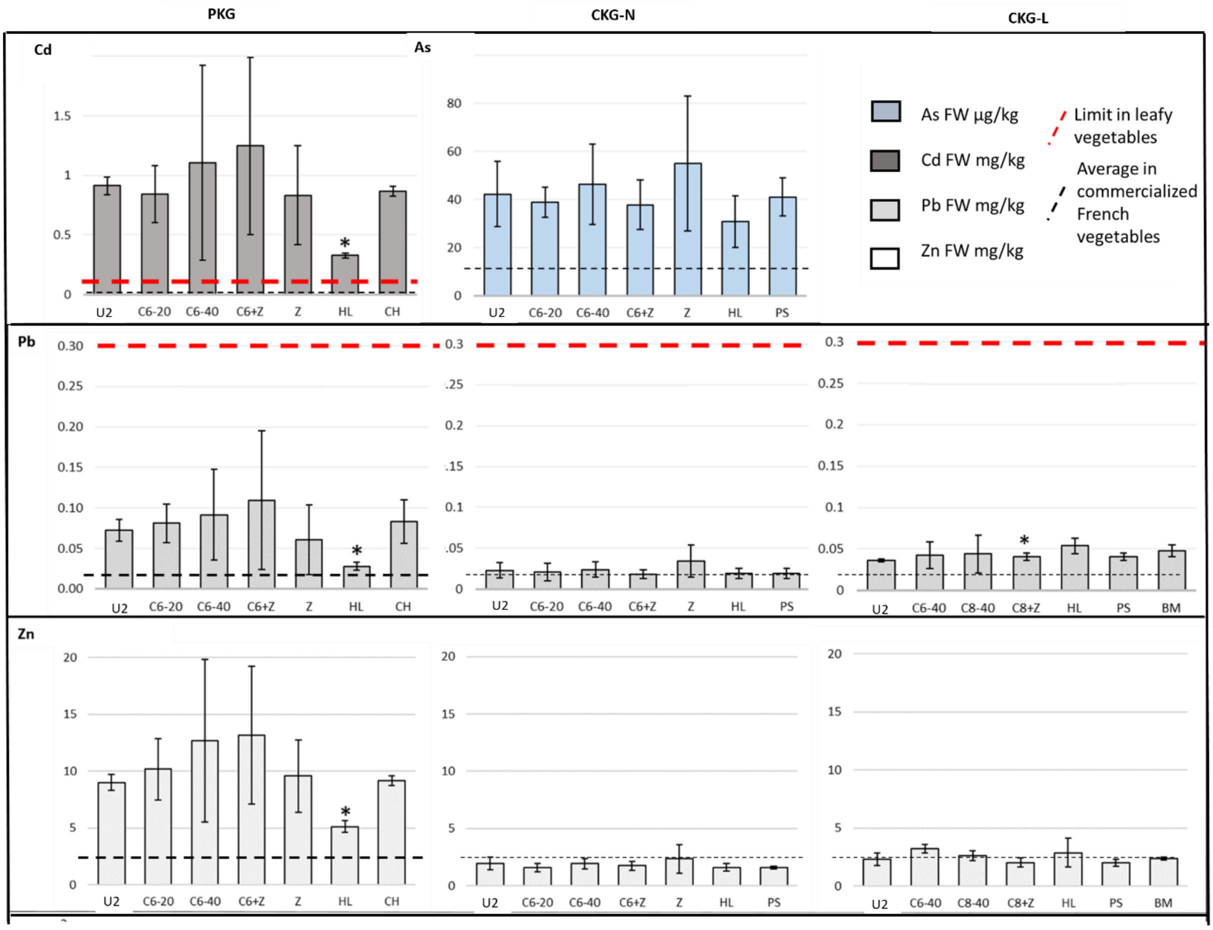


Figure 4-5. **Metal(loid) concentrations (in mg kg^{-1} FW) in lettuce grown on unamended an amended planted PKG, CKG-N, and CKG-L in comparison to EU limits for leafy vegetables and French averages for commercialized vegetables. U2: unamended and planted control; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. * denotes a significant difference ($p < 0.05$) between the control U and a given condition as evaluated by a Student t-test.**

The bioaccumulation of Pb in lettuce can be related back to its fractionation in the soil and its presence in soil pore water. PKG contains 5.2% of its Pb in Fraction A, whereas CKG-N contains 1.9% and CKG-L 2.0%. Thus Pb is more than twice as mobile in PKG soil. In soil pore water, 34 µg L^{-1} of Pb, was present for PKG, whereas 1.9 µg L^{-1} and 3.0 µg L^{-1} were present for CKG-N and CKG-L, respectively, making Pb more than 10 times more available. By percentage, lettuce grown on PKG accumulated four times that of the CKG-N soil and two times that of the CKG-L soil despite comparable pseudo-total concentrations of the element of 264, 238, and 384 mg kg-^{1}, respectively. Studies have shown that Pb bioaccumulation depends upon soil pH, EC, clay content, OM content, CEC, nutrients, and other physical or mechanical soil characteristics (Smical et al., 2008). Specifically, Pb uptake into lettuce tissues are typically not linearly correlated with soil Pb. This concentration has a better correlation with plant tissue Al content (McBride et al., 2014). However, there was no significant relationship between lettuce Pb and Al in

Experiment 2. Though Pb and Al are accumulated similarly in the field at neutral soil pHs, this moreso indicates surface adherence or contamination as a result of aerial deposition or splash from rainfall (Egendorf et al., 2021).

Table 4-7. **Bioconcentration factors (BCF) of As, Cd, Pb, and Zn in lettuce grown on unamended and amended planted PKG, CKG-N, and CKG-L after 6 weeks of growth**

		As	Cd	Pb	Zn
PKG	U2	nd	3.56 ± 0.35	0.004 ± 0.001	0.40 ± 0.05
	C6-20	nd	2.68 ± 0.36	0.004 ± 0.000	0.39 ± 0.02
	C6-40	nd	2.45 ± 0.29*	0.003 ± 0.001	0.34 ± 0.02
	C6+Z	nd	2.81 ± 0.45b	0.004 ± 0.000	0.40 ± 0.04
	Z	nd	1.87 ± 0.22*	0.003 ± 0.000	0.33 ± 0.01
	HL	nd	0.94 ± 0.03*	0.002 ± 0.000*	0.26 ± 0.01*
	CH	nd	3.38 ± 0.53	0.004 ± 0.001	0.38 ± 0.03
CKG-N	U2	0.023 ± 0.003	nd	0.001 ± 0.000	0.330 ± 0.117
	C6-20	0.023 ± 0.002	nd	0.001 ± 0.001	0.338 ± 0.081
	C6-40	0.020 ± 0.004	nd	0.001 ± 0.000	0.328 ± 0.057
	C6+Z	0.028 ± 0.004	nd	0.002 ± 0.000	0.402 ± 0.049
	Z	0.016 ± 0.008	nd	0.001 ± 0.001	0.299 ± 0.111
	HL	0.026 ± 0.003	nd	0.001 ± 0.000	0.330 ± 0.021
	PS	0.024 ± 0.003	nd	0.001 ± 0.000	0.401 ± 0.023
CKG-L	U2	nd	nd	0.002 ± 0.000	0.107 ± 0.040
	C6-40	nd	nd	0.001 ± 0.000	0.084 ± 0.018
	C8-40	nd	nd	0.001 ± 0.000	0.089 ± 0.009
	C6+Z	nd	nd	0.002 ± 0.001	0.066 ± 0.008
	HL	nd	nd	0.002 ± 0.000	0.122 ± 0.013
	PS	nd	nd	0.002 ± 0.000	0.077 ± 0.009
	BM	nd	nd	0.001 ± 0.000	0.077 ± 0.005

U2: unamended and planted control; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn . nd: non determined; * denotes a significant difference ($p < 0.05$) between the control U and a given condition as evaluated by a Fisher test

Zinc

Lettuce grown on PKG contained 9.0 mg kg^{-1} of Zn in the control soil (U2; Figure 4-6). As observed for Pb, the addition of HL significantly lowered the accumulation of this metal by 44%, to 5.1 mg kg^{-1} of fresh weight. No other amendment resulted in a significant change in Zn uptake in comparison to the control soil. However, compared to PKG's control soil and as with Pb, lettuce of both CKG-N and CKG-L accumulated less Zn by fresh weight of plant. CKG-N and CKG-L control lettuces (U2) contained 2.0 and 2.3 mg kg^{-1} of Zn on average respectively. In neither of these two soils, the control lettuces exhibited significant differences with other conditions. Compared to Chinese regulations, the three soils fall below the limit of 50 mg kg^{-1} of Zn in the fresh weight of lettuce. Lettuce grown of the CKG-N and CKG-L soils accumulated more than 5 times less than this limit. Nevertheless, concerning the average values of Zn in French vegetables of 2.34 mg kg^{-1}, this was not the case. All conditions in PKG uptook more Zn than average by up to 4 times. For CKG-N, only the addition of Z (2.36 mg kg^{-1}) was associated with a weak exceeding the average. For CKG-L, all conditions except U, C8+Z, and PS slightly exceeded the average.

Concerning the BCF, lettuce collected in unamended PKG, CKG-N, and CKG-L (U2) showed ratios of 0.40, 0.33, and 0.11 (Table 4-7). As for the concentration in the fresh weight of the plant, lettuce accumulated the most Zn in the PKG soil. Lettuce in CKG-L clearly bioconcentrated the least Zn. On PKG, as with for Cd and Pb, the addition of HL resulted in a significant decrease in the BCF to 0.26 in addition to significantly decrease the accumulation of the metal in the fresh weight of the lettuce (Figure 4-6). Amendments other than C6-20, C6+Z, and HL also had the tendency to reduce the BCF on this soil. For CKG-N and CKG-L, no amendment significantly changed the BCF. However, there was a slight tendency for Z in CKG-N to decrease this ratio to 0.299, this amendment having the lowest BCF for this soil. On CKG-L, no amendment significantly changed the BCF but all amendments, except HL, tended to decrease the ratio slightly, from 0.11 until 0.066. In the literature, Zn BCFs in lettuce grown in contaminated environments tend to range from 0.05 to 21.8 (Chaney et al., 2009; Mtisi & Gwenzi, 2019).

2. Discussion

The aim of this chapter is to assess how the establishment of a crop in combination with amendments influences the environmental availability and phytoavailability of metal(loid)s. This question is discussed from three different perspectives, shown in Figure 4-6.

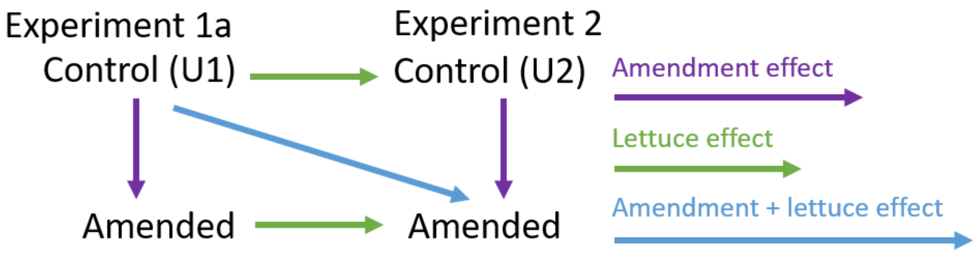


Figure 4-6. Summary of the Chapter 4 flow of results presentation and discussion of results

The effect of amendments on the behavior of metal(loid)s in the three kitchen gardens was previously assessed in the plant-free soil medium in Experiment 1a (*cf* Chapter 3). In the present chapter, their effect in the planted system is presented by comparing an unamended planted soil (U2) with amended planted soils, and discussed in this section (purple arrow). The effect of the lettuce on the metal(loid) behavior (green arrow) was then discussed in unamended and amended soils by comparing results from Experiment 2 to those previously observed in Experiment 1a. Finally, the changes in soil parameters observed between unamended/unplanted soils (U1) and amended/planted ones (U2) allowed for the discussion of the combined effect of amendments and lettuce on metal(loid) behavior in the three kitchen gardens (blue arrow).

2.1 Amendment effects on metal(loid)-contaminated kitchen garden soils in a planted system

Principal component analyses (PCA) were performed on the physico-chemical, biological, and metal(loid) availability for each separate planted soil. Amendments were added as supplementary variables. The PCA multivariate test in Figure 4-7 shows linear combinations of the original data collected on the planted PKG, CKG-N, and CKG-L soils. This data is explained on multiple axes, or components, after interpretation with eigenvalues and variance information. This analysis shows which parameters and amendments are responsible for data variability in a large data set. In summary, this analysis considers the strength of multiple variables and indicates their links together. Pearson correlation matrixes were also carried out for each soil, in order to identify significant linear correlations and relationships between soil physico-chemical parameters, biological parameters, and metal availability results for a given soil (Annexes 4-5, 4-8, and 4-9). This indicates data significance, but cannot identify links or correlations to amendments.

PKG

It is seen that this soil has the best relationship between its data, with the weights accounting for physico-chemical parameters, biological parameters, and metal availability results explaining 55.4% of data variability. As seen in Figure 4-7, the first axis (41.0%) was characterized by soluble C_{org}, $CaCO_3$, P_2O_5, EC, Cd in SPW, Zn in SPW, Zn extracted by EDTA on its right, positive side. The squared cosines of the centroids of the conditions Z and HL lay on this side of the axis as well. On the left negative side, this axis was characterized by Cd and Zn extracted by NH_4NO_3 and all soil fractions of Cd and Pb. The squared cosines of the centroids of the conditions C6-20, CH, and the control U appear on this side of the axis. Notably, HL lays in close proximity to the positive side of the first axis, suggesting its link to the aforementioned parameters. Particularly, it is seen that the variables P_2O_5 and $CaCO_3$ lay close to each other, as well as with the addition of HL. The addition of all amendments significantly increased $CaCO_3$ content from 1.12 g kg^{-1}, with HL increasing this value significantly more to 3.62 g kg^{-1} due to its buffering capacity. Moreover, the addition of HL resulted in a significant increase in available P from 0.47 to 0.80 g kg^{-1}. Lime has also been cited as an effective amendment on acidic soils because of its ability to raise P (Mkhonza et al., 2020; USDA, 1995), further suggesting a relationship. The second axis (14.3%) was characterized by global bacterial activity and the first three soil fractions of Zn on its positive right side, and Pb is SPW and the residual (F4) fraction of Zn on its negative left side. The compost condition C6-40 lied closely to this axis on the negative side. Specifically, C6-40 was in close proximity to the Zn found in soil Fraction A on the PCA, suggesting an influence.

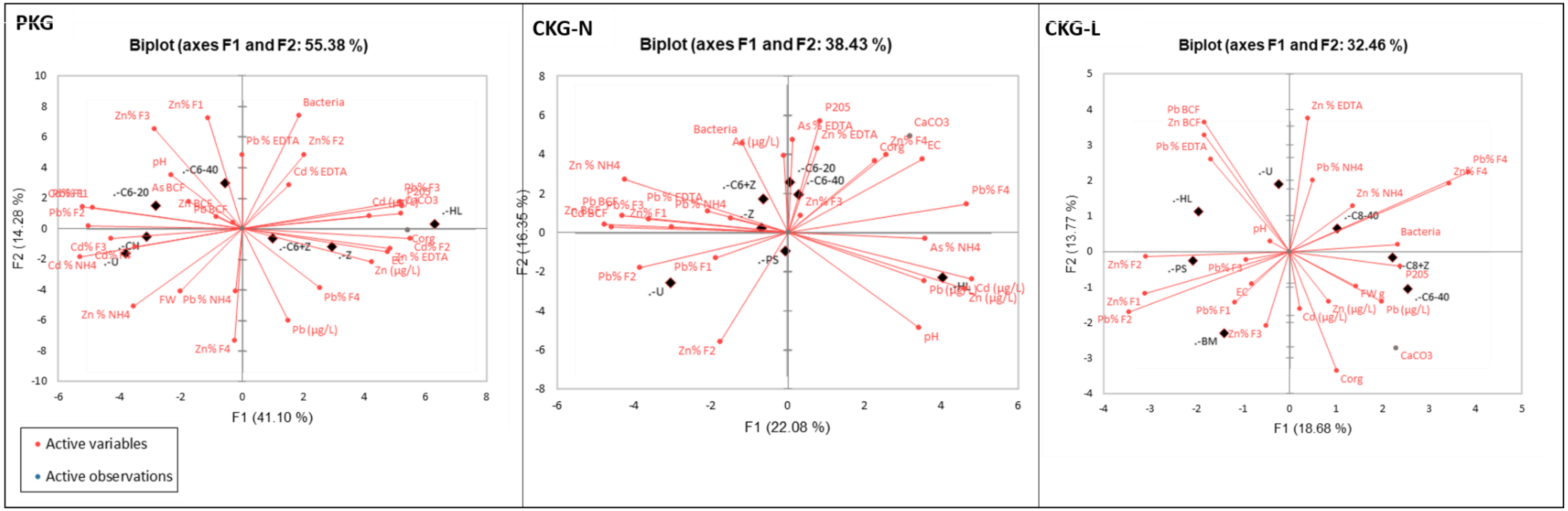


Figure 4-7. Principal component analysis of physico-chemical, biological, and metal(loid) availability analyses and their relationships with conditions tested on planted PKG, CKG-N, and CKG-L. Bacteria: global enzymatic activity analysis; C_{org}: sum of NaOH-soluble carbon; F1-F4: soil fractions; NH_4: NH_4NO_3 extraction; (µg/L): soil pore water reading; U: unamended control; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn.

➢ Cd availability negatively correlates with C_{org}, available P, and $CaCO_3$

Considering correlations between soils parameters and metal(loid) availabilities themselves, the PCA shows that the most available soil fraction of Cd negatively corresponded with changes in C_{org} (Pearson coefficient = -0.92), available P (Pearson coefficient = -0.89), and $CaCO_3$ (Pearson coefficient = -0.84) (Annex 4-5). This suggests that amendments that increased these parameters decreased exchangeable Cd. Indeed, the NH_4NO_3 extraction that can reveal additional information about exchangeable, quickly environmentally available Cd is negatively and significantly correlated with the same three parameters (Pearson coefficients = -0.86 through -0.89) (Annex 4-5). The bioconcentration of Cd in lettuce (Cd BCF), which has been shown to correspond to these two fractions, also had negative relationships with these three parameters. The PCA also shows that available soil P, $CaCO_3$, and C_{org} positively correlated with each other for PKG with Pearson coefficients from 0.83 to 0.90 (Figure 4-7). The extractions and ways of estimating environmental availability correlated, with the BCF and NH_4NO_3 extraction having a Pearson coefficient of 0.92, and the BCF having a correlation of 0.77 with Cd found in the exchangeable soil fraction. The extraction and soil fraction A correlated as well (Pearson coefficient = 0.85) (Annex 4-5). The second soil fraction, however, positively corresponded with C_{org} (Pearson coefficient = 0.96), available P (Pearson coefficient = 0.92) and $CaCO_3$ (Pearson coefficient = 0.92), and negatively with the BCF of Cd and its extractability (Annex 4-5). This suggests the increase of these parameters can increase reducible Cd. As established, both Z ($\cos^2 = 0.54$) and HL ($\cos^2 = 0.91$) lay on the same side of the same axis as the correlated variables C_{org}, $CaCO_3$, available P, and EC, suggesting their positive relationship with these parameters. Notably, Corg, available P, and $CaCO_3$ are anticorrelated with NH_4NO_3-extractable Cd (Pearson coefficients = -0.86 through -0.90). Z and HL lay on the opposite side of the first axis as Cd extracted by NH_4NO_3 (and all soil fractions of Cd and Pb), so these amendments were thus linked to negative relationship with this Cd extraction. Indeed, Z and HL were linked to decreases in Cd mobility and availability in soil Fraction A and NH_4NO_3-extractions, and increases in EDTA-extractions (Annex 4-6), a parameter which lies on the same side of the axis as these variables.

➢ Cd availability linked with compost doses

As previously presented, the addition of C6-20 to U2-PGK soil resulted in i) a significant increase in EDTA extractable Cd from 47% to more than 55%, ii) a significant increase in EDTA extractable Pb from 46% to more than 71%, and a decrease in soil F2 (Annex 4-7), and iii) a significant decrease in NH_4NO_3-extractable Cd. The doubled dose C6-40, however, significantly lowered the Cd BCF in lettuce, NH_4NO_3-extractable Cd, and did not increase Cd-EDTA extractability. This compost condition was the only one to fall on the same PCA axis as global bacterial activity, suggesting the increase in bacterial activity brought by the higher dose of compost might have mitigated its long-term risk as evaluated by EDTA.

This compost's success in lowering Cd uptake could be linked to its addition of P and K relative to the control soil (U2). Growth media rich in plant essential nutrients cause trace elements to compete with those nutrients to be absorbed (Gothberg et al., 2004). This suggests that this Cd uptake can be disfavored in some conditions. Compost amendments were able to significantly decrease NH_4NO_3-extractable Cd, but in some cases favored significant increases in EDTA-extractable Cd (*i.e.,* C6-20 and C6+Z).

CKG-N

As for PKG, it was seen that physico-chemical and biological parameters as well as metal availability results explained 38.4% of data variability on CKG-N. As seen in Figure 4-8, the first axis (22.1%) was characterized by $CaCO_3$, EC, and As extracted by NH_4NO_3 on its right, positive side. The left negative side of the first axis was characterized by the BCF of Pb and Zn and Pb in soil fractions B-R, as well as Zn in soil fractions A and B. The squared cosine of the centroid of the control condition U2 appears on this side of the axis. The positive side of the second axis characterized by pH, and HL lies upon its axis in this direction. The negative side of the second axis (16.4%) is characterized by available P, C_{org}, and EDTA-extractable As and Zn, and the compost amendments tested C6-20 and C6+Z.

- *Relationship between HL, pH, and As*

The link between HL and pH is clear on the PCA, with both lying on the same side of the same axis, thus exhibiting a link. Indeed, the addition of HL to the CKG-N soil significantly increased pH, and was the only amendments to not significantly increase EDTA-extractable As. This makes HL's influence on pH, and EDTA-extractable As's negative relationship with this parameter for this soil, clear. Typically, pH increases mobilize As in soils (Lienard et al., 2016; Cerqueira et al., 2022; Jiang et al., 2023). However, despite increasing pH, HL added in the presence of ferrous sulfate can decrease As mobility (Warren et al., 2003; Yang et al., 2022). Ferrous sulfate is likely to be present in this soil because of its geogenous origins, which could explain HL's efficacy.

- *Relationships between compost amendments, available P, and EDTA-extractable As*

The addition of all composts significantly increased soil available P and soluble carbon, with C6+Z evoking the biggest shift from 4.76 mg g^{-1} to 5.82 mg g^{-1} of the former (Table 4-1). All compost amendments (C6-20, C6-40, C6+Z) significantly increased EDTA-extractable As as well. This was likely linked with the increase in available P, closely grouped with EDTA-extractable As and Zn on the PCA. Organic-matter rich and siliceous amendments such as zeolite are known in the literature to increase available P, because of their capacity to promote ion exchange (Rodriguez-Salgado et al., 2016). Additionally, C_{org} and available P contents typically positively correlate in soils (USDA, 1995; Reichman, 2002; Rengel, 2002; Mkhonza et al., 2020). Indeed, in this study, available P and C_{org} have a Pearson coefficient of 0.90 (Annex 4-8). The relationship between As mobility and available P are variable, with phosphate often mobilizing As because of its competition for sorption sites due to its chemical similarity. Studies more often cite the immobilizing effect of the addition of P-rich amendments on bioaccessibility (Cai et al., 2017; Li et al., 2017).

CKG-L

On CKG-L, the variables tested explained 32.5% of the data variability. On the first axis (18.9%) lay the residual fraction of Zn in the positive direction, along with the centroids of the compost amendments (C6-40, C8-40, C8+Z). In the negative direction lay the second and last soil fractions of Pb as well as the first two soil fractions of Zn. The positive side of the second axis (13.8%) was described by EDTA-extractable Pb and Zn, and their BCFs, whereas the negative side was described by $CaCO_3$ and C_{org}, with the centroid of BM also on this axis.

➢ *Weak relationships in a heterogeneously contaminated soil*

As previously observed in the chapter, the addition of the larger quantities of 8-month-old compost (C8-40, C8+Z at D2) resulted in a significant increase in available P and all amendments resulted in a significant pH increase (Table 4-1). C6-40 and other composts were also associated with the highest $CaCO_3$ contents of all amendments, and a significant increase in EDTA-extractable Pb (Figure 4-4). Despite their effects, the CKG-L soil had very few significant correlations among extractions and amendments. This Pb soil concentration was, however, positively correlated with both the BCF of Pb and Zn in lettuce, as with CKG-N (Pearson coefficients = 0.74 and 0.65 respectively) (Annex 4-9). Notably, this soil also had a lack of correlations among soil characteristics studied and metal(loid) extractability or uptake into the plant.

2.2 Effects of the plant model

This section discusses the results and trends in lettuce germination, biomass, essential element content, and contamination from Experiment 2. The effect of the lettuce on metal(loid) behavior (green arrow) assessed by comparing results of the Experiment 2 with those of Experiment 1a is also assessed. This comparison was made in order to show trends that arise when the soils (unamended and amended) were influenced by a lettuce plant system.

2.2.1 Changes in unamended soils with the addition of a plant system

Table 4-8 resumes data already presented in Chapter 3 and in the first part of this chapter in order to compare the physico-chemical parameters and the extractability of metal(loid)s obtained in unamended soils of Experiment 2 (U2) to those from the Experiment 1a in plant-free conditions (U1).

The presence of lettuce significantly increased pH value in the slightly acidic PKG soil (U1) from 6.0 to 6.3. This is due to the well-known phenomenon that soil pH increases with the release of root exudates (McLaughlin et al., 1997). The other two alkaline soils (CKG-N, CKG-L) had soil pHs which did not significantly change with the addition of a plant system. The absence of change with lettuce could be explained by the alkaline pH and the high content of $CaCO_3$ of these soils. CKG-N and CKG-L carbonate contents stayed relatively stable after the lettuce growth whereas they were significantly decreased by two in PKG. The solubility of $CaCO_3$ can decrease as temperature rises, which could contribute to explaining this shift between the first experiment, performed at stable cool temperatures, and the greenhouse experiment (Coto et al., 2012). Before planting (U1), PKG, CKG-N, and CKG-L were associated with EC of approximately 1,769, 96, and 231 µS cm^{-1}, respectively. The high salinity of PKG could be at the origin of the toxicity observed during the germination. For PKG, this average halved with the addition of lettuce. For CKG-N and CKG-L, soil EC stayed approximately the same after lettuce growth.

Soil EC, which corresponds directly with soil salinity, is negatively affected by soil pH and soil moisture (Aizat et al., 2014; Pathak and Rao, 1998). Increasingly alkaline soils have smaller relative amounts of soluble salt, which explains the relatively lower EC's of CKG-N and CKG-L (Provin et al., 2001). The decreasing effect of the lettuce on EC in PKG could be explained by the natural leaching of soil nutrients and salts in high-EC soils with watering when there is ample irrigation water (Schoups et al., 2005; Kaman et al., 2006; Geerts et al., 2008). Nevertheless, Nagaz & Mechlia (2013) also found that when lettuce was watered as needed, soil salinity and conductivity can even decrease over time. Another hypothesis to explain this decrease could be the nutrient absorption by lettuce. The highest biomass was measured indeed for lettuce from PKG suggesting a better supply of nutrients. However, no difference in the macro- and micro-element concentrations was noted in lettuce between soils. The availability of salts, mainly influenced by soil pH, could be also different between soils, and explain why such decrease with lettuce was not observed in CKG-N and CKG-L soils. This hypothesis was reinforced by the fact that PKG soil showed also higher available P content than the two others.

Without a plant system, available P contents were indeed 0.69 g kg^{-1} for PKG whereas they were of 0.31 g kg^{-1}, and 0.45 g kg^{-1} for CKG-N, and CKG-L, respectively (U1). In the presence of lettuce (U2), this average fell to 0.47 g kg^{-1} for PKG, and stayed nearly the same for CKG-N and CKG-L at 0.35 g kg^{-1} and 0.41 g kg^{-1} respectively. P availability tends to flourish on soils with pHs between 6.0 and 7.5 like PKG and CKG-N (USDA, 1995). In these acidic and neutral soils, phosphorous could be sorbed by Fe and Al limiting therefore its availability. This phenomenon should occur below 5.5 and between 7.5 and 8.5 (Lear et al., 2004) or below 7.0 (Barrow, 2017). The former pH conditions reduce soil microbial activity and thus decrease OM mineralization rates (Lear et al., 2004), and the latter case (like with

CKG-L) limits phosphate availability to plants due to P fixation in secondary minerals by Ca (USDA, 1995).

Table 4-8. **Comparison of the unplanted (U1) and planted (U2) unamended soils (PKG, CKG-N and CKG-L) in terms of physico-chemical parameters and extractability of metal(loid)s**

		PKG		CKG-N		CKG-L	
		U1	**U2**	**U1**	**U2**	**U1**	**U2**
	pH	6.02	6.27*	7.12	7.13	7.86	7.77
	CaCO$_3$ (g kg^{-1} DW)	2.27	1.12*	1.10	0.96	69	72
	EC (µS cm^{-1})	1,769	887*	96	107	231	187
	P$_2$O$_5$ (g kg^{-1} DW)	0.66	0.47*	0.34	0.35	0.42	0.41
NH$_4$NO$_3$ extractable	**Cd**	1.8%	2%	-	-	-	-
	Pb	0.35%	0.09%*	0.47%	0.07%*	0.04%	0.03%
	Zn	1.3%	0.23%*	0.68%	0.02%*	0.009%	0.01%
	As	-	-	0.23%	0.1%*	-	-
EDTA extractable	**Cd**	70%	47%*	-	-	-	-
	Pb	66%	46%*	14%	17%*	48%	42%
	Zn	50%	34%*	17%	13%*	14%	22%*
	As	-	-	7.4%	3%*	-	-

U1: Unplanted and unamended control from experimentation 1a; U2: Planted and unamended control planted with lettuce from experimentation 2. .* denotes a significant difference with the addition of lettuce for a given parameter and soil as evaluated by a Student test. Red signifies a significant increase in extractability and green a significant decrease after planting.

For PKG, the introduction of lettuce resulted in a significant increase in NH$_4$NO$_3$-extractable Pb, whereas NH$_4$NO$_3$-extractable Zn, and EDTA-extractable Cd, Pb, and Zn decreased (Table 4-9). For CKG-N, NH$_4$NO$_3$-extractable and EDTA extractable Pb significantly increased, and NH$_4$NO$_3$-extractable and EDTA-extractable Zn and As significantly decreased with the addition of lettuce. For CKG-L, the addition of a plant model resulted in few significant differences, with only EDTA-extractable Zn decreasing in presence of lettuce. The difference of extractability for Pb and Zn between soils was mainly due to pH as hypothesize for nutrients including available P.

2.2.2. Changes in amendment responses with the addition of a plant system

Table 4-9 shows the evolution of the amendment effects between before and after lettuce growth on common physico-chemical parameters and simple extraction results. On PKG, in the unplanted soil, amending had no effect on the short-term environmental availability of metals as analyzed by NH_4NO_3 whereas in the presence of lettuce, amending the soils (with the same doses of the same amendments) globally decreased the environmental availability of Cd and Zn in comparison to the control. However, before planting, there were fewer negative long-term effects associated with amending. In Experiment 1a, the addition of C6-20, C6-40, and CH resulted in an increase in EDTA-extractable Cd in comparison to the control corresponding to an increase in $CaCO_3$. After planting, C6-20 and C6-40 also increased EDTA-extractable Pb. Conversely, CH became less problematic in the presence of lettuce as the only amendment not to significantly increase the long-term availability of a metal(loid). For CKG-N, before planting, the short-term environmental availability of metal(loid)s was varied depending on the added amendment.

Notably, whereas the composts added alone increased As availability, C6+Z and PS decreased it. In the long-term, an EDTA extraction determined that no amendments increased metal(loid) availability in plant-free system, and PS would stay an effective amendment for As in the long-term. However, after planting, as evaluated by EDTA, all amendments except HL posed a potential problem in increasing availability As. CKG-N is the only soil for which differences in extractability correspond to differences in pH, $CaCO_3$, EC, and/or available P. Whereas there are mixed responses of As associated with changes in pH, it was seen that (i) mobilized Zn mobility as analyzed by NH_4NO_3 and pH had an inverse relationship, (ii) As mobility as analyzed by EDTA had a direct relationship with pH, (iii) mobilized As analyzed by EDTA corresponds to increased available P, and iv) immobilized As corresponded to increased EC. For CKG-L, before planting, both the environmental availability of metal(loid)s as evaluated by NH_4NO_3 and EDTA were not changed with amendment. After planting, the trend that no amendment changed short-term environmental metal(loid) availability stayed a trend.

Table 4-9. **Changes in physico-chemical parameters and metal(loid) extractability (based on NH_4NO_3- and EDTA-extractants) in comparison to unamended control soils in the unplanted Experiment 1a (U1) and planted Experiment 2 (U2)**

		Unplanted				Planted				Unplanted		Planted	
Soil	*Amendment*	pH	$CaCO_3$	EC	P_2O_5	pH	$CaCO_3$	EC	P_2O_5	NH_4NO_3	EDTA	NH_4NO_3	EDTA
PKG	C6-20					↑	↑			-	↑ Cd	↓ Cd ↓ Zn	↑ Cd ↑ Pb
	C6-40						↑			-	↑ Cd	↓ Cd ↓ Zn	↑ Pb
	C6+Z						↑			-	-	↓ Cd	↑ Cd ↑ Pb ↑ Zn
	Z		↓				↑	↑	↑	-	-	↓ Cd	↑ Cd ↑ Zn
	HL						↑	↑	↑	-	-	↓ Cd ↓ Zn	↑ Cd ↑ Zn
	CH						↑			-	↑ Cd	↓ Zn	-
CKG-N	C6-20	↑					↑		↑	↑ As	-	-	↑ As
	C6-40	↑					↑		↑	↑ As	-	-	↑ As
	C6+Z	↑				↓	↑	↑	↑	↓ As	-	-	↑ As
	Z	↑				↓	↑			-	-	-	↑ As
	PS	↓		↑			↑			↓As ↑ Zn	↓ As	-	↑ As
	HL	↑			↑		↑			↓ Zn	↑ As	-	-
CKG-L	C6-40	↓			↑	↑	↑			-	-	-	↓ Pb
	C8-40	↓	↓	↑	↑	↑			↑	-	-	-	↓ Pb
	C8+Z		↑		↑	↑			↑	-	-	-	↓ Pb
	PS					↑	↑			-	-	-	-
	HL				↑	↑			↓	-	-	-	↓ Pb
	BM				↑	↑	↑			-	-	-	↓ Pb ↓ Zn

C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. Whereas an (↑) and red denotes a significant increase, (↓) and green denotes a significant decrease ($p < 0.05$), orange represents a mix of both, and (-) represents no significant results with the addition of amendment as evaluated by a Student test

3. Combined effects of amendments- and plant- on metal(loid) behavior in three kitchen garden soils

This section discusses the combined effect of amendments and lettuce on metal(oid) behavior in the three soils assessed by comparing the Experiment 1a control (U1) with the Experiment 2 amended values, as visualized in Table 4-10. Ratios between the control and amendments were calculated and shown in Annex 4-10, whereas a ratio under 1 signifies that extractability decreased with the effect of the amendment and plant and is represented by a down arrow.

The combined effect of amending and planting had an overall positive effect on metal(loid) extractability. Thus, for PKG, no amendment and plant mix resulted in an increase in Cd, Pb, or Zn extractability. All amendments were at least associated with a decrease in the extractability of all tested metals. In fact, all tested amendments significantly decreased NH_4NO_3-extractable Pb and Zn, and EDTA-extractable Cd and Zn, between the onset of Experiment 1a and the end of Experiment 2. C6-40, Z, and HL also significantly decreased NH_4NO_3-extractable Cd and EDTA-extractable Pb and CH significantly reduced EDTA-extractable Pb. By comparison, just the addition of a plant system (U2) tended to increase NH_4NO_3 Cd, significantly increased extractable Pb, and significantly decreased extractable Zn. The addition of lettuce also significantly decreased EDTA-extractable Cd, Pb, and Zn in U2. Thus, the benefit of adding amendments to reduce environmentally available Cd and Pb in the short-term is clear. However, composts are not significantly effective over time as analyzed by the EDTA, long-term extraction, likely due to OM degradation.

For CKG-N, similarly, all amendments were associated with a decrease of all the metal(loid)s measured by both extractions. This decrease was significant regarding NH_4NO_3-extractable Pb and Zn, and for all amendments except HL, for As. All amendments were effective to significantly reduce EDTA-extractable As and Zn, and all amendments except Z reduced Pb. The addition of lettuce to the unamended control soil resulted, however, in a significant increase in NH_4NO_3 and EDTA-extractable Pb, and a significant decrease in extractable Zn and As. Thus the interest of adding amendments in the presence of a plant system to decrease extractable Pb is evident.

For CKG-L, different tendencies emerged. Despite no significant effect was observed for metal extractability after amending and planting, amendments tended to increase NH_4NO_3-extractable and EDTA extractable Zn. This was significant for all amendments on EDTA. Nevertheless, amending and planting tended to decrease Pb extractability, with this decrease being significant for EDTA when C6-40, C8+Z, and BM were added. Concerning just the addition of the plant system, few trends were visible, but EDTA-extractable Zn significantly increased in the control. Thus the addition of amendments did not change this trend, but the addition of C6-40, C8+Z, and BM did decrease EDTA-extractable Pb.

Table 4-10. **Changes in metal(loid) extractability (based on NH_4NO_3 and EDTA extractants) calculated between Experiment 2 compared to the unamended unplanted control soils (U1) in Experiment 1a**

			NH_4NO_3				EDTA			
Soil	*Amendment*	Unplanted control	**Cd**	**As**	**Pb**	**Zn**	**Cd**	**As**	**Pb**	**Zn**
PKG	C6-20	**NH_4NO_3:** Cd = 1.8% Zn = 1.3% **EDTA** Cd = 70% Pb = 66% Zn = 50%	↓	nd	🟩 ↓	🟩 ↓	🟩 ↓	nd	↓	🟩 ↓
	C6-40		🟩 ↓	nd	🟩 ↓	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟩 ↓
	C6+Z		↓	nd	🟩 ↓	🟩 ↓	🟩 ↓	nd	↓	🟩 ↓
	Z		🟩 ↓	nd	🟩 ↓	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟩 ↓
	HL		🟩 ↓	nd	🟩 ↓	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟩 ↓
	CH		↓	nd	🟩 ↓	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟩 ↓
CKG-N	C6-20	**NH_4NO_3:** Zn = 0.68% As = 0.23% **EDTA** Pb = 14% Zn = 17% As = 7.4%	nd	🟩 ↓	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟩 ↓	🟩 ↓
	C6-40		nd	🟩 ↓	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟩 ↓	🟩 ↓
	C6+Z		nd	🟩 ↓	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟩 ↓	🟩 ↓
	Z		nd	🟩 ↓	🟩 ↓	🟩 ↓	nd	🟩 ↓	↓	🟩 ↓
	PS		nd	🟩 ↓	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟩 ↓	🟩 ↓
	HL		nd	↓	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟩 ↓	🟩 ↓
CKG-L	C6-40	**NH_4NO_3:** Pb = 0.04% Zn = 0.01% **EDTA** Pb = 48% Zn = 14%	nd	nd	↓	↑	nd	nd	🟩 ↓	🟥 ↑
	C8-40		nd	nd	↓	↑	nd	nd	↓	🟥 ↑
	C8+Z		nd	nd	↓	↑	nd	nd	🟩 ↓	🟥 ↑
	PS		nd	nd	↓	↑	nd	nd	↓	🟥 ↑
	HL		nd	nd	↓	↑	nd	nd	↓	🟥 ↑
	BM		nd	nd	↓	↑	nd	nd	🟩 ↓	🟥 ↑

C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. Whereas red denotes a significant increase, and green denotes a significant decrease ($p < 0.05$) as evaluated by a Student test and nd means non-determined.

4. Summary

In this chapter, the effects of a selection of amendments on metal(loid) behavior were assessed in planted conditions by analyzing physico-chemical soil characteristics, metal(loid) extractability (NH_4NO_3, EDTA, sequential extractions, passive extraction) and response in the plant (germination, biomass, and metal(loid) bioconcentration). The influence of plants as well as combined effects of amendments and plants were also discussed. These results revealed several meaningful trends in the relationships among soil characteristics and metal(loid) mobility for the three described soils.

An overview of the results examines the conditions which invoke a decrease in metal(loid) availability as evaluated by extractions and lettuce metal(loid) bioconcentration. Table 4-11 summarizes the statistically significant positive effects for PKG and CKG-L, and the highly effective amendments for CKG-N as there was an absence of statistically significant results.

Table 4-11. **Summary of the statistically significant metal(loid) availability reductions on PKG and CKG-L (in bold) and notable reductions for CKG-N.**

			PKG	CKG-N	CKG-L
Chemical extractions	**NH_4NO_3**	***As***	nd	PS	nd
		Cd	**C6-20, C6-40, C6+Z, Z, HL**	nd	nd
		Pb	-	C6-Z, HL, PS	-
		Zn	**C6-20, C6-40, C6+Z, Z, HL, CH**	-	-
	EDTA	***As***	nd	-	nd
		Cd	-	nd	nd
		Pb	-	HL, PS	**C6-40, C8-40, C8+Z, HL, BM**
		Zn	-	PS	**BM**
	Fraction A	***As***	nd	HL, Z	nd
		Cd	**Z, HL**	nd	nd
		Pb	**C6+Z, Z, HL**	C6-20	-
		Zn	-	-	**C6-40**
Concentration in soil solution		***As***	nd	PS	nd
		Cd	-	**nd**	nd
		Pb	**C6-20**	Z	-
		Zn	-	-	-
Lettuce BCF		***As***	nd	HL	nd
		Cd	**C6-40, Z, HL**	nd	nd
		Pb	**HL**	C6+Z, HL	-
		Zn	**HL**	HL	-

nd = not determined because of absence of metal(loid); (-) = no change; BCF = bioconcentration factor; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. Whereas amendments in bold showed a statistically significant ($p < 0.05$) reduction in metal(loid) availability

Markedly, for PKG, C6 mixes showed success in mitigating the availability of Cd, Pb, and Zn. All tested amendments showed success on this soil. Among the most successful amendments which were effective in reducing availability as analyzed by multiple methods include C6-20, C6-40, C6+Z, Z, and HL. C6-40, Z, and HL were clearly some of the most effective amendments, with their additions limiting the bioconcentration of metal(loid)s in the lettuce plant model. Specifically, HL was seen to be effective for all metal(loid)s in this soil, though its addition significantly decreased biomass.

For CKG-N, no amendment significantly reduced metal(loid) availability as analyzed by the experiments detailed above. However, several amendments reduced metal(loid) availability more than other amendment tested. PS, HL, C6+Z, and Z were effective for multiple metal(loid)s and tests. Specifically, C6+Z and HL reduced metal(loid)s uptaken into lettuce.

For CKG-L, composts, HL, and BM had some success in reducing metal(loid) availability. Both BM and C6-40 were seen to reduce the availability of both Pb and Zn. However, as very little metal(loid) was concentrated in the plants, their success was difficult to distinguish. Nevertheless, both BM and C6-40 tended to reduce metal(loid)s accumulation in the lettuce, as suggested by the results for the other extractions.

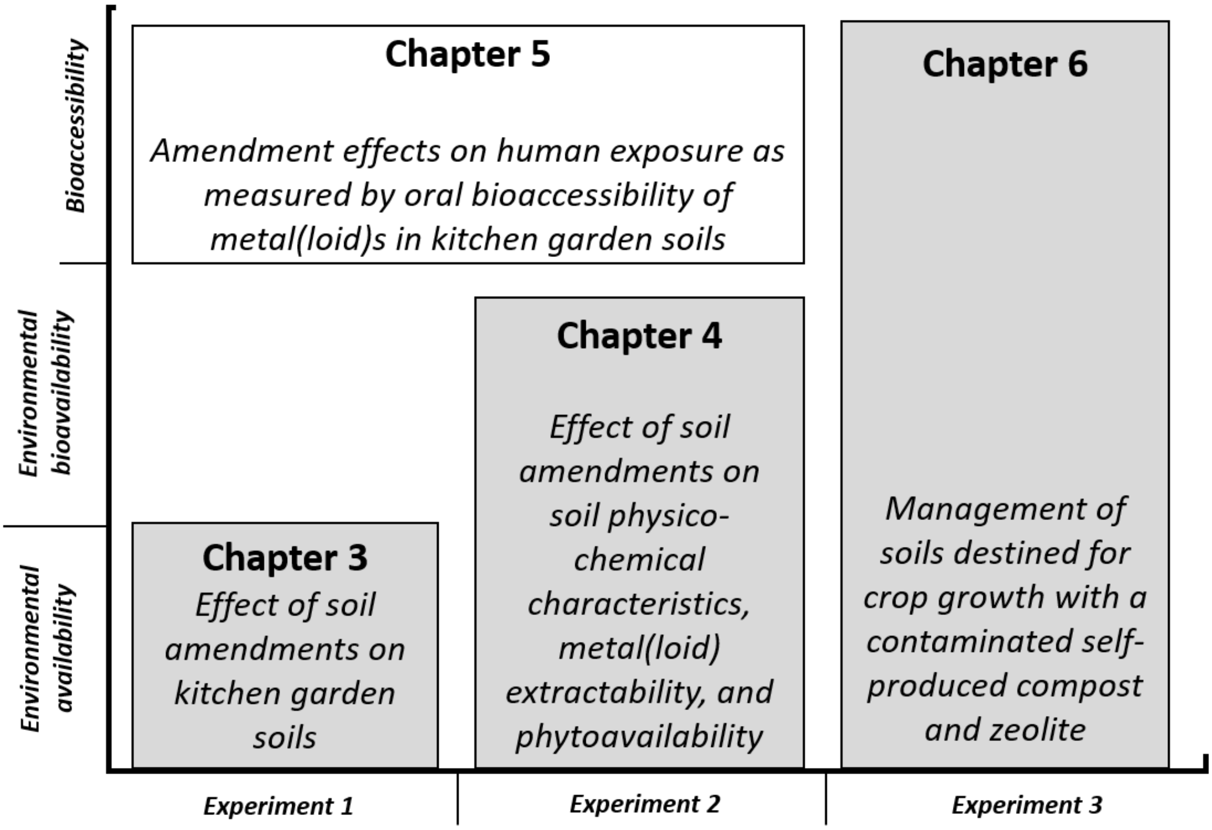
Chapter takeaways

Chapter 4 showed that amendments had distinct effects on different kitchen garden soils based upon the physico-chemical changes brought to the soils on which they were applied. Effects on physico-chemical parameters, metal(loid) extractability, and lettuce uptake were strongest on the slightly acidic, anthropogenically-contaminated soil PKG.

Specifically:

- PKG
    - Strongest correlations and relationships between amendments and physico-chemical or biological soil changes, between soil characteristics and metal(loid) extractabilities, and among extractions themselves
    - The addition of HL and Z were responsible for the majority of physico-chemical and biological soil changes, with HL specifically linked to positive relationships with P_2O_5 and $CaCO_3$ and decreased Cd mobility in the presence of lettuce
    - Positive correlation between the BCF of Cd, NH_4NO_3-extractable Cd, and Cd in soil fraction A
    - P_2O_5, soluble C_{org}, $CaCO_3$ positively correlated with each other and negatively correlated with Cd in soil Fraction A
    - Slowest germination rate but the most lettuce biomass
    - (Hyper-)accumulatory character of lettuce for Cd on this soil
- CKG-N
    - Addition of HL positively correlated with pH
    - Addition of C6-40 positively correlated with P_2O_5
    - All compost additions increase C_{org}, with marked correlation with C6-20 and C6+Z
    - Correlation of Pb, Zn, and As BCF’s to their respective concentrations in lettuce
    - Reduction of Pb long-term availability (EDTA extraction) by PS
- CKG-L
    - Correlation between P_2O_5 and $CaCO_3$ was found in this soil
    - C8 amendments linked with pH and P_2O_5
    - Compost amendments positively correlated with bacterial activity, whereas the reverse was observed for HL
    - Correlation between Pb and Zn BCFs and their respective concentrations in the soil
    - C6-40, C8-40, C8+Z, HL, and BM lowered EDTA Pb extractability

Chapter 5: Amendment effects on human exposure as measured by oral bioaccessibility of metal(loid)s in kitchen garden soils



Chapter 5: Amendment effects on human exposure as measured by oral bioaccessibility of metal(loid)s in kitchen garden soils

The previous chapters showed that addition of some amendments allows to reduce mobility, extractability, and phytoavailability of metal(loid)s in soils. This chapter focuses on the effects of the proposed management of the moderately contaminated KGs studied on human health. This is done through the assessment of population exposure related to the non-intentional ingestion of soil particles. Population exposure is estimated using oral bioaccessibility measurements, which is an increasingly used method of analysis evaluating the human exposure to metal(loid)s specifically targeted to help manage contaminated areas (Ruby et al., 1996; Hamel et al., 1999; Basta & Gradwohl, 2000; Juhasz et al., 2007; Roussel et al, 2010; Pelfrêne et al., 2011). Although the consumption of contaminated homegrown vegetables can pose health risks, the impact of the ingestion of soil particles is particularly hazardous. This danger is present because the majority of metal(loid)s present in soils are associated with the fine fraction (<250 µm), which is the most likely to be ingested or inhaled as it remains more easily on hands or suspended in the air after soil or plant manipulation (Pelfrêne, 2016). Children represent a particularly at-risk group because of hand-to-mouth activity. The exposure accumulated during garden maintenance can also be especially dangerous for gardeners, who can ingest between 200 and 480 mg of resuspended particles per day when working the soil (Ineris, 2015).

As seen in Figure 5-1, this chapter first considers the bioaccessibility of metal(loid) in the three soils by analyzing their unamended controls from Experiment 1a in plant-free conditions (U1) and in the presence of lettuce (U2), as represented by the green line. Then the effect of amendments on oral bioaccessibility of metal(loid)s in presence of lettuce is analyzed with results from the planted control and amended soils from Experiment 2 (amendment effect, purple line), in order to estimate a real-life *in situ* scenario in a kitchen garden while still being able to maintain certain parameters such as temperature, humidity, and irrigation. Finally, the effect of both the amendment and lettuce effect is analyzed (blue line).

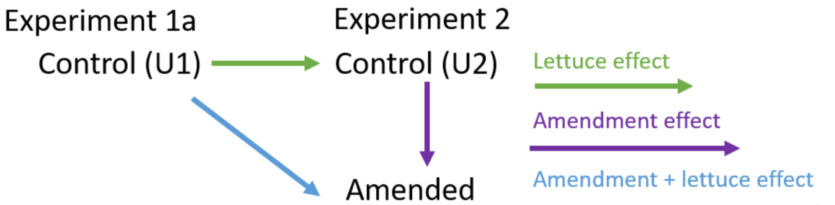


Figure 5-1. **Flow of Chapter 5 bioaccessibility result presentation from both Experiment 1a and Experiment 2**

1. Effect of the presence of lettuce on metal(loid) bioaccessibility in three contaminated kitchen garden soils

Table 5-1 presents the values in both G and GI phases in the unamended control soils without (U1) and with lettuce culture (U2) in order to determine the effect of a plant system on oral bioaccessibility of Cd, Pb, and As.

Table 5-1. Bioaccessibility of Cd, Pb and As in gastric (G) and gastro-intestinal (GI) phases in both unplanted (U1) and planted (U2) unamended soils of PKG, CKG-N and CKG-L (mean values expressed in % of pseudo-total concentrations) and their physico-chemical parameters

		PKG		CKG-N		CKG-L	
		U1	U2	U1	U2	U1	U2
G-bioaccessible	Cd	64%	65%	nd	nd	nd	nd
	As	nd	nd	26%	16%*	nd	nd
	Pb	65%	52%*	26%	16%*	77%	70%
GI-bioaccessible	Cd	14%	32%*	nd	nd	nd	nd
	As	nd	nd	24%	16*%	nd	nd
	Pb	10%	13%	0.9%	6%*	0.9%	2%
	pH	6.02	6.27*	7.12	7.13	7.86	7.77
	$CaCO_3$ (g kg^{-1} DW)	2.27	1.12*	1.10	0.96	69	72
	EC (µS cm^{-1})	1,769	887*	96	107	231	187
	P_2O_5 (g kg^{-1} DW)	0.66	0.47*	0.34	0.35	0.42	0.41

nd = not determined; * denotes a significant difference with the addition of lettuce for a given parameter and soil as evaluated by a Student test. Red signifies a significant increase and green a significant decrease in metal(loid) bioaccessibility after planting

1.1 Plant-free condition (U1)

The gastric and gastrointestinal bioaccessibility of Cd, Pb, and As was measured in three unamended, unplanted kitchen garden soils (U from experiment 1a, U1) (Table 5-1).

Cadmium

The PKG soil contained elevated levels of anthropogenic non-essential metals Cd and Pb related to smelting activities. Of the pseudo-total amount of Cd, 64% was present in the G phase, and 14% in the

GI phase. The difference in bioaccessibility between the G- and GI- phases can be explained by the acidic pH of the stomach environment (pH = 1.2), which induces an acidification of the organic salt functions and protonation of the Fe, Al, and Mn oxide/oxyhydroxide surfaces (Waterlot et al., 2017). During the GI phase, the bioaccessible fraction of Cd decreased considerably. In near neutral pH and in the carbonate- and phosphate-rich environment of the intestine phase, this metal may be stabilized in solution by processes of complexation or adsorption in remaining soil particles or other indigestible materials present in chime and/or by precipitation as relatively insoluble compounds, allowing it to be less bioaccessible (Basta & Gradwohl, 2000; Grøn & Andersen, 2003). The values of Cd bioaccessibility measured fall in a similar range of those found in a study by Pelfrêne et al. (2013) carried out in the same environmental context (*n* = 440); with Cd being between 57.4% - 90.1% G-bioaccessible and 21.1% - 42.9% GI bioaccessible. These rates of bioaccessible Cd corresponded to those found in fraction A and B. As observed in our experiments, Cd was mainly linked to carbonates and Fe/Mn oxides than to OM. However, the former two constituents have a greater tendency to be destroyed in the gastrointestinal matrix (Pelfrêne et al., 2011).

Arsenic

On the CKG-N soil, Pb and As have a primarily geogenous origin from a vein of micaschist running through the bedrock of the garden. The unplanted, unamended soil's As was 26% bioaccessible in the G phase and 24% in the GI phase. These similar concentrations between phases are observed by several studies (Barsby et al., 2012). Some suggest that As tends to be slightly less bioaccessible in the GI phase because of solubilized As' adsorption to newly precipitated iron oxides after the pH shift (Li et al., 2015; Bari et al., 2021). Geogenously contaminated soils (*n* = 91) in Northern Ireland have been shown to exhibit As bioaccessibilities from 5.2– 24.4% in the G-phase and 5.9 – 22.6% in the GI-phase as measured by the UBM protocol (Barsby et al., 2012). CKG-N was slightly more bioaccessible in terms of As, but as France and Northern Ireland have different geochemical backgrounds, this profile fits the geogenously-contaminated CKG-N soil to some extent.

Lead

The PKG soil contained elevated levels of anthropogenic Pb related to smelting activities. Of the pseudo-total amount of Pb in the soil, 65% was bioaccessible in the G phase, and 10% in the GI phase. These values fall in a similar range of those found in a study by Pelfrêne et al. (2013) carried out in the same environmental context (*n* = 440); with Pb being 45.9% - 73.7% G-bioaccessible and 11.7% - 37.3% GI-bioaccessible. Another study on urban and peri-urban soils contaminated by mining and smelting (*n* = 4) showed that Pb (SBRC assay) can be 54.8 ± 21.9% (*n* = 13) bioaccessibility in the G phase (Smith et al., 2011). For anthropogenically-contaminated soils, lower ranges of bioaccessibility are typically associated with mining, and the presence of Pb species such as Pb- sulfates and phosphates, whereas upper ranges are associated with smelter emissions and highly soluble Pb oxides and carbonates (Ruby et al., 1999; Porter et al., 2004; Smith et al., 2011). Thus this difference in bioaccessibility is due not only to Pb speciation and particle size, but also reactive soil phases and soil composition.

On the CKG-N soil, the unplanted, unamended soil's Pb was 26% gastrically bioaccessible and 0.9% gastrointestinally bioaccessible. Geogenously contaminated soils (*n* = 91) in Northern Ireland have been shown to exhibit Pb bioaccessibilities between 6% and 60% in the G phase, and 2.8% - 19.1% 10.9 ± 8.11 % in the GI phase as measured by the UBM protocol (Barsby et al., 2012). The CKG-N soil falls within the range of gastrically bioaccessible Pb, but its Pb is much less gastrointestinally bioaccessible.

The CKG-L soil is anthropogenically and heterogeneously contaminated by urban fill and exposure to highway traffic. This unplanted, unamended soil's Pb was 77% gastrically bioaccessible and 0.9% gastrointestinally bioaccessible. For soils anthropogenically contaminated with urban fill (*n* = 31) like CKG-L, G-bioaccessibility (SBRC) of Pb has been found to have ranges including 65.9 ± 19.2%, and GI-bioaccessibility from 2.05 ± 1.45% (Smith et al., 2011). This aligns with the CKG-L results, as it is a heterogeneous urban garden associated with waste material deposits.

Between the G and GI phases, Pb bioaccessibility decreased for all soils; by 54%, 25% and 76%, for PKG, CKG-N, and CKG-L, respectively. This change in bioaccessibility between phases is globally seen for this element (Ruby 1999, Roussel et al., 2010, Wragg et al., 2011). This phenomenon occurs because in near neutral pH and in carbonate-rich environments, this metal can be complexed or adsorbed on remaining soil particles or indigestible materials present in the matrix (Basta & Gradwohl, 2000; Grøn & Andersen, 2003; Garau et al., 2019; Pelfrêne et al., 2020). This shift in pH can also lead to the precipitation of Fe as ferrihydrite, which can bind Pb and reduce its GI-bioaccessibility (Smith et al., 2011). The Pb in the geogenically-contaminated soil, CKG-N, was more than two times less gastrically-bioaccessible than PKG and CKG-L. Differences in gastric bioaccessibility are likely due to soil origins and forms of Pb. Geogenous Pb, often occurring in mineralized or difficultly available forms, is generally regarded to be less bioaccessible than anthropogenic Pb because of the forms of the metal present (Walraven et al., 2015; Ruby et al., 1999). Indeed, bioaccessible Pb corresponds to its chemical form, which can be influenced by its origins (Walraven et al., 2015; Ruby et al., 1999). As seen in Figure 5-2, some of the least bioaccessible forms of Pb include minerals such as lead (II) sulfide, followed by oxides, sulfides, and phosphates, and then oxidized or carbonate bound or ionized forms of Pb, which could explain the links between Pb origin, species, and gastric bioaccessibility.

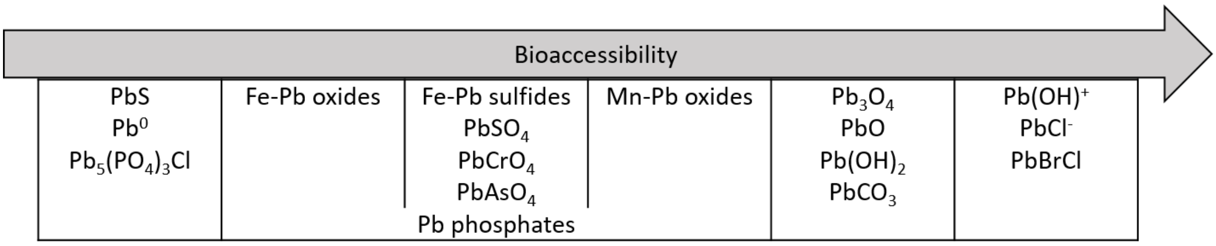


Figure 5-2. Overview of Pb chemical forms influencing its bioaccessibility in soils (adapted from Ruby et al., 1999)

In the GI phase, however, less difference was present among soils. Both community kitchen gardens (CKG-N and CKG-L) had 0.9% gastrointestinally bioaccessible Pb, whereas PKG was more than 10 times more accessible in this phase. This shows that Pb was not less bioaccessible in the geogenously contaminated soil. These differences in GI-phase Pb bioaccessibility could be influenced Pb's separation in the different soil fractions (*cf* Chapter 4; Figure 4-2). Indeed, Pb present in soil can be dissolved and redistributed by adsorption or precipitation with soil constituents like OM and reactive Fe, changing its bioaccessibility depending on soil characteristics (Ruby et al., 1999). Pb in the more available soil fractions was linked to anthropogenic origins and higher G- and GI- bioaccessibility (Hiller et al., 2022; Farmer et al., 2011; Li et al., 2001; Kelepertzis et al., 2021). Furthermore, anthropogenic Pb gastrointestinal bioaccessibility can vary by sources of pollution. The gastrointestinal bioaccessibility of **city waste Pb** (lead linings, paints, glazes, containing lead oxides such as Pb_3O_4; PbO, 5-600 µm) < **diffuse Pb** (Pb in manure and fertilizer; small particle sizes that have passed through cow intestine) ≈ **gasoline Pb** (*e.g,* PbBrCl, Pb oxides, Pb sulphates; 0.015 µm – 1 µm) < **car battery Pb** < **Pb bullets and pellets** (5-150 µm) (Walraven et al., 2015). Concretely, a RIVM *in vitro* gastrointestinal bioaccessibility test (Oomen et al., 2003) found that soils contaminated with Pb residue in the form of bullets and pellets were between 60.7% and 79.0 bioaccessible, whereas soils heterogeneously polluted by waste containing Pb paint and glaze were between 0.5% to 8.3% bioaccessible (Walraven et al., 2015). Other studies have shown that of anthropogenically contaminated sites, Pb gastrointestinal bioaccessibility tends to be lower at mining sites because of their associated with insoluble forms of Pb (Cotter-Howells & Thorton, 1991; Davis et al., 1992; Gasser et al., 1996).

1.2 Influence of lettuce

After addition of a lettuce model and 6 weeks of growth, the analyzed PKG soil contained Cd and Pb that were 65% and 52% G-bioaccessible, and 32% and 13% GI-bioaccessible, respectively. The Pb and As present in CKG-N was 16% G-bioaccessible, and 6% and 16% GI-bioaccessible, respectively. For CKG-L, Pb was 70% G-bioaccessible and 2% GI-bioaccessible. As seen in Table 5-1, there was a 75%, 65%, and 97% decrease in Pb G- and GI- bioaccessibility on these soils in the presence of the vegetal model.

For PKG, after lettuce growth and harvesting, the bioaccessibility of Cd did not change whereas those of Pb became significantly lower, dropping by 13% of the pseudo-total. In the GI phase, the addition of the plant model brought more than double the concentration of bioaccessible Cd, with this value increasing significantly. The concentration of GI-bioaccessible Pb stayed steady, however, despite a tendency to be slightly more bioaccessible in the presence of the plant model. These changes in the presence of the plant model corresponds with an increase in pH from 6.0 to 6.3, but a decrease in $CaCO_3$ from 2.27 to 1.12 g kg^{-1}, in EC from 1,769 to 887 µS cm^{-1} and in available P from 0.66 to 0.47 g kg^{-1}. The latter two changes are likely explained by nutrient uptake from the soil into the plant.

In the CKG-N soil, the bioaccessibility of Pb in the G phase experienced a decrease of 10% the pseudo-total with the addition of lettuce. In the GI phase, the bioaccessibility of Pb significantly increased by almost sevenfold in the presence of lettuce. A similar behavior was highlighted for As in both phases, where the G- and GI-bioaccessibility fell by 10% and 8% of the pseudo-total, respectively, reflecting a decrease of 38% between conditions. These changes in the presence of the lettuce model were not associated with significant changes in the measured soil physico-chemical parameters. For CKG-L, no significant differences between the percentage of G- and GI-bioaccessible Pb in the unplanted and planted controls were seen. There were also no significant changes in the physico-chemical parameters measured between the unplanted and planted experiment.

The difference in bioaccessibility between the G- and GI- phases increased for each soil in the presence of lettuce, with G-bioaccessible Pb tending to decrease in the presence of lettuce, while GI-bioaccessible Pb tended in increase in the presence of lettuce, for all the tested soils. Studies on the parameters responsible for Pb G- and GI- bioaccessibility suggested that the presence of carbonates, EC, and pH play a role in Pb G-bioaccessibility (Gonzalez-Grijalva et al., 2019; Roussel et al., 2009; Pelfrêne et al., 2013). In the present study, no measured physico-chemical parameter followed the same trend for all three soils, making it more likely that the global decrease in Pb G-bioaccessibility is due to another parameter brought by the plant model. Studies have cited lettuce's influence on soil microbiomes, with its germination on multiple different soil types invoking the colonization bacterial genera such as *Sphingomonas*, *Rhizobium*, *Pseudomonas*, and *Variovorax* (Schrieter et al., 2014). Pb GI-bioaccessibility itself can be dependent on the presence of kaolinite and calcite in the soil, contaminant types, and Al and Fe oxide content (Gonzalez-Grijalva et al., 2019; Lake et al., 2021). In this experiment, Pb GI-bioaccessibility increased with the addition of a lettuce plant model in greenhouse conditions for all control soils. However, the increase in bioaccessibility with the addition of a plant model is rarely seen in literature. A study analyzing the effect of a plant model grown in a greenhouse on oral bioaccessibility of Pb found that the addition of a *Miscanthus* culture in greenhouse conditions invoked a decrease in Pb GI-bioaccessibility. This phenomenon was linked to decreases in pH and increases in organic carbon contents (Pelfrêne et al., 2015). Similarly, Attenyake et al. (2017) found that lettuce culture in the field was linked to decreases in soil pH from 7.08 to 6.66, but this result was not linked to bioaccessibility results. In field conditions, it was reported that GI-bioaccessible (PBET) Pb measured from Pb-contaminated soils planted with carrot decreased during the growth period from 9.1 to 7.5%. This decrease over time was not significant, despite changes in Pb speciation favoring Pb linked to Fe-oxyhydroxides and to hydroxypyromorphite (Smith et al., 2011; Obrycki et al., 2016; Hashimoto et al., 2011). Indeed, a study performed by Gonzalez-Grijalva et al. (2019) found that GI- bioaccessible Pb (IVBA; USEPA Method 1340) decreased with increasing Al and Fe oxide content.

As pH did not significantly change with plant addition for all of the soils (except in PKG; *cf* Chapter 4), it could be postulated that the increase in GI-bioaccessibility was a result of a decrease in Al- and/or Fe- oxides. Considering that the study of the metal(loid)s present in the lettuce showed that they contained Al and Fe, which is presumably uptaken from the soils following the dissolution of oxides present in the acidic rhizosphere, this could explain the tendency for the GI-bioaccessibility increase (Smith et al., 2011). Fe (oxy)hydroxides and OM create surface sorption and chelation sites for Pb^{2+}, and pH increases mean fewer H^+ ions are able to compete with Pb^{2+} for binding sites, and Pb forms complexes with phosphorus (Hettiarachchi & Pierzynski, 2004; Rieuwerts et al., 1998, Zia et al., 2011, Finzgar et al., 2007; Walraven et al., 2015). This means that Pb present in soil can be dissolved and redistributed by adsorption or precipitation with soil constituents like OM and reactive Fe. Specifically, after anthropogenic Pb resides within the soil, it can shift to more stable forms than that which is found in soil Fraction A, including that which is bound to organic matter, clay, reactive iron or other reactive phases, or even mineralized forms (Walraven et al., 2015).

Indeed, as noted by Pelfrêne et al. (2011), soil Fraction A can positively contribute to Pb GI-bioaccessibility. Figure 5-3 further supports that Pb's GI-bioaccessibility can be related to Pb's source and thus separation in the different soil fractions (*cf* Chapter 4; Figure 4-2) (Walraven et al., 2015). Regarding the unamended planted soils, PKG, CKG-L, and CKG-N contain 13%, 6% and 2% of Pb in their GI-phases, respectively (Figure 5-x). PKG contains 5.2% of its Pb in the exchangeable soil Fraction A, whereas CKG-N contained 1.9% of its Pb in Fraction A, and CKG-L 2.0% (Figure 5-3). This accounts for 40%, 32%, and 100% of the total GI-accessible Pb content for these three soils, respectively. A Pearson correlation matrix performed on the three soils' controls (Annex 5-1) revealed that the GI-bioaccessibility of Pb and Fraction A (Pearson coefficient = 0.86) significantly correlate.

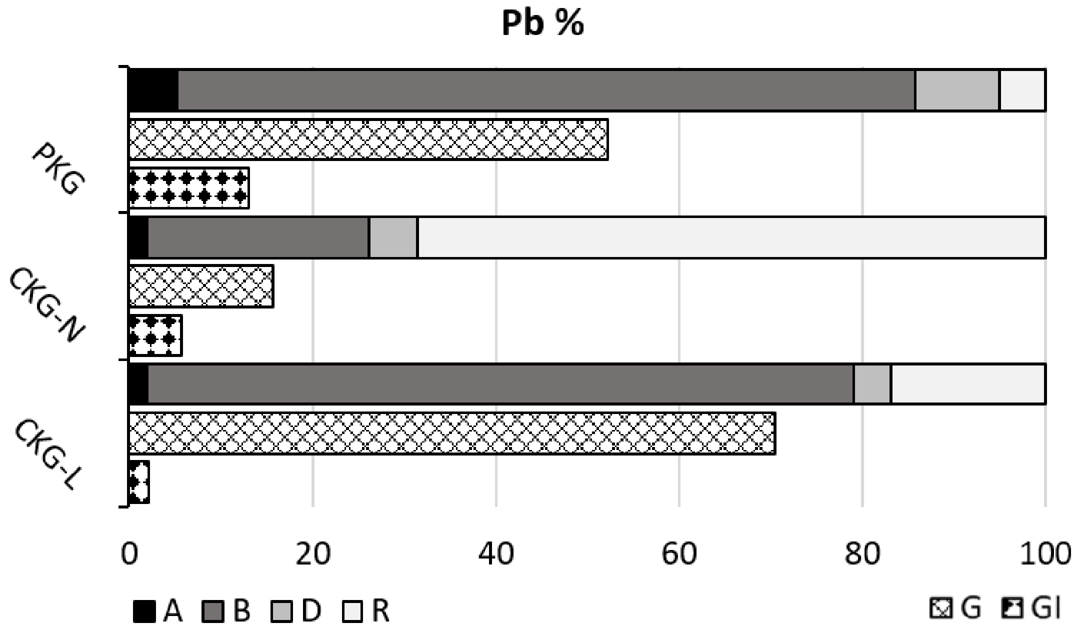


Figure 5-3. Comparison of the distribution of Pb in the unamended planted controls (U2) of PKG, CKG-N and CKG-L with their oral gastric (G-) and gastrointestinal (GI-) bioaccessibilities

Additionally, soil Fraction D can also positively contribute to GI-phase Pb concentrations (Pelfrêne et al., 2011), with these soils' controls significantly correlating (Pearson coefficient = 0.98) (Annex 5-1). PKG contained 9.1% of its Pb in this oxidizable soil fraction complexed to OM, whereas CKG-N contained 5.4% and CKG-L 4.2%. This accounts for 70%, 90%, and over 100% of the total GI-phase Pb for these soils, respectively. Both Fraction D Pb and GI-phase Pb can be found in forms complexed to OM (Basta & Gradwohl, 2000; Grøn & Andersen, 2003; Garau et al., 2019; Pelfrêne et al., 2020), which could explain their similar extractabilities.

2. The effect of amendments on metal(loid) G- and GI- bioaccessibility in planted kitchen garden soils

2.1 Bioaccessibility of Cd in the PKG soil

Figure 5-4 shows the influence of amendments on the G and GI bioaccessibility of Cd in the PKG soil in terms of percent of the pseudo-total Cd soil content. After lettuce growth, the bioaccessibility of Cd was on average of 64% in the G phase and 32% in the GI phase on the unamended and planted control soil (U2). With the addition of amendments, G bioaccessibility of Cd ranged from 58% to 73%. No statistical differences were present despite this variation. There was, however, a tendency for both the Z-amended and HL-amended soils to have slightly less G-extractable Cd than the control. Concerning GI-bioaccessible Cd, which ranged from 21% to 33% accessible, more significant changes occurred. Indeed, bioaccessibility was significantly reduced with all amendment additions excepting CH. The addition of C6-20, C6-40, C6+Z, Z, and HL were associated with GI-bioaccessibility values of 27%, 24%, 25%, 23%, and 21%, respectively. Their addition led to significant drops in bioaccessibility of at least 16% in comparison to the control.

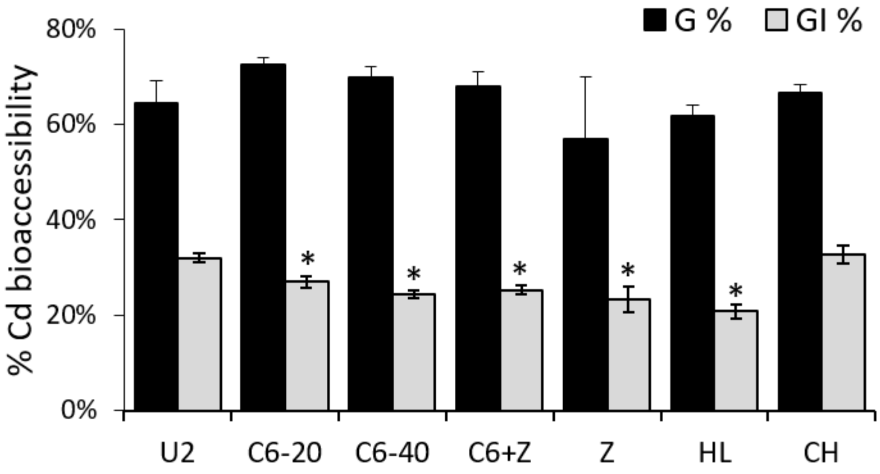


Figure 5-4. **Influence of amendments on G- and GI-bioaccessibility of Cd in the PKG soil. U2: unamended and planted control; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; Z: chabazite zeolite; HL: hydrated lime; CH: crushed horn. * denotes a significant difference ($p < 0.05$) between the unamended control U and a given condition for a given soil as evaluated by a Student test.**

In literature, several authors showed that amendments, in particular organic amendments (compost, peat, biochar), have the ability to decrease Cd bioaccessibility by increasing soil pH, CEC, EC, OM, soil nutrient content, and microbial activity otherwise negatively affected by Cd toxicity (Vargas et al., 2019; Li et al., 2022; Lehmann et al., 2011; Hiller et al., 2022). A study on the effect of different organic matter-rich amendments added at 3% to a highly Cd-contaminated soil (41 mg kg^{-1}) planted with Chinese cabbage in greenhouse conditions found that Cd GI-bioaccessibility (assessed by SBET) depends heavily upon these same parameters (Bashir et al., 2018). In this study, Cd GI-bioaccessibility decreased by more than 20% in comparison to the planted control with the addition of various biochars. The authors found that complexation and electrostatic interactions were particularly important mechanisms responsible for Cd immobilization and oral bioaccessibility reduction. Increases in soil pH and EC may have provided adsorption sites for Cd in the soil (Park et al., 2011; Bian et al., 2013). It has also been suggested that organic matter and organic amendments that contain dolomite and siliceous minerals as Z and HL can promote Cd immobilization when added to soils (Usman et al., 2016). This is because their chemical species allow Cd to become complexed and stabilized, especially when coupled with EC increases (Usman et al., 2016). Indeed, these two amendments significantly increased soil EC. The presence of micropores in siliceous amendments and their ability to complex Cd with EC increases, as well as their ability to promote bacterial activity, could suggest why HL and Z were effective amendments in the PKG soil, especially considering both significantly increased soil C_{org}, an indicator of bacterial activity.

2.2 Bioaccessibility of As in the CKG-N soil

Figure 5-5 illustrates the G- and GI-bioaccessibility of As in the CKG-N soil. In the G phase, it was found that As on the unamended control soil (U2) was on average 16% extractable, with no significant differences were seen among amendment conditions ranging from 14% to 16%. In the GI phase, while the bioaccessibility of As did not significantly change after passage through the stomach, significant differences were observed for some conditions. Indeed, the addition of C6-40 and PS, two organic matter–rich amendments, resulted in significant but slight decreases in GI-bioaccessibility to 15%. Notably, the addition of C6-40 was also associated with a significant increase in available P by 26% in comparison to the control soil, as seen in Chapter 4. Indeed, available P is known to have a negative link with the GI bioaccessibility of As. The addition of organic matter-rich amendments has been linked to As mobilization in anthropogenically-contaminated soils as evaluated by simple extractions and bioaccessibility tests (Fleming et al., 2013; Cao and Shiralipour, 2006; Wang and Mulligan, 2006; Manning and Goldberg, 1996). It is widely seen that these additions increase As bioaccessibility as their doses increase (Fleming et al., 2013; Cao and Shiralipour, 2006; Wang and Mulligan, 2006). This is because OM addition can be linked to soil pH increases, which reduce As' adsorption strength to soil minerals (Manning and Goldberg, 1996). OM addition can also lead to As dissolution in anthropogenically contaminated soils because it competes for adsorption sites with its organic acids, Ca, and P brought to soil, and thus promote As' reduction into arsenite or other mobile forms (Sarkar et al., 2007; Adriano, 2001; Chen et al., 2002; Hartley et al., 2010).

Notably, the As assessed in CKG-N has geogenous backgrounds, however, and thus may contain different As species. In the present study, these amendments did not increase soil pH, and were added at relatively low rates such that there was likely not a significant impact on soil OM. In fact, their additions were associated with a slight decrease in P and Ca present in the plant. This could suggest that there was also less P and Ca present in these soils, as well, which could have promoted As immobilization. Another study found that because of OM's elevated OC content in comparison to soils, As is significantly less gastrically bioaccessible in OM–rich amendments such as composts, than in a similarly contaminated urban community garden soil (Hiller et al., 2022). The study implied that the addition of composts to urban kitchen garden soils has the ability to decrease As bioaccessibility, as supported by C6-40's effect in this study.

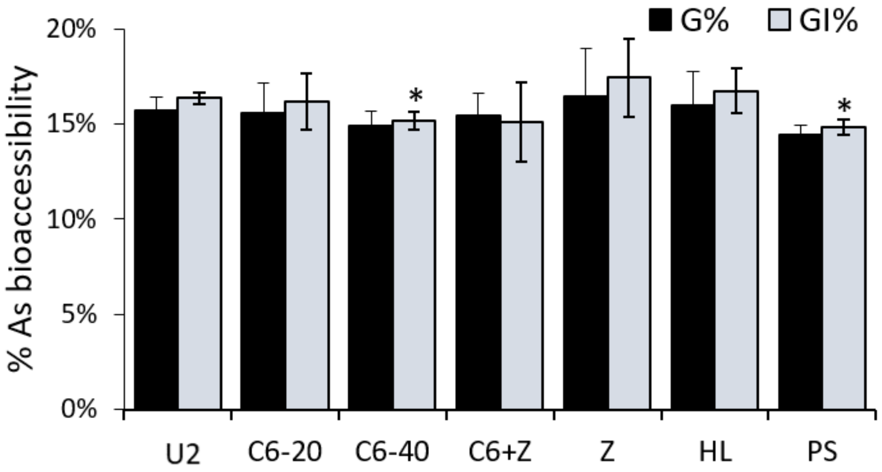


Figure 5-5. Influence of amendments on G- and GI- bioaccessibility of As in the CKG-N soil. U2: unamended and planted control; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil. * denotes a significant difference ($p < 0.05$) between the unamended control U and a given condition for a given soil as evaluated by a Student test.

The addition of phosphate amendments and carbonate-rich substances can help remediate As-contaminated soils and in unique cases, reduce As bioaccessibility (Cai et al., 2017; Cao and Shiralipour, 2006; Manning and Goldberg, 1996). Specifically, Cai et al. (2017) performed bioaccessibility tests (PBET) on As- and Pb- contaminated orchard soil containing lead arsenate and urban soil contaminated with Pb-based paints and leaded gasoline previously treated with either peat, Ca phosphate ($Ca(PO_4)_2$), or Fe oxide in the field. As was found to be between 20-35% G- and GI- bioaccessible in the urban soil, and G-bioaccessibility was significantly decreased with the addition of the phosphate amendment, a tendency which followed into the GI-phase. This result was likely due to phosphate's ability to inhibit arsenate absorption in the intestinal phase (Villa-Bellosta & Sorribas, 2008; Li et al., 2017). This may have been a reason for the available P-rich C6-40's ability to decrease GI-bioaccessible As. The influence of phosphate amendments on As are variable, however, and P amendments are linked to As' increased soil mobility (Li et al., 2017; Cai et al., 2017; Cai et al., 2007; Bradham et al., 2011). In some cases, the G-phase phosphate can desorb As from soils and prevent its reabsorption on Fe oxides in the GI phase, increasing-bioaccessibility (Juhasz et al., 2014; Smith et al., 2014; Li et al., 2017).

2.3 Bioaccessibility of Pb in the three kitchen garden soils

Figure 5-6 shows the influence of amendments on G- and GI- bioaccessibility of Pb in the PKG, CKG-N, and CKG-L soils. In the G phase, Pb was on average between 41% and 55% in PKG, between 12% and 16% in CKG-N, and between 63% and 70% in CKG-L. In the GI phase, Pb was on average between 10 and 13% in PKG, between 4% and 6% in CKG-N, and between 1% and 3% in CKG-L. Regarding the effect of amendments, they had a minimal effect on Pb bioaccessibility in both phases. Indeed, significant amendment-led changes only happened on the PKG soil, where the addition of HL in both phases and C6-40 only in the GI phase invoked a decrease, by 21% in the G phase and 17% in the GI phase for both amendments.

Nevertheless, for each soil there were certain tendencies and links with other physico-chemical soil characteristics and metal(loid) extraction results. Overall, it was seen that the gastric availability of Pb is correlated to its BCF in lettuce (Pearson coefficient = 0.752). The percentage of metal available after passage through the acidic environment of the stomach led to a decrease in the percentage to 12%, or a 77% drop after passage through the stomach matrix. The addition of amendments in the form of C6-40 and HL led to a significant decrease in bioaccessibility to 10%, making these two amendments both effective reducers of human exposure to metal(loid)s for this soil and phase. All amendments that reduced (significantly or not) bioaccessibility significantly increased $CaCO_3$ in comparison to the control soil, and were linked to increased EC and available P. Additionally, C6+Z and HL are linked with significantly less Pb in the most available soil fraction in comparison to that of the control. This could suggest that the increased EC promoted ion exchange, and P_2O_5 and $CaCO_3$ helped bind free Pb.

For CKG-N, there was no significant change in extractability among the tested conditions, though there was a tendency for bioaccessibility to decrease with the addition of C6-40, C6+Z, Z, HL, and PS. All of these effective amendments significantly increased $CaCO_3$, and tended to increase soluble organic C, which are both linked to complexation abilities. G-bioaccessible Pb is seen to be correlated with EDTA-extractable Pb for this soil (Pearson coefficient = 0.784), which extracted 17% of the pseudo-total Pb on the control soil. This EDTA extractability fell significantly to 14% with the addition of PS, which was also the amendment associated with the lowest Pb G-bioaccessibility for this soil. Regarding GI bioaccessible metal(loid)s, those of Pb fell to 6%, with no significant differences occurring with amendment.

All amendments tended to decrease G-bioaccessibility of Pb on CKG-L. All of these effective amendments significantly increased soil pH, which promotes Pb-complex formation. In the GI phase, bioaccessibility decreased, with Pb being 2% extractable. At this stage, no significant differences were present among conditions, though C6-40 had the tendency to decrease its availability by more than 43%. No significant correlations with bioaccessibility and other parameters were seen for this soil.

For the common amendments of the three soils (C6-40 and HL), it was observed that they tended to reduce G- and GI- bioaccessibility of Pb while these soils are located in different environmental contexts and present different physico-chemical parameters and contamination origins. Notably, though HL reduced bioaccessible Pb for each soil, it did not have the same physico-chemical effect on each soil. The success of the compost amendment, however, could be linked to compost's relatively lower Pb bioaccessibility in comparison to soil because of its relatively higher OC content, as supported by study on self-produced composts hailing from urban community kitchen gardens showing that Pb in this matrix is significantly less gastrically bioaccessible (Hiller et al., 2022). The study implied that the addition of composts to urban kitchen garden soils could have the ability to decrease Pb bioaccessibility, as supported by C6-40's effect on both As and Pb in this study.

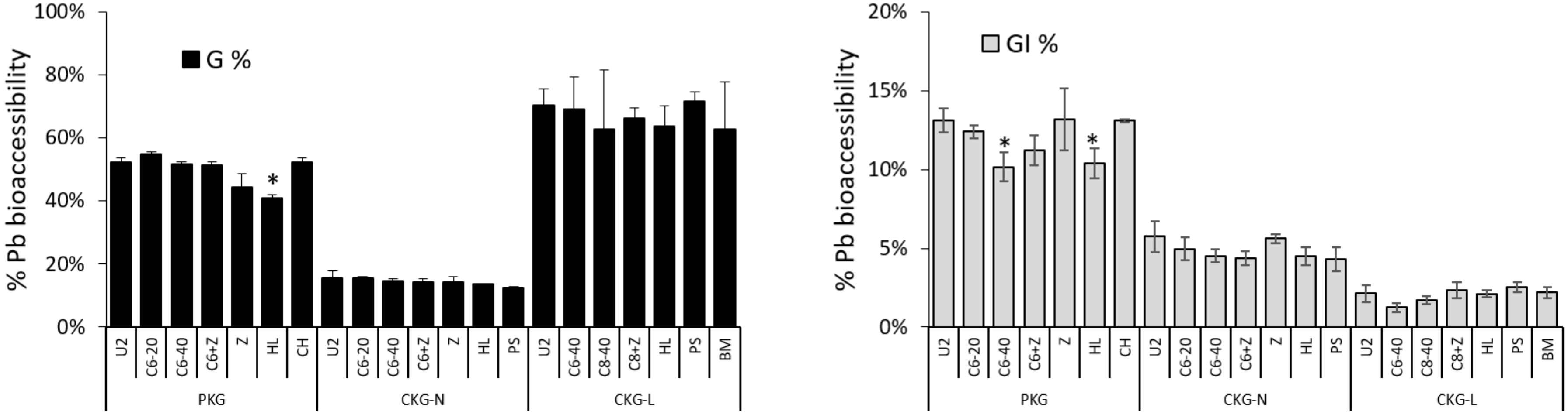


Figure 5-6. Influence of amendments on G- and GI- bioaccessibility of Pb in the PKG, CKG-N, and CKG-L soils. U2: unamended and planted control; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; Z: chabazite zeolite; HL: hydrated lime; CH: crushed horn; PS: potting soil; BM: bone meal. * denotes a significant difference ($p < 0.05$) between the unamended control U for a given soil and a given condition for the same soil as evaluated by a Student test.

3. Study of the influence of both lettuce and amendments on metal(loid) bioaccessibility in three contaminated kitchen garden soils

This section discusses the combined effect of amendments and lettuce on metal(loid) bioaccessibility in the three kitchen garden soils by comparing the Experiment 1a control (*i.e.*, U1; unamended and unplanted condition) with the Experiment 2 values (*i.e.*, U2; amended and planted conditions) (Table 5-2). To study this combined effect, changes with the addition of the different amendments selected for each KG soil and the control U1 were evaluated. Down arrows (↓) signify that bioaccessibility of metal(loid)s has decreased in the presence of both the amendment and plant, whereas up arrows (↑) show an increase of bioaccessibility with the amendment-plant system. Colors indicate significance of the results, with green showing a significant decrease and red a significant increase. The results highlighted mixed effects depending on phase, metal(loid), and to some extent, amendment.

In the presence of both amendments and the plant model, Cd G-bioaccessibility in the PKG soil was significantly increased by at least 4% with the addition of all tested compost amendments (C6-20, C6-40, C6+Z) and CH (Annex 5-2). The other two amendments tested, Z and HL, significantly reduced Cd G-bioaccessibility by at least 4%. The comparison of the unplanted (U1) and planted (U2) controls showed that with the addition of a plant model, little changes in Cd G-bioaccessibility were seen; thus these effects are likely brought by the amendments. In the GI phase, however, all amendments were associated with a non-significant but not negligible increase in Cd bioaccessibility by at least 47% in comparison to U1 (Annex 5-2). Likewise, Cd in U2 was more GI-bioaccessible than U1. However, all amendments besides CH decreased GI-phase Cd in comparison to U2. Thus Cd seems to have been mobilized by the plant into the GI-phase, as reflected in the hyperaccumulatory BCF results for this element.

For As, present on the CKG-N soil, the combination of amendments and the plant system significantly reduced its G- and GI- bioaccessibility by at least 30% (Annex 5-2). As there was little change in As G- or GI- bioaccessibility with amendment addition in comparison to U2, it is likely the plant that brought this reduction in As' G-bioaccessibility. This was not associated with any significant changes in measured soil physico-chemical parameters. Because As is immobilized by Fe compounds, it is possible that the rhizosphere of the plant provoked local pH changes or microbial changes that dissolved oxides and allowed for the liberation of Fe (Smith et al, 2011).

Pb was present and analyzed on all three soils. The G-bioaccessibility of this element was reduced in each soil by at least 7% with the addition of all amendments as compared to U1 (Annex 5-2). This decrease was significant for the PKG and CKG-N soils. In the GI phase, however, Pb bioaccessibility was increased significantly for all amendments added to the CKG-N soil, by at least 454% in comparison to

U1, in CKG-L amended with HL (273% increase), and slightly on most PKG amended soils. Only C6-40 and HL were associated with decreases of 4% and 6% in comparison to the unplanted control U1, respectively (Annex 5-2). These were the two amendments that significantly reduced Pb GI-bioaccessibility compared to the Experiment 2 planted control. As the same trends in G- and GI- phase Pb happen on all soils, changes in bioaccessibility between U1 and U2 seem to be a plant-led trend.

Table 5-2. **Changes in metal(loid) bioaccessibility calculated between Experiment 2 amended (U2), planted soils and the unamended unplanted control soils in Experiment 1a (U1)**

		G			GI		
Soil	*Amendment*	**Cd**	**As**	**Pb**	**Cd**	**As**	**Pb**
PKG	C6-20	🟥 ↑	nd	🟩 ↓	↑	nd	↑
	C6-40	🟥 ↑	nd	🟩 ↓	↑	nd	↓
	C6+Z	🟥 ↑	nd	🟩 ↓	↑	nd	↑
	Z	🟩 ↓	nd	🟩 ↓	↑	nd	↑
	HL	🟩 ↓	nd	🟩 ↓	↑	nd	↓
	CH	🟥 ↑	nd	🟩 ↓	↑	nd	↑
CKG-N	C6-20	nd	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟥 ↑
	C6-40	nd	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟥 ↑
	C6+Z	nd	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟥 ↑
	Z	nd	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟥 ↑
	PS	nd	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟥 ↑
	HL	nd	🟩 ↓	🟩 ↓	nd	🟩 ↓	🟥 ↑
CKG-L	C6-40	nd	nd	↓	nd	nd	↑
	C8-40	nd	nd	↓	nd	nd	↑
	C8+Z	nd	nd	↓	nd	nd	↑
	PS	nd	nd	↓	nd	nd	↑
	HL	nd	nd	↓	nd	nd	🟥 ↑
	BM	nd	nd	↓	nd	nd	↑

C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. Whereas red denotes a significant increase, and green denotes a significant decrease ($p < 0.05$) compared to U1 values as evaluated by a Student test. nd means non-determined.

4. Summary

Thus, the results shown in this section responded to the analysis of the effects of both the plant, the amendments, and the plants and amendments combined on the oral bioaccessibility of Cd, As, and Pb in the KG soils. The G- and GI- bioaccessibility of Cd was measured on the PKG soil, and summarized in Figure 5-7. Globally, gastrointestinally-bioaccessible Cd increases with the addition of a lettuce model, whereas GI-phase Cd stays relatively stable. Regarding the addition of amendments, all excepting CH significantly decreased GI-phase Cd in comparison to the U2 planted control. For this anthropogenically-contaminated soil, excepting for Z and HL in the G-phase, these amendment-led changes were relatively weak in comparison to plant-led changes. Compared to the unplanted control (U1), amendment addition invoked global increases in gastrically- and gastrointestinally-available Cd.

For As, G- and GI- bioaccessibility measurements on unamended, unplanted (U1) control and unamended, planted (U2) control CKG-N soils show that the addition of the lettuce model was linked to global decreases in gastric and gastrointestinal As bioaccessibility. Furthermore, with the addition of C6-40 and PS on this planted soil, G- and GI- phase bioaccessible As decreased significantly more. For this geogenously-contaminated soil, decreases in G- and GI- phase bioaccessible As are led both by the C6-40 and PS amendments, and to a greater extent, the addition of the lettuce model.

Notably, the G- and GI- bioaccessibility of Pb was analyzed on all soils, as well as the effects of the common amendments C6-40 and HL. Their common effects on all three soils are summarized in Figure 5-7. Globally, it is seen that gastrically-bioaccessible Pb decreases with the addition of a lettuce model, but gastrointestinally-bioaccessible Pb increases for all of the control soils studied. In terms of amendments, for all soils, both C6-40 and HL tended to reduce both G- and GI- bioaccessible Pb in comparison to the U2 planted control. However, these amendment-led changes in bioaccessibility were weaker in comparison to the combined plant-amendment led changes in bioaccessibility, which had much more influence on both G- and GI- phase Pb when compared to the unplanted (U1) control soils. Conclusively, C6-40 and HL can reduce bioaccessible Pb on planted soils, but this effect is not enough to compensate for the increase in GI-bioaccessible Pb brought by the addition of lettuce on the CKG-N and CKG-L soils.

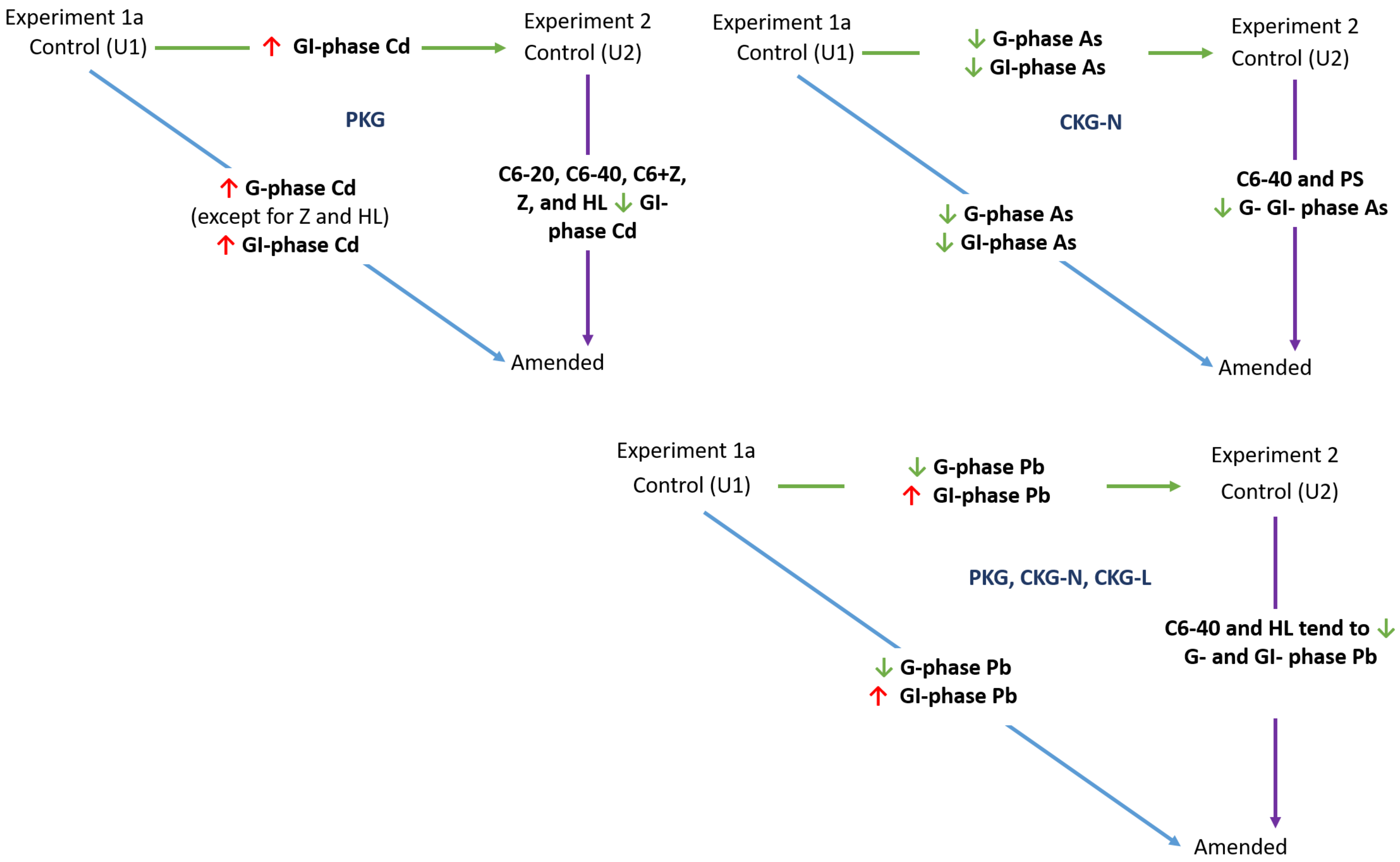
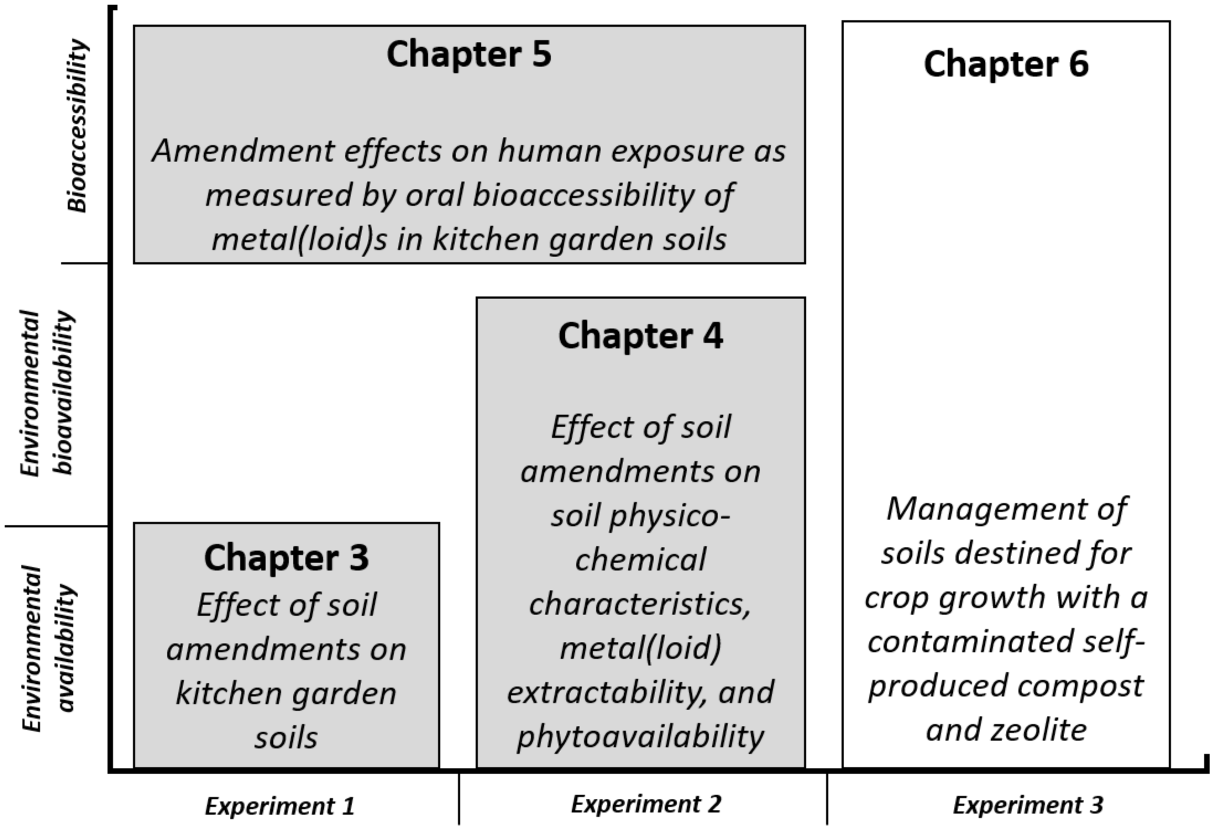


Figure 5-7. Major impacts of lettuce planting and amending on Cd, As, and Pb bioaccessibility measured in PKG, CKG-N, and CKG-L soils

Chapter takeaways

Chapter 5 shows several trends in metal(loid) bioaccessibility. Pb's gastric bioaccessibility was seemingly governed by metal(loid) origins, whereas its GI bioaccessibility was more influenced by its fractionation in the soil. The addition of a plant model tended to lead to decreases in Pb G-bioaccessiblity and increases in Pb GI-bioaccessibility. Several amendments reduced both the G- and GI- bioaccessibility of all the tested metal(loid)s present in a given soil. For PKG, Z and HL reduce the G- and GI-bioaccessibility of both contaminants present on this soil, Cd and Pb. For CKG-N, the OM-rich amendments C6-20, C6-40, C6+Z, and PS reduce G- and GI- bioaccessible Pb and As. On CKG-L, C6-40, C8-40, and HL decrease the G- and GI- bioaccessibility of Pb.

Chapter 6: Management of soils destined for crop growth with a contaminated self-produced compost and zeolite



Chapter 6: Management of soils destined for crop growth with a contaminated self-produced compost and zeolite

The previous chapters showed that the addition of two industrial composts (C6 and C8), collected on the Agriopale composting platform (that meets the quality standard NF U44-051), alone or in combination with zeolite (Z) can reduce metal(loid) mobility, extractability, phytoavailability, and/or oral bioaccessibility in three kitchen garden soils located in different environmental contexts. Many gardeners, however, produce their own composts, which can show variable quality and be contaminated by metal(loid)s present in the amendment's parent material (*e.g.* green garden waste, garden soil). Research carried out on self-produced composts further suggest their potential dangers. A study carried out on kitchen gardens near the former metal smelter MetalEurop found that on average, the composts collected (n=52) contained between 1.9 – 34.5 mg kg^{-1} Cd and 76 – 865 mg kg^{-1} Pb (Pelfrene et al., 2019) . On average, these samples exceeded the legislation concentration limits of Cd and Pb (3.0 and 180 mg kg^{-1}, respectively) for organic amendments. More recently, a study was conducted in Nantes (Kohli et al., 2022), in which the authors showed that up to 85% of self-produced composts exceeded organic farming thresholds for Pb and Zn . Additionally, little is known about the agronomic and environmental interest of these composts when used as an amendment in soils destined for crop growth.

This chapter aims to study a self-produced compost hailing from a contaminated context's release of metals (Cd, Pb and Zn) in soils, and the interest of a co-application of natural zeolite with compost to immobilize these pollutants. The experiment was carried out in two phases. In the first phase, the objective was to study the metal(loid) immobilizing effect of different doses of chabazite zeolite (Z) combined with a self-produced compost (C). The objective of the second phase was to study the environmental and toxicological interest of the co-application of this compost and different doses of Z to manage kitchen garden soils, in particular a non-contaminated (NCS) soil and a contaminated soil (CS) corresponding to CKG-L.

The steps taken to meet these objectives and the results obtained were the subject of an article submitted in Environmental Geochemistry and Health in July 2022, authored and titled as follows:

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Is the co-application of self-produced compost and natural zeolite interesting to reduce environmental and toxicological availability in metal-contaminated kitchen garden soils?

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Abstract

Composting can turn organic waste into a valuable soil amendment that can improve physical, chemical, and biological soil quality. Compost amendments can also contribute to the remediation of areas anthropogenically degraded by metals. However, it well known that compost, particularly self-produced compost, can show enrichment in metals. An experimental study was conducted to examine the short- and long-term distribution and the mobility of metals in soils amended with a self-produced compost when it was added alone or in combination with different doses of a natural zeolite to soil. The aim was also to study the interest of managing moderately metal-contaminated kitchen garden soils by assessing the chemical extractability, phytoavailability and oral bioaccessibility of metals. When zeolite was added to compost alone, it had the tendency to better reduce extractability of Cd and Zn at 25%, and those of Pb at 15%. When the self-produced compost alone or in co-application with zeolite at these doses was applied to soils, the results showed (i) a decrease of NH_4NO_3-extractable Zn; (ii) a reduction of Pb environmental availability, but not Pb bioaccessibility, and (iii) an increase of rye grass biomass. Nevertheless, the risk posed by the self-produced compost was minimal when applied at the proper rate (0.6% w/w). In the selected experimental conditions, the study recommends that self-produced compost be mixed with 15% zeolite to maximize vegetal biomass and minimize environmental risk. The question of sustainability of the results with repeated compost addition is also raised.

Keywords: Contaminated soil; Metals; Amendments; Extractability; Bioaccessibility; Phytoavailability

1. Introduction

The use of composts is one of the most common practices used by farmers and gardeners. Numerous studies have shown the immediate beneficial effect of amending soils with compost. Indeed, compost addition increased plant biomass production, improving soil fertility parameters, such as plant nutrient concentrations in soil, soil structure, water-holding capacity, but also microbial population density and enzyme activity (e.g., De Bertoldi, 1993; Estrella-Gonzaléz et al., 2020; Waitt and Rankin, 2022). Moreover, compost amendments can contribute to the remediation of anthropogenically degraded areas. This includes not only in physical degradation, as the case with for example compacted soils which are poor in organic matter and with low biodiversity, but also chemical degradation with soils contaminated by metallic elements. In the latter case, compost amendments can help reduce food-chain transfer of pollutants (Al Mamun et al., 2016; Awasthi et al., 2019; Das et al., 2016; Gunes et al., 2014;

He et al., 2019; Kumpiene et al., 2019; Li et al., 2015; Liénard et al., 2016; McBride et al., 2014; Szolnoki et al., 2013). The use of composts made from municipal solid wastes, biosolids and their combinations has received great attention in the past four decades. Concerns have been expressed on the high levels of metals in these composts due to the contamination of raw products (e.g. household dust, batteries, disposable household materials) and their possible adverse effects when used as amendments on agricultural soils and the potential hazards of metals to crops, animals and humans. In urban areas, composting has become the major pathway of organic waste disposal for beneficial utilization. Indeed, recycling organic waste to create self-made composts is seen as an increasingly trendy, economically, socially, and environmentally conscious way to find alternatives of recovering household and garden waste (vegetable peelings, grass cuttings, animal excrement, etc.).

Concerns were also raised regarding the quality of these self-produced composts from garden waste. While composts produced on industrial platforms are regularly monitored and are subject to regulations defining, in particular their concentrations of undesirable elements, this is not the case for self-produced composts in vegetable gardens. Indeed, composts produced in the context of kitchen gardens, especially in disturbed areas by past and current anthropogenic activities, can show enrichment in metals (Al Mamun et al., 2016). An overview of self-produced composts found that they typically contain from 1.9 to 34.5 mg kg^{-1} Cd, 8 to 865 mg kg^{-1} of Pb, and 31 to 689 mg kg^{-1} of Zn (Al Mamun et al., 2016; Alvarenga et al., 2008; Attanayake et al., 2015; Barrena et al., 2014; Chelinho et al., 2019; Garau et al., 2019; Pelfrene et al., 2019; Storino et al., 2016; Vasquez et al., 2017; Vaverkova et al., 2020). Thus, regarding this data, it appears that some composts do not comply with reference values, and exceed Cd, Pb and Zn limits for some sellable composts, with the most exigent setting upper limits of 0.7 mg kg^{-1}, 45 mg kg^{-1}, and 200 mg kg^{-1} of Cd, Pb, and Zn, respectively (Biological agriculture 889/2008, WRAP 2014). These metals present in self-made composts hail from contaminated soil, water, and air matrices. Indeed, metals can be uptaken from soil or water into plants and/or be deposited directly on leaves via dust particles. During the composting process, metals in raw materials tend to concentrate as organic matter deteriorates (Richard, 1992).

Questions were also raised about the use of these contaminated composts as amendment on kitchen garden soils in terms of leaching, toxicity to plants and soil microbial activities, as well as sanitary issues in connection with the ingestion of soil particles and vegetables produced. The leachability of metals from composts mainly depends on their composition in humic and non-humic materials which are linked to the degradation degree of organic matter (Murray et al., 2011). These humic substances have a high affinity for metals. Thus, organic matter has the ability to form stable, soluble complexes with metals while maturing, and can play an important role in their dissolution and transfer in the soil profile. Some studies reported that compost amendments may result in the lixiviation of mobile metal-organic complexes in the soil solution (Kaschl et al., 2002; Planquart et al., 1999). Specifically, it has been shown that metal cations can substitute for exchangeable calcium in the inorganic and organic compost fractions. It can therefore be inferred that metals and organic compounds present in self-made composts can impact the fate of the pollutants in the environment and their availability for biosphere including man. Few studies have been carried out on the behavior of metals after application of contaminated self-produced compost to soil. Research has instead focused specifically on the extractability of metals from soils amended with sewage sludge composts or municipal waste composts which tend to be rich in metal (Businelli et al., 2009; Chen et al., 2010; Fang et al., 2017). These studies have suggested that the repeated applications of metal-rich industrial composts can lead to a significant enrichment in metal loadings in the amended topsoils over a long time-period, as well as fresh releases of metals (Businelli et al., 2009; Fang et al., 2017).

To mitigate the effect of the assumed metals present in composts derived from household wastes, literature cites various adsorbents such as peat and coir as potential additives during composting process that could reduce metal leachability (Grimes, 1999). A recent literature review reported that additives (i.e., zeolite, clinoptolite and biochar) significantly reduced by more than 40% the estimated metal bioavailability (i.e., Zn, Pb, Ni, Cu, Cr and Cd) in the final compost products (Abdelrahman et al., 2022). Natural clay minerals such as zeolites have been cited to provoke metal sorption when added to soil or water alone, partly due to the formation of complexes with hydroxyl groups (Cheng and Hseu, 2002; Chlopecka and Adriano, 1997; Kim et al., 2012; Lin et al, 1998; Mahabadi et al., 2007; Oren and Kaya, 2006; Querol et al., 2006; Zhu et al., 2012). This aluminosilicate is moreover commonly available at garden supply shops and relatively inexpensive. It is postulated that zeolites could also help bind metals present in their exchangeable forms in the compost. Studies performed specifically on the effect of natural zeolites in composting process suggested that its addition could reduce maturation time by promoting organic matter degradation, and thus promote the creation of humic acids and buffer pH in a compost (Al Mamun et. al., 2016, Liu et al., 2019, Waqas et al., 2019; Wang et al., 2017; Zhang et al., 2015). Despite the lack of studies on the impact of zeolite-amended compost on the behavior of metals, it was reported that zeolite-amended mature compost can reduce the mobility of Cd, Pb, and Zn in the soil as well as their accumulation in plants grown on amended soil, and shift them to a form linked to organic matter and oxides (Singh et al., 2014; Hamidpour et al., 2017; Herwijnen et al., 2007; Vrînceanu et al., 2019).

The present research seeks to evaluate the effect of using self-produced compost in an environment contaminated by the past activities of a Pb smelter on soil intended for vegetable cultures. The study first examines the addition of a natural chabasite zeolite to compost at different doses and its presumed effects on the immobilization (or behavior) of Cd, Pb, and Zn when contaminated compost is applied to a vegetable garden soil. The most pertinent of these conditions were then tested on two soils presenting different physico-chemical characteristics and degree of contamination, first without vegetation and then with rye grass, to analyze: (i) realistic situations of metal leaching from compost, (ii) the effect of compost alone or in combination with zeolite and (iii) the simultaneous influence of amendment and plant on the environmental and toxicological availability of metals from soil (using chemical extractions and oral bioaccessibility). The end goal of the study was to clarify the role of compost addition in the (im-)mobilization processes of metals from both soil and compost, and therefore assess the interest of zeolite to reduce the potential mobilization.

2. Materials and Methods

2.1 Collection and preparation of materials studied

Experimental *ex situ* assays were conducted on a compost, used alone and in combination with a zeolite, mixed with two soils collected in northern France. Self-produced compost (C) made from garden scraps and grass clippings was collected from a private kitchen garden, which is located in Evin-Malmaison (France) in the former coal-mining area of northern France where considerable atmospheric dust emissions of Cd, Pb and Zn were generated by the former lead smelter Metaleurop Nord (Noyelle-Godault, France). The compost was collected from a plastic composter, and the resulting material was dark brown and highly degraded. After collection, it was gently sieved to 2 mm. This compost containing 22% of organic matter (OM) is well degraded since it composed by 74% of soluble compounds, 7% of hemicellulose, 18% of cellulose, and 1% of lignin. It presented a pH value of 3.6, an electric conductivity (EC) of 4,620 µS cm^{-1}, a C/N of 11, and contained 3.6 g kg^{-1} of available phosphorous (Table 1). The compost also had a cationic exchange capacity (CEC) of 33 cmol+ kg^{-1}, with 17 cmol+ kg^{-1} of Ca^{2+}, 1 cmol+ kg^{-1} of Mg^{2+}, 0.4 cmol+ kg^{-1} of $Na^{+,}$ and 15 cmol+ kg^{-1} of K^+. In terms of contamination degree, the concentrations of Cd, Pb and Zn in the compost were 3.8, 213, and 315 mg kg^{-1}, and exceeded the limits set by NF U44 051 (2006) for organic amendments, and very largely the values provided by EU Eco Label, Biological Agriculture, and WRAP (Waste and Resources Action Program, 2014) by at least three times for Cd and twice for Pb (Table 1). Natural zeolite used in this experiment is commercialized by Chabasite France. It contained 69% chabasite, 20% potassium feldspar, and 2% of other elements. The zeolite had a pH of 8.1, an EC of 115 µS cm^{-1}, a CEC of 102 cmol+ kg^{-1} (with 17 cmol+ kg^{-1} for Ca^{2+}, 0.4 cmol+ kg^{-1} for Mg^{2+}, 10 cmol+ kg^{-1} for Na^+, and 75 cmol+ kg^{-1} for K^+). It was lower in carbonates and available phosphorous than the compost and contaminated soil (Table 1). This amendment was ground to 250 µm before application to favor its homogenization.

Two soil samples, one non-contaminated (NCS) and one contaminated (CS), were collected. On average, the soil texture is silt loam to loam for both samples according to the USDA textural soil classification. The NCS corresponds to the ploughed horizon of an agricultural soil located near Lille in northern France. The CS was collected from a recently closed community garden located in Lille. The soil of this garden is derived from fill and has been under the influence of atmospheric fallout related to past industrial activities (e.g. brickworks, household waste incineration plant) and the proximity of a highway. For each soil, a composite sample was made up of about ten samples taken between 0 and 25 cm in depth. Soil samples were first air-dried at a temperature below 40°C, homogenized, and gently crushed to pass through a 2-mm stainless steel sieve according to the ISO 11464 standard (AFNOR, 1995). Table 1 presents the physico-chemical parameters and degree of contamination of these soil samples. The total carbonate and organic matter contents were higher in CS than in NCS. The pH values were neutral in NCS to slightly alkaline in CS. Compared to the regional agricultural values, the CS was associated with minimal concentrations of Cd and high concentrations of Pb and Zn, while NCS presented concentrations in Cd, Pb and Zn close to the regional geochemical background values (Table 1).

Table 1. Physico-chemical parameters and degree of contamination of zeolite (Z), compost (C) and non-contaminated (NCS) and contaminated (CS) soils in comparison with regulation limits and regional values

	Amendments		***Compost regulation limits***				***Soils***		
	Z	***C***	***NF U 44-051***[a]	***EU Eco Label*** [b]	***Biological agriculture***[c]	***WRAP*** [d] ***(2014)***	***CS***	***NCS***	***Regional values***[e]
pH H_2O	8.1	3.6	-	-	-	6-8	7.7	6.9	-
EC (µS cm^{-1})	115	4,620	-	-	-	600 – 1,500	134	86	-
CEC (cmol+ kg^{-1})	102	33	-	-	-	-	-	-	-
OM (%)	-	22.37	≥20	-	-	-	9.42	3.11	-
C/N	-	10.9	>8				33	0.6	
$CaCO_3$ (g kg^{-1})	2	0.3	-	-	-	-	119	0.1	-
P_2O_5 (g kg^{-1})	0.19	3.92	<30	-	-	-	0.42	0.25	-
Cd (mg kg^{-1})	0.10	3.80	3.00	1.00	0.70	<0.50	0.58	0.37	0.40 ± 0.20
Pb (mg kg^{-1})	47.7	213	180	100	45	<50	384	75	32 ± 17
Zn (mg kg^{-1})	54.5	315	600	300	200	<150	399	55	68 ± 25

[a] NF U 44-051, 2006. Amendements organiques - Dénominations spécifications et marquage.

[b] Waste and Resources Action Program (WRAP), 2014

[c] Biological agriculture (CE n°889/2008)

[d] Mean values and standard deviation (*n* = 232) from Sterckeman et al. (2002).

2.2 Experimental setup

This experiment was carried out in two phases (Figure 1). The first phase aimed to study the effects of zeolite addition at different doses (w/w) on the behavior of the metals present in the self-produced compost after six weeks of exposure. More specifically, the self-produced compost C (100 g) was put in polyethylene pots and mixed well with Z at five rates (0%, 10%, 15%, 20%, and 25% w/w). Each treatment was replicated 3 times. Water (4/5 osmosis, 1/5 tap) was added to 60% of water holding capacity (WHC, pH water = 7) and the pots were stored in a cool, dark place at constant temperature and humidity for a period of 6 weeks. After this time of exposure, samples were collected from each pot and were then air dried and sieved to 2 mm.

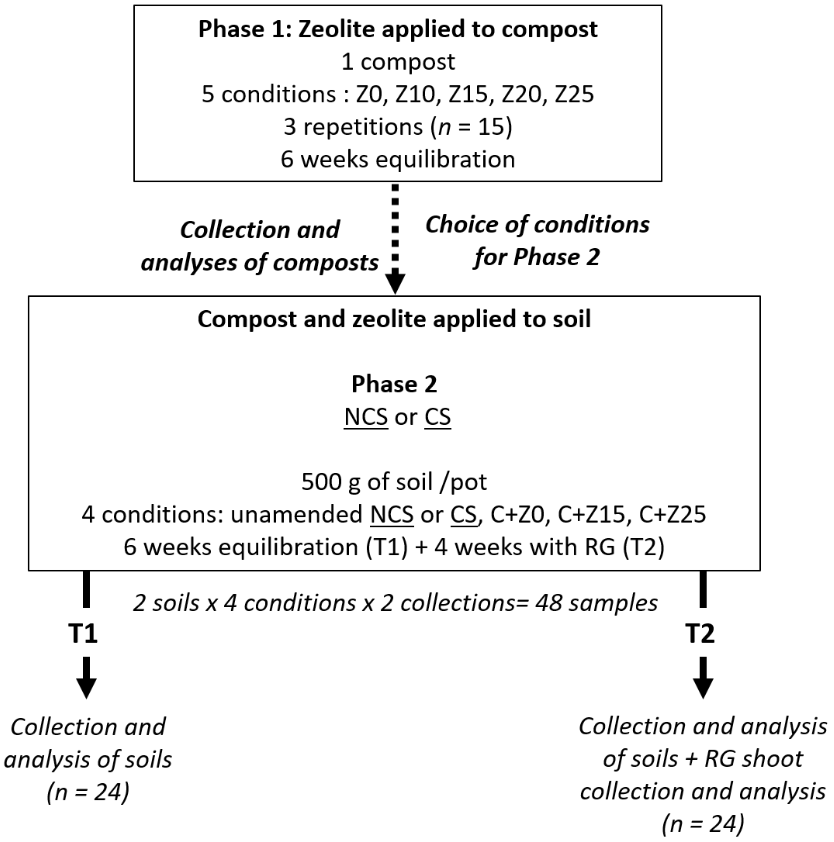

Fig. 1. Experimental design of the study. CS: contaminated soil; NCS: non-contaminated soil; C: compost applied at 0.6% by dry mass; Z0: no zeolite added; Z10, Z15, Z20 and Z25: 10%, 15%, 20%, and 25% respectively of zeolite applied to compost by dry mass; C+Z0: no zeolite mixed with 0.6% of compost and applied to soil; C+Z15 and C+Z25: 15% and 25%, respectively, of zeolite mixed with 0.6% of compost and applied to soil; RG: rye grass.

At the end of this preliminary phase, the doses of Z that best met expectations were selected. The selected compost-zeolite mixtures were then tested in phase 2 on NCS and CS, in conjunction with a vegetal model (i.e., ray grass). More specifically, NCS (500 g) and CS (500 g) were put in pots and mixed well with compost alone (C+Z0) and in combination with zeolite at two rates (C+Z15 and C+Z25). Non-amended soil was used as control (NCS or CS). The rate of 6 g of compost per soil kg, or 0.6% w/w was chosen in concurrence with the recommended value regarding agricultural practices. Each treatment was replicated 6 times (*n* = 24 for each soil). As for phase 1, water was added to 60% of soil WHC and the pots were stored in a cool, dark place at constant temperature and humidity for a period of 6 weeks. At the end of the six-week equilibration period (T1), half the pots (*n* = 12 for each soil) were dried, sieved, and ground for analysis while the other half of the soil-amendment mixes were removed to the greenhouse and seeded with 0.75 g of *Lolium perenne* L. (English rye grass) seeds in each pot. Plants were regularly irrigated with the water mix. After 4 weeks of cultivation (T2), aerial parts of the grass were harvested, double-washed, and dried at 40°C before being ground to 250 µm for analysis. Remaining soil (*n* = 12 for each soil) was removed, dried at 40°C, and sieved to 2 mm and/or ground to 250 µm for further analysis.

2.3 Analytical methods

2.3.1 Physico-chemical parameters of compost and soils

All samples (i.e., compost alone or with zeolite, unamended control soils, and amended soils) were analyzed in the same manner. The pH was measured in a 1:5 volume ratio of 2 mm sieved material to osmosis water suspension, according to NF ISO 10390. Total carbonate content was obtained by measuring the volume of CO_2 released after a reaction with HCl (NF ISO 10693). Conductivity was measured using 1:5 ratio of material sieved to 2 mm and double-distilled water, rotated for 2 hours and then centrifuged at 1,000 *g* for 10 minutes before being measured in the supernatant using a Cond330i/SET – 2C20-0011 with automatic temperature compensation. Assimilated P (expressed in g P_2O_5 kg^{-1}) was measured using an extraction by ammonium oxalate solution followed by the spectrocolorimetric determination of the phosphomolybdic blue complex at 825 nm (NF X31-161) according to the Joret-Hébert method.

2.3.2 Degree of contamination

The pseudo-total metal concentrations in the different materials (amendments, soils, and rye grass) were obtained by Hot Block system-assisted digestion (Environmental Express® SC100, Charleston, SC, USA) and determined by atomic absorption spectrometer (AAS, AA-6800 Shimadzu) for Cd, Pb, and Zn as described by Waterlot et al. (2012). Specifically, 300 mg of each ground soil sample was digested in a mixture of 1.5 mL HNO_3 (70%) and 4.5 mL HCl (37%), namely *aqua regia*, at 95°C for 90 min. Plant samples were mixed with 5 mL HNO_3 (70%), heated for 75 minutes at 95°C, and then digested with 5 mL of H_2O_2 (30%) added over 15 minutes before being heated for 180 minutes more. After mineralization, digestion products were completed to 25 mL with bidistilled water (resistivity 10 MΩ cm^{-1}), filtered using a 0.45 µm cellulose acetate filter and stored at 4°C prior to analysis.

Quality control was based on the use of internal reference soils and reference vegetal matter and provided good recoveries for Cd, Pb, and Zn (102-114%, 100-101%, 98-100%, and 88-90%, respectively, for soil, and 114, 100, and 95% recovery for Cd, Pb, and Zn for vegetal matter).

2.3.3 Extractability of metals

The metals (Cd, Pb, and Zn) in the tested matrices were fractionated using the modified sequential extraction procedure from the SM&T program (Rauret et al., 2000), fully described by Waterlot et al. (2012). Each fraction was noted as F1, F2, F3, or F4 and defined respectively as (i) exchangeable, water- and acid-soluble (40 mL of 0.11 M acetic acid was added to 1 g of soil sample and the mixture was shaken at room temperature for 16 h); (ii) reducible (40 mL of 0.5 M hydroxylammonium chloride was added to the residue from the previously step and the mixture was shaken for 16 h); (iii) oxidizable (H_2O_2 at 30%, followed by 50 mL of 1.0 M ammonium acetate at pH 2 and mixing for 16 h); and (iv) residual (*aqua regia*). The soil pellet was washed with water between each step. Extractable Cd, Pb, and Zn were assessed used a 0.01 M $CaCl_2$ extraction using 3 g of material (i.e., compost alone or in combination with zeolite) ground to 250 µm agitated with 30 mL of solution for 2 hours before being centrifuged at 4,500 *g* for 20 minutes, and then filtered with a 0.45 µm cellulose acetate filter. Ammonium nitrate-extractable metals were analyzed using 10 g of matrix sieved to 2 mm agitated with 25 mL of a 1 M NH_4NO_3 solution for 1 hour and 20 minutes. Samples were centrifuged at 1,500 *g* for 10 minutes, and then filtered with a 0.45 µm cellulose acetate filter (NF ISO 19730). EDTA salt-extractable metals were quantified using 4 g of matrix sieved to 2 mm agitated with 40 mL of a 0.05 M EDTA solution with a pH of 7 for 1 hour as according to the BCR method (Quevauviller, 1998). Samples were then centrifuged at 4,500 *g* for 20 minutes, and then filtered with a syringe and 0.45 µm cellulose acetate filter. All extracted metal concentrations were determined using AAS and verified using certified materials.

2.3.4 Oral bioaccessibility of Pb

In vitro oral bioaccessibility was only determined for Pb on the contaminated soil (CS) and was evaluated according to UBM (Unified Bioaccessibility Method; ISO 17924) adapted by Pelfrêne et al. (2020), where gastrically- and gastrointestinally-available metal was determined. The degree of contamination of Cd in the CS soil was too low to allow for the determination of bioaccessible Cd. Briefly, 0.6 g of dry unamended and amended soils were placed in centrifuge tubes and mixed with 9 mL of simulated saliva fluid. After a quick manual shaking (10 s), 13.5 mL of simulated gastric fluid were added, and the pH of the solution was adjusted to 1.2 ± 0.05 with HCl (37%). The tubes were shaken end-oved-end at 37°C for 1 hour and centrifuged at 4,500 *g* for 5 min. The supernatant constitutes the gastric-only phase. Then, the gastro-intestinal phase was prepared with gastric-only phase, in which 27 mL of simulated duodenal fluid and 9 mL of simulated bile solution was added. The final pH should be ranged from 5.8 to 6.8 by adjusting with NaOH (10 M). Tubes were shaken end-over-end at 37°C during 4 h and centrifuged at 4,500 *g* for 5 min. Bioaccessible concentrations of Pb in supernatant of both phases were measured by AAS. To evaluate analytical recovery, a blank and a NIST standard reference material (SRM2710a) were used. Mean recoveries in SRM 2710a ($n = 4$) were 106% for Pb in the gastric phase, and 110% in the gastro-intestinal phase. The bioaccessibility of Pb was expressed as a ratio between the extracted concentrations in gastric (G) or gastrointestinal (GI) phases and the pseudo-total concentrations in the soil.

2.4 Data treatment

All data was analyzed using three replicates for each modality of each phase. Based upon parametricity, differences between controls and amended modalities were calculated using a student T-test or Wilcoxon test for data collected at the same time. Differences among conditions were calculated using a one-way ANOVA and a post-hoc Tukey test. A one-way ANOVA and a post hoc Bonferroni test were used to find differences among data collected over time, between T1 and T2. Analyses were done using XLSTAT 2019.3.2 and Microsoft Excel 2016.0.4966.

3. Results and discussion

3.1 Effects of zeolite addition on physico-chemical parameters and extractability of metals from compost

In phase 1 of the experiment, compost was amended with 0%, 10%, 15%, 20% and 25% of zeolite. Table 2 presents the effects of these additions on physicochemical parameters of the matrices and the availability of metals as evaluated by various chemical extractions of varying strengths (i.e., $CaCl_2$, NH_4NO_3 and EDTA). The addition of all rates of zeolite was linked with no significant change in a compost's pH. None of the zeolite rates tested was able to buffer the compost mixes since their pH remained between 3.6 and 3.8 units of pH (Table 2). The acidic characteristic of the compost studied is not ordinary for a mature compost. Mature composts are thus generally neutral to slightly alkaline (from 7 to 9 pH units), with typical commercialized composts having a pH between 6 and 8 (Avnimelech et al., 1996; Forster et al., 1993; Table 1). This acidic character could be explained by raw materials (mainly made with grass clippings and garden green wastes) and anaerobic composting conditions which confer to the compost a particular distribution of the ligno-cellulosic compounds, rich in soluble compounds and poor in lignin and cellulose (73% of soluble compounds, 7% of hemicellulose, 19% of cellulose and 2% of lignin). The degradation of cellulose in anaerobic condition leads to the formation of soluble organic acids which explains the high and low amounts of soluble and cellulose fractions respectively and the acid pH of the compost (Leschine, 1995). Additionally, the tested compost had an OM content of 22%, whereas a typical commercialized compost has no more than 20% OM. Nevertheless, regardless of its acidity and OM content, the compost studied can be considered as mature due to other indicators. A mature compost is indeed characterized by a C/N ratio of less than 25 and a CEC value more than 60 meq per 100 g of OM (Iglesias-Jimenez & Perez-Garcia, 1989; Roletto et al., 1985). The compost studied effectively presents a C/N of 11 and a CEC of 33 $cmol^+ kg^{-1}$ corresponding to 1,392 meq per 100 g of OM (Table 1). This compost complied also with the C/N reglementary values for commercialized compost which have to be more than 8 (Table 1). However, its EC value exceeded from 3 to 8 times the values of commercialized composts (Table 1). Generally, the addition of zeolite during composting is associated with an increase of pH and a decrease of salt content (Chan et al., 2016; Liu et al., 2022; Mao et al., 2019; Soudejani et al., 2019; Wang et al., 2017). In Phase 1, a significant decrease in conductivity from 4.3 mS cm^{-1} to 3.8 mS cm^{-1} occurred with the addition of zeolite, as did for available phosphorous from 3.9 g kg^{-1} to 3.1 g kg^{-1} with the addition of 15%, 20%, and 25% zeolite (Table 2). The slight decrease of EC with zeolite amount increase could be also explained since chabazite has also a good selectivity for univalent cations with low charge density as NH_4^+ or Na^+ which might be released from the compost (Colella, 1999). This could also suggest that the addition of zeolite reduced the formation of or adsorbed metallic salts, which increase EC (Moreno et al., 1997).

Table 2. Effects of the addition of zeolite (Z) at different doses to compost (C) on its physico-chemical parameters and metal extractability (mean values and standard deviation)

		C+Z0	C+Z10	C+Z15	C+Z20	C+Z25
pH water		3.6 ± 0.1a	3.7 ± 0.01a	3.7 ± 0.01a	3.8 ± 0.03a	3.7± 0.2a
EC (mS cm^{-1})		4.3 ± 0.1a	4.0 ± 0.05b	3.9 ± 0.05b	3.8 ± 0.03b	3.8 ± 0.08b
P_2O_5 (g kg^{-1})		3.9 ± 0.2a	3.3 ± 0.3a	3.2 ± 0.3b	3.0 ± 0.2b	3.1 ± 0.04b
Pseudototal (mg kg^{-1})	Cd	3.4 ± 0.2a	3.5 ± 0.3a	3.0 ± 0.1a	3.5 ± 0.9a	3.4 ± 0.1a
	Pb	232 ± 6a	224 ± 9a	220 ± 6a	210 ± 15a	207 ± 12a
	Zn	304 ± 5a	285 ± 9a	266 ± 3a	244 ± 7a	246 ± 4a
$CaCl_2$ (%)	Cd	51.6 ± 8.5a	28.6 ± 4.1b	32.9 ± 4.0b	13.8 ± 3.2b	19.0 ± 14.5b
	Pb	0.18 ± 0.1a	0.09 ± 0.04a	0.11 ± 0.04a	0.15 ± 0.01a	0.13 ± 0.04a
	Zn	19.1 ± 0.8a	16.5 ± 0.6b	15.5 ± 0.2b	15.4 ± 0.1b	13.9 ± 0.2b
NH_4NO_3 (%)	Cd	25.4 ± 0.6a	22.6 ± 3.4a	22.6 ± 3.2a	22.9 ± 2.8a	23.6 ± 3.3a
	Pb	0.83 ± 0.03a	0.57 ± 0.04b	0.41 ± 0.07b	0.38 ± 0.02b	0.33 ± 0.03b
	Zn	20.2 ± 0.4a	18.8 ± 0.4b	17.7 ± 0.2b	18.7 ± 0.4b	17.4 ± 0.5b
EDTA (%)	Cd	97.7 ± 7.9a	88.3 ± 8.5a	92.2 ± 2.8a	78.1 ± 18.1a	77.9 ± 7.5a
	Pb	44.5 ± 1.3a	36.9 ± 0.6b	32.5 ± 2.5b	60.0 ± 2.6c	57.3 ± 2.3c
	Zn	50.4 ± 1.1a	49.5 ± 1.8a	49.9 0.3a	50.0 ± 1.0a	47.3 ± 0.9b

C+Z0: no zeolite mixed with 0.6% of compost, C+Z10, C+Z15 and C+Z25: 10%, 15% and 25% of zeolite respectively mixed with 0.6% of compost. Letters indicate significant differences between the conditions ($p < 0.05$).

The effect of zeolite on the Cd, Pb and Zn availability from non-conforming compost was assessed through chemical extractions. Metal extractions by $CaCl_2$ and NH_4NO_3, which simulate metal fraction in soil pore water, was used to provide an estimate of the displacement of easily soluble metals (cation exchange process) and are suitable to predict the metal uptake by plants from contaminated soils though these extraction reagents have similar ionic strength that exists in soil solution. Their unbuffered character causes reactions and interactions that occur at the pH of the soil (Gryschko et al., 2004; Houba et al., 2000; Lebourg et al., 1998; Vincreanu et al., 2019). EDTA, a strong chelator which can compete with more strong binding sites in soil (complexation processes), was used to assess the pool of metals absorbed both by organic matter, (hydr-)oxides (Fe, Al, Mn) and carbonates of soil with low carbonate contents (Quenea et al., 2009; Sahuquillo et al., 2003). Some authors consider that EDTA could be reliable to predict plant availability of metal(loid)s (Dai et al., 2008; Zhu et al., 2012). As expected, Cd, Pb and Zn in non-conforming compost were highly extracted by EDTA (98, 45 and 50% respectively) compared to the two other extractants due to its high extraction strength. Some differences appeared between the extraction ability of $CaCl_2$ and NH_4NO_3. Calcium chloride was able to extract more Cd than NH_4NO_3 (52 vs 25%), suggesting that a major part of Cd was weakly bound to compost constituents. The reverse was observed for Pb (0.2 vs 0.8%), whereas a similar extraction capacity was noted for Zn (approximately 20% extractable by both $CaCl_2$ and NH_4NO_3). Although EDTA removed similar amounts of Zn and Pb (50% and 45% respectively), $CaCl_2$ and NH_4NO_3 extracted 20 times more Zn than Pb from the compost. This suggests that Zn could be distributed both in the soluble/exchangeable and organic fractions of this compost. Thus, the metals present in this compost can be classified according to their availability as follows: Cd > Zn > Pb.

Metals present in the compost reacted differently to the addition of zeolite as analyzed by the three extractions. Exchangeable Cd as analyzed by the $CaCl_2$ extraction was reduced by the addition of any rate of zeolite (from 52 to 14%), a tendency which also presented itself in the NH_4NO_3 extractions (from 25 to 23%) (Table 2). Though no significant difference between the control and other conditions were found with EDTA extractions, all zeolite-amended composts were associated with less available Cd, especially with 20 and 25% zeolite for which a decrease of approximately 20% in the extracted Cd was observed (Table 2). Concerning Pb, the $CaCl_2$ extraction showed no difference with zeolite's addition (Table 2). However, exchangeable Pb as analyzed by NH_4NO_3 was significantly reduced as the rate of applied zeolite increased. With doses including and above 15% of zeolite, extractability was at least halved in comparison to the control. A similar trend was observed with EDTA extractions. Additions of 10% and 15% of zeolite generated significantly less extracted Pb than the control (37 and 33% vs 45% respectively). However, with 20% and 25% of zeolite, extraction of Pb was significantly increased, with EDTA removing 1.3 times more than in the control, and between 1.5 to 1.8 times than the lower zeolite mix doses (Table 2). Exchangeable Zn measured with $CaCl_2$ and NH_4NO_3 extractions slightly decreased with the addition of zeolite by between 1.4 and 5.2% in comparison to the control (Table 2). However, no significant difference or clear trend in mobility was seen for Zn extracted with EDTA, aside from small decrease in availability with the addition of 25% zeolite (Table 2).

The comparison of extractability trends observed among metals and extractants reveals information about immobilization mechanisms and metal speciation in the compost. Cation exchange, adsorption processes, and precipitation/coprecipitation mechanisms controlled by insoluble/soluble products interacting with zeolites govern compost-metal reactions (Belviso, 2020; Ibrahimi and Sayyadi, 2015; Misaelides, 2011). The decrease of $CaCl_2$ and/or NH_4NO_3 Cd and Zn extractability observed with the addition of zeolite suggests that these elements were mainly present as free ions and immobilized by zeolite through ion exchange (Lebourg et al., 1998). For Cd and Zn, however, no differences were seen with the EDTA extraction in presence of zeolite. For Pb, since extractable NH_4NO_3 and EDTA-extractable Pb decreased with amendment, the mechanism involved was different. Considering that the extraction rate of Pb by relatively weak $CaCl_2$ and NH_4NO_3 was lower as compared to EDTA and the other metals, Pb was likely precipitated or complexed (Hettiarachchi et al., 2003). This metal was likely mainly bound to (hydro)-oxides or organic compounds contained in the compost, as composts contain inorganic components such as Fe, Mn, Al oxides which can bind metals through irreversible processes (Hettiarachchi et al., 2003). The complexation of metals (i.e., Cd, Ni, Zn, Cu, Pb) can also occur with organic functional groups such as carboxyl, carbonyl and phenols of humic substances or with more broadly dissolved organic matter (DOM), abundantly contained in composts (Ahmad et al., 2017; Pennanen et al., 2020; Welikala et al., 2018). It has been shown in particular that compost has a greater adsorption affinity for Pb than Cd and Zn (Pennanen et al., 2020). Indeed, Pb could be co-precipitated with (hydr-)oxides contained in both compost and zeolite, or bound in metal-organic complexes formed at a pH of less than 6.5 (Hettiarachchi et al., 2003; Lebourg et al., 1998; Quenea et al., 2009; Sahuquillo et al., 2003; Shi et al., 2009a). The increased doses of zeolite could be accompanied by a rise of (hydr-) oxides that enhanced the formation of EDTA-extractable $Pb(OH)_2$ precipitates Moreover, zeolite could have a dispersive effect on OM that would induce an increase of DOM concentration and consequently a high metal leaching caused by metal-DOM complexes (Oste et al., 2002). The more zeolite rate increased, the more DOM content increased and Pb leached, thus explaining the increase of EDTA-extractable Pb from 20% of zeolite. Zeolite also exhibits a selectivity for cations such as H^+ ions in an acidic medium like this compost. More specifically, it exhibits preference for specific cations. This alumino-silicate generally has a higher affinity for weakly bound monovalent cations (e.g., NH_4^+, Cs^+) than divalent cations (e.g., Cd^{2+}, Pb^{2+}, Zn^{2+}) (Phillips, 1998). Concerning divalent cations specifically, chabasite exhibits selectivity for divalent cations with low hydration energy such like Pb^{2+}. However, it binds to a much lower extent divalent cations with high hydration energy such as Cd^{2+} and Zn^{2+} (Colella, 1999). Moreover, the efficiency of zeolite in metal(loid) immobilization decreases when multiple contaminants exist due to competition (Reddy et al., 2014). This could explain the difference in zeolite efficiency according to the metal and the amount of zeolite tested in this study. This is specifically relevant to explain the increase of Pb extractability by EDTA with doses including and exceeding 20% of zeolite added to non-conforming compost.

Based upon results of this experiment testing various rates of zeolite on extractable metals in a self-produced compost, the compost amended with 15% and 25% of zeolite (C+Z15 and C+Z25, respectively) were considered the most pertinent conditions to test applied to soils.

3.2 Assessment of the co-application of compost and zeolite on NCS and CS soils

3.2.1 Effect of the co-application of compost and zeolite on soil physico-chemical parameters

Table 3 presents physico-chemical parameters of unamended and amended NCS and CS by considering the amendment effects before seeding rye grass (T1) and after rye grass growth (T2). For NCS at T1, the addition of acidic compost with or without zeolite resulted in a significant decrease of 0.3 units in soil pH. To a lesser extent, this decrease was also observed after rye grass growth (T2). The decrease of pH observed in the amended NCS could be due to the production of acidic compounds during compost oxidation on an acidic soil (Hamidpour et al., 2017). Regarding T1, the growth of ryegrass (T2) increased the soil pH between 0.3 to 0.5 units of pH (Table 3). At both sampling times, the addition of amendments significantly increased EC, from 112 µS cm^{-1} to 169 µS cm^{-1} for T1 and from 85 µS cm^{-1} to 143 µS cm^{-1} at T2. Moreover, EC raised as the amount of zeolite increased. The EC was significantly weaker after the rye grass growth in NCS (85 µS cm^{-1}) and C0+Z25 (143 µS cm^{-1}) compared with unplanted soils T1 (112 and 169 µS cm^{-1} respectively). The same trend was noted for C+Z0 and C+Z15 with 112 and 130 µS cm^{-1} vs 146 and 156 µS cm^{-1} respectively. However, amendments (T1) alone or with ryegrass (T2) did not impact the carbonate and available P contents, except for C+Z0 associated with a significant loss of $CaCO_3$ and, for C+Z25 at T2, where a slight increase of available P was observed.

The effect of the contaminated compost addition on physicochemical parameters of a moderately contaminated kitchen garden soil (CS) were also analyzed (Table 3). For this soil before the rye grass growth (T1), the addition of compost alone (C+Z0) slightly but significantly decreased soil pH in comparison to the control, from 7.7 to 7.5, as observed for NCS. This was probably due to the compost's high acidity (3.6 units, Table 1) although the CS's $CaCO_3$ content was higher in comparison to NCS (70 vs 0.6 g kg^{-1}) and compost addition rate was small (0.6%). This acidity seemed to be offset by zeolite since no significant effect was observed in C+Z15 and C+Z25 compared with CS. Though amendments had little significant effect on physicochemical parameters studied, EC tended to increase with the addition of the amendments and increasing amounts of zeolite (Table 3). This trend was also observed after rye grass growth (T2) with a significant EC increase in soil amended with C+Z15 compared with CS (190 vs 156 µS cm^{-1}). The decrease of carbonate content observed for this condition might be linked with a heterogeneity of this component suggested by variation in $CaCO_3$ concentrations noted between the original and pot experiment soils (119 vs 70 g kg^{-1} in T1 and 81 g kg^{-1} in T2). Compared with T1, the growth of rye grass (T2) in CS induced an increase from 0.1 to 0.3 units of soil pH in all conditions excepting C+Z25, as well as a significant decrease of about 1.4 times in EC for all conditions excepting C+Z0, as observed in NCS. The absence of a pH increase in the mix with highest zeolite amount could be due to the buffering ability of zeolite because of its affinity for cations among which H^+ ions (Usman et al., 2005). Between T1 and T2, $CaCO_3$ increased for the unamended (CS) and C+Z0 soil whereas the addition of zeolite had no impact on carbonates contents. These differences could be a result of heterogeneous soil $CaCO_3$ or could suggest a link between the addition of zeolite to compost, and the subsequent decrease of $CaCO_3$.

Compared with both soils (NCS and CS) at T1, the growth of rye grass (T2) induced a global increase in soil pH, as well as a decrease in EC. These common findings could be a result of the effects of the rhizosphere, in particular the release of root exudates and plant uptake of nutrients from soil solution (Reichman, 2002; Rengel, 2002). The decrease of soil EC was presumably linked with uptake by the plant. The overall effects of amendments on these two parameters can be explained by the acidic nature of the compost and the richness of zeolite and compost in salts (i.e., 115 and 4,620 µS cm^{-1} respectively; Table 1) though applied to soil at a relatively low rate of 0.6%. Concerning $CaCO_3$, its content tended to increase in CS in the presence of the plant system. Additionally, for CS, for both the control and the C+Z0 amended soils, this increase was significant between T1 and T2. When mixed with increasing amounts of zeolite, soil $CaCO_3$ and its byproducts can be trapped by zeolites in greater quantities as they capture carbon gases, especially in the presence of CaO, $CaOH_2$, amorphous silicates, and an acidic environment like that of the compost (Wee, 2013). This capture is further aided in the presence Na^+ ions, present at 10 cmol+ kg^{-1} Na in the zeolite and 0.4 cmol+ kg^{-1} in the self-made compost studied (Monasterio-Guillot et al., 2020.) The compost's low pH, and to a smaller extent, its Na^+ content, could partially determine the ability of zeolite to trap $CaCO_3$ and render it less available. Exchangeable Ca and Na would need to be studied in order to have further information about the plausibility of this theory.

Table 3. Physico-chemical parameters of NCS and CS soils unamended and amended with compost alone (C+Z0) or in combination with zeolite 15% (C+Z15) and 25% (C+Z25) before (T1) and after (T2) rye grass growth presented with mean values and standard deviation

	NCS				CS			
	Unamended	C+Z0	C+Z15	C+Z25	Unamended	C+Z0	C+Z15	C+Z25
Amendment effect "T1"								
pH	7.0 ± 0.0a	6.7 ± 0.0b	6.7 ± 0.0b	6.8 ± 0.0b	7.7 ± 0.0a	7.5 ± 0.0b	7.6 ± 0.0a	7.7 ± 0.0a
EC (µS cm^{-1})	112 ± 6a	146 ± 9b	156 ± 10b	169 ± 7b	225 ± 29a	239 ± 21a	271 ± 13a	265 ± 8a
$CaCO_3$ (g kg^{-1})	0.6 ± 0.2a	0.6 ± 0.1a	0.3 ± 0.2a	0.5 ± 0.3a	70 ± 1a	71 ± 2a	72 ± 1a	72 ± 2a
P_2O_5 (g kg^{-1})	0.26 ± 0.00a	0.27 ± 0.00a	0.27 ± 0.00ab	0.29 ± 0.00b	0.40 ± 0.01a	0.41 ± 0.01a	0.40 ± 0.02a	0.39 ± 0.01a
[Cd] mg kg^{-1}	0.47 ± 0.06a	0.43 ± 0.09a	0.55 ± 0.08a	0.57 ± 0.07a	1.08 ± 0.10a	1.19 ± 0.07a	1.27 ± 0.19a	1.15 ± 0.17a
[Pb] mg kg^{-1}	110 ± 6a	113 ± 2a	117 ± 1a	119 ± 4a	402 ± 36a	563 ± 124a	510 ± 91a	485 ± 119a
[Zn] mg kg^{-1}	56 ± 2a	59 ± 1a	59 ± 1a	61 ± 4a	381 ± 16a	400 ± 13a	403 ± 6a	379 ± 29a
Plant + amendment system effect "T2"								
pH	7.3° ± 0.0a	7.2° ± 0.0b	7.1° ± 0.0b	7.2° ± 0.1b	7.8 ± 0.0a°	7.8 ± 0.0a°	7.9 ± 0.0a°	7.7 ± 0.2a
EC (µS cm^{-1})	85° ± 5a	112 ± 15a	130 ± 16b	143° ± 5c	156± 11a°	160 ± 17a	190 ± 10b°	188 ± 16a°
$CaCO_3$ (g kg^{-1})	0.5 ± 0.0a	0.2 ± 0.2a°	0.2 ± 0.2a	0.7 ± 0.1a	81± 2a°	80 ± 4a°	71 ± 2b	75 ± 3a
P_2O_5 (g kg^{-1})	0.31° ± 0.00a	0.31° ± 0.00a	0.32° ± 0.02a	0.31° ± 0.00a	0.43 ± 0.01a	0.42 ± 0.01a	0.43 ± 0.01a	0.44 ± 0.01b
[Cd] mg kg^{-1}	0.14 ± 0.07a	0.20 ± 0.06a	0.16 ± 0.02a	0.49 ± 0.15b	0.68 ± 0.13a	0.67 ± 0.19a	0.66 ± 0.08a	0.73 ± 0.03a
[Pb] mg kg^{-1}	111 ± 6a	118 ± 8a	122 ± 4a	130 ± 18a	464 ± 80a	555 ± 169a	368 ± 11b	352 ± 16b
[Zn] mg kg^{-1}	55 ± 2a	57 ± 1a	65 ± 7a	62 ± 2a	391 ± 2b	413 ± 21b	384 ± 11b	352 ± 16a

Different letters indicate significant differences between the control soil and a given condition, * denotes a difference between C+Z0 and other mixes, and ° denotes a difference between T1 and T2 for a given condition. T1: after 6 weeks of equilibration, T2: after 6 weeks of equilibration and 4 weeks of rye grass growth in greenhouse.

3.2.2 Effect of the co-application of compost and zeolite on soil metal fractionation

Sequential extractions were performed on Pb and Zn for both the NCS and CS (Figure 2 and Figure 3, respectively). At both T1 and T2, the amount of Cd in each fraction of soils was below the limit of detection, and consequently not shown in Figure 2. At T1, the chemical distribution of Pb in NCS showed that this element was not very mobile, as 4% was found in Fraction 1 whereas 77% was in Fraction 2, 7% in Fraction 3, and 12% in Fraction 4. The addition of compost alone or in combination with zeolite did not impact the distribution of Pb in NCS in spite of a slightly significant increase of Pb present in Fraction 3 (+1%) was observed for C+Z0 and C+Z15 in comparison with the NCS control. In CS, the distribution of Pb was similar to those of NCS, with 1% in Fraction 1, 74% in Fraction 2, 4% in Fraction 3, and 21% in Fraction 4 (Figure 4). The addition of amendments in this soil also did not change the chemical distribution of Pb. However, Abbaspour and Golchin (2011) and Hamidpour et al. (2017) reported that, with the addition of compost and zeolite, Pb concentrations can increase in the organic soil fraction (F3), and decrease in more available carbonate-bound (F1) and Fe- and Mn- bound fractions (F2) due to Pb fixed by humic substances. This could be explained results obtained for C+Z0 and C+Z15 in NCS. For Zn in NCS (T1), there is significantly less Zn present in Fraction 1 of the soil amended with C+Z15 than the unamended control (Figure 3). A similar trend was observed for C+Z25. Fractionation of Zn in the CS is similar to NCS, with 18% being found in F1, 35% being found in F2, 16% in F3, and 31% in F4 (Figure 4). There are no significant differences among conditions.

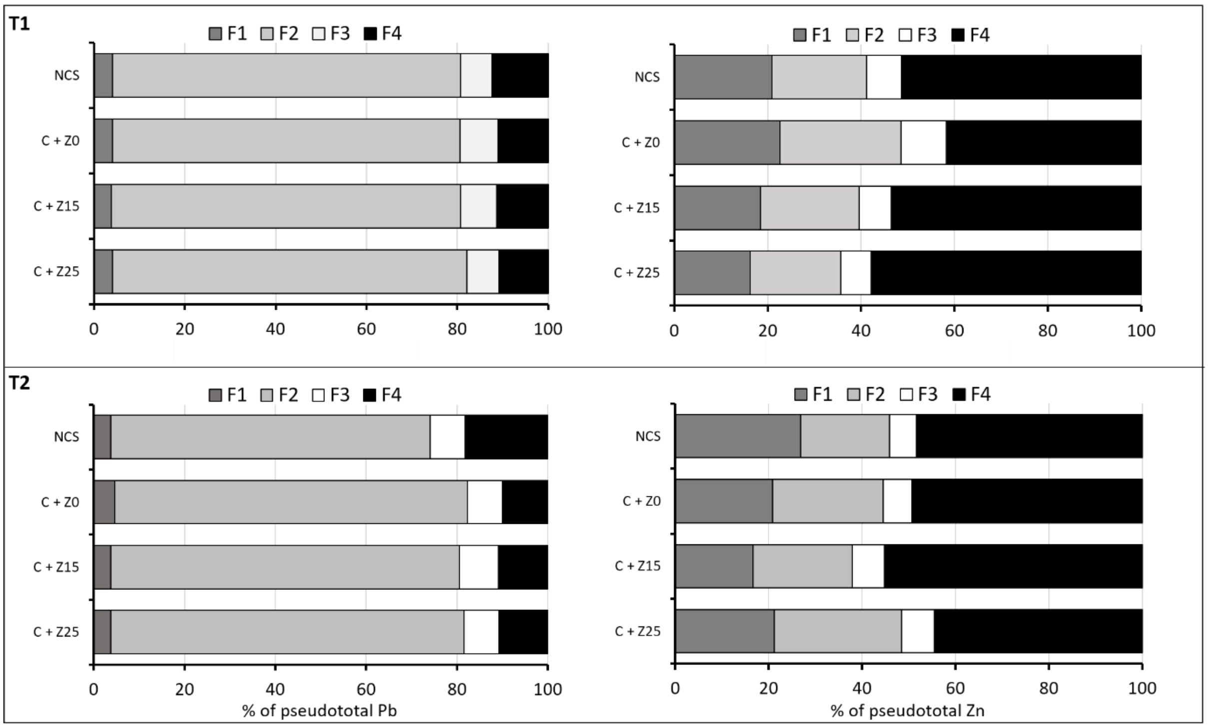

Fig. 2. Fractionation of Pb and Zn at T1 and T2 in NCS (non-contaminated soil); C: compost applied at 0.6%; Z0: no zeolite applied, Z15: 15% of zeolite applied to compost by dry mass, Z25: 25% of zeolite applied to compost (w/w), T1: after 6 weeks of equilibration, T2: after 6 weeks of equilibration and 4 weeks of rye grass growth in greenhouse.

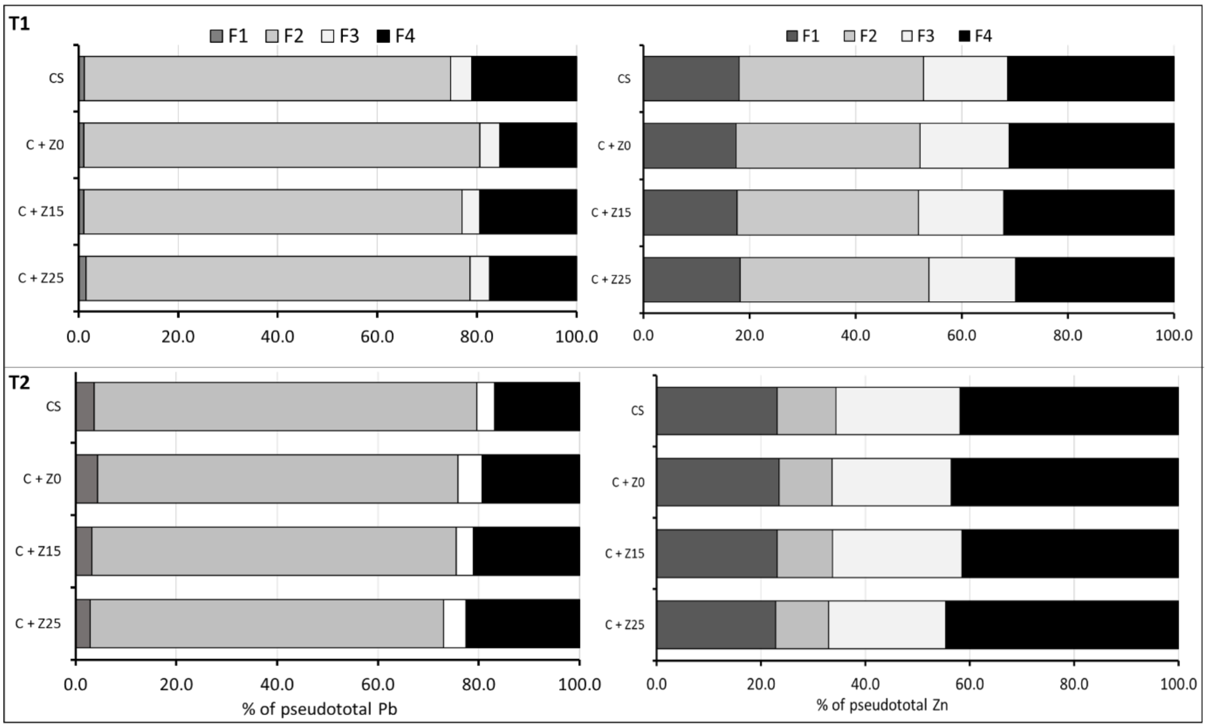

Fig. 3. Fractionation of Pb and Zn at T1 and T2 in CS (contaminated soil); C: compost applied at 0.6%; Z0: no zeolite applied, Z15: 15% of zeolite applied to compost by dry mass, Z25: 25% of zeolite applied to compost (w/w), T1: after 6 weeks of equilibration, T2: after 6 weeks of equilibration and 4 weeks of rye grass growth in greenhouse.

At T2, there is no significant change in fractionation for any condition compared with T1 in NCS (Figure 2). However, for CS, each condition had significantly more Pb present in Fraction 1 than at T1 (3% increase) whereas no effect of amendments was observed in other fractions (Figure 3). This could suggest that the rhizosphere mobilized Pb already present in the CS soil. Though one study found that the aging of applied compost on soil can affect Pb speciation, the effect of the rhizosphere was shown to sometimes mitigate this effect (Attanayake et al., 2017). Indeed, a lack of change in Pb speciation over time was attributed to the acidifying effect of the rhizosphere of certain plants such as tomatoes (Hashimoto et al., 2011). Zinc was mainly found in residual fraction (F4, 51%), 20% were in each F1 and F2, and 7% were in F3 (Figure 2). Likewise, a study on the partitioning of Zn in municipal solid waste composts found that the majority of Zn was found in F4 or in F2 bound to iron oxides (Paradelo et al., 2011). Due to data variability, there were no significant differences among conditions for any metal at T2 with the introduction of rye grass. For the CS, Zn was similarly found mostly in the residual fraction (42%) (Figure 3). However, much more Zn was found in F1 and F3 (23% and 24%, respectively) than in F2, which had the lowest concentration of Zn at 11% (Table S1 in Supplementary materials). Regarding the effect of compost with or without zeolite at T2, there is no significant difference in Pb fractionation among conditions for both NCS and CS. This suggests that rye grass cultivation did not alter Pb fractionation significantly. There is, however, a tendency for the compost-amended soil C+Z0 to accumulate more Pb in the most available soil fractions in comparison to the control soil alone, and, to a lesser extent, the Z-amended compost additions. Thus, with plant system, the addition of zeolite to compost and a non-contaminated soil may mitigate the impacts of compost Pb leachates into the two most available soil fractions. This could simply be due to the effect of the rhizosphere and subsequent shifts in pH and metal(loid) availabilities as well.

3.2.3 Effect of the co-application of compost and zeolite on metal environmental availability

The environmental availability of metals from compost (with or without zeolite) and/or soils was assessed by NH_4NO_3 and EDTA extractions. The Figures 4 and 5 present the results obtained on NCS and CS, respectively. For NCS, the soil presenting a very low degree of contamination, it appeared that metals (i.e., Cd, Pb and Zn) in the unamended (i.e., control) NCS were weakly extracted by NH_4NO_3, where less than 0.01 mg kg^{-1} (4%) Cd, and 0.07 and 0.04 mg kg^{-1} (about 0.1%) Pb and Zn were removed. This extraction thus extracted less Pb and Zn than Fraction A of the sequential extraction. By contrast, metals were more extractable by EDTA. This extractant removed all Cd, up to18.7 mg kg^{-1} (33%) of Pb, and up to 12.1 mg kg^{-1} (25%) of Zn. For the CS, similar amounts of metals were extracted by NH_4NO_3. Up to 0.01 (2%), 0.07 (0.02%), and 0.15 (0.04%) mg kg^{-1} of Cd, Pb, and Zn were extracted. With the stronger extractant (EDTA), more metals were extracted: up to 0.53 (52%), 9.22 (19%), and 73.07 (67%) mg kg^{-1} of Cd, Pb, and Zn as in NCS. It is seen that by concentration of pseudo-total metals in mg kg^{-1}, the weaker extraction removed comparable amounts in both NCS and CS soils. The stronger extraction removed less Cd and Pb in the NCS by concentration of pseudo-total metals, and more Zn. This, however, translates to more Cd and Pb extracted by percentage in the less contaminated NCS soil, and more Zn extracted in the contaminated CS soil. In Phase 1, on the compost alone, nearly all Cd was removed by EDTA and 45% of Pb, and 50% of Zn, not dissimilarly from the NCS and CS soils. These results suggest that most Pb and Zn is not exchangeable but bound tightly with soil constituents. Pb is mainly bound with (hydr)-oxides of Fe, Al, and Mn (77%), whereas Zn is found in crystallized fraction (51%) as shown their chemical distribution in NCS (Figure 2).

None of the amendments resulted in a significant change in Cd extractability with NH_4NO_3 extraction before (T1) and after (T2) the rye grass growth in comparison to the control NCS (Figure 4). By contrast, Cd extracted from soil mixes by EDTA tended to slightly increase with additions of zeolite in T1. At T2, the amount of Cd extracted by EDTA was significantly higher with compost mixed with 25% of zeolite than for the other conditions (from 0.14 mg kg^{-1} to 0.34 mg kg^{-1}). This result indicates the leaching of 100% of the total Cd (0.16 mg kg^{-1}) included in the soil-compost mix. This could be explained by the supposed increase in soil salinity and soluble complexes with the addition of zeolite (Usman et al., 2005). Solubilization of Cd was less pronounced when lower quantities of zeolite were added to the Cd-rich compost. Moreover, the plant and amendments had a combined effect on Cd availability since Cd, highly extracted by EDTA, was significantly lower in T2 than in T1 for all the modalities including the non-amended soil (NCS) (Figure 4). The slight overall increase in soil pH and available P as well as the decrease in EC observed in T2 (Table 2) could explain the decrease of Cd availability after the growth of rye grass.

Pb availability did not change with the addition of amendments (T1) regardless of the extractant. However, with plant system (T2), Pb extractability with EDTA slightly but significantly decreased with compost and 25% of zeolite whereas values were under the detection limits when Pb was extracted by NH_4NO_3. This finding corresponds with a significantly higher EC of soils in this condition, as zeolite addition to compost tends to increase EC (Hamidpour et al., 2017). Both extractants revealed opposite behavior of Pb in amended NCS with the growth of rye grass. An increase in EDTA-extractable Pb was observed after rye grass cultivation whereas the opposite trend was found for NH_4NO_3. This discrepancy before and after ray grass growth could be explained by both the affinity of EDTA for organically bound metal and the root exudates rich in low-molecular weight organic acids known to be reactive with metals (Koo et al., 2010; Montiel-Rozas et al., 2016).

For Zn, results for T1 and T2 showed an enhancement of the extractability with the compost adding and the zeolite amount increase, with a stronger effect with 25% of zeolite. Although Zn was found in majority in crystalline lattice of soil (i.e., 51%), the chemical distribution study showed that 20% were exchangeable, 20% bound with Fe, Mn and Al (hydr-)oxides, and 7% organically bound corresponding to the half of the total Zn (Figure 2). No significant effects of amendments on metal chemical distribution were noted. Such as observed for Cd, the plant coupled with amendments decreased the Zn availability.

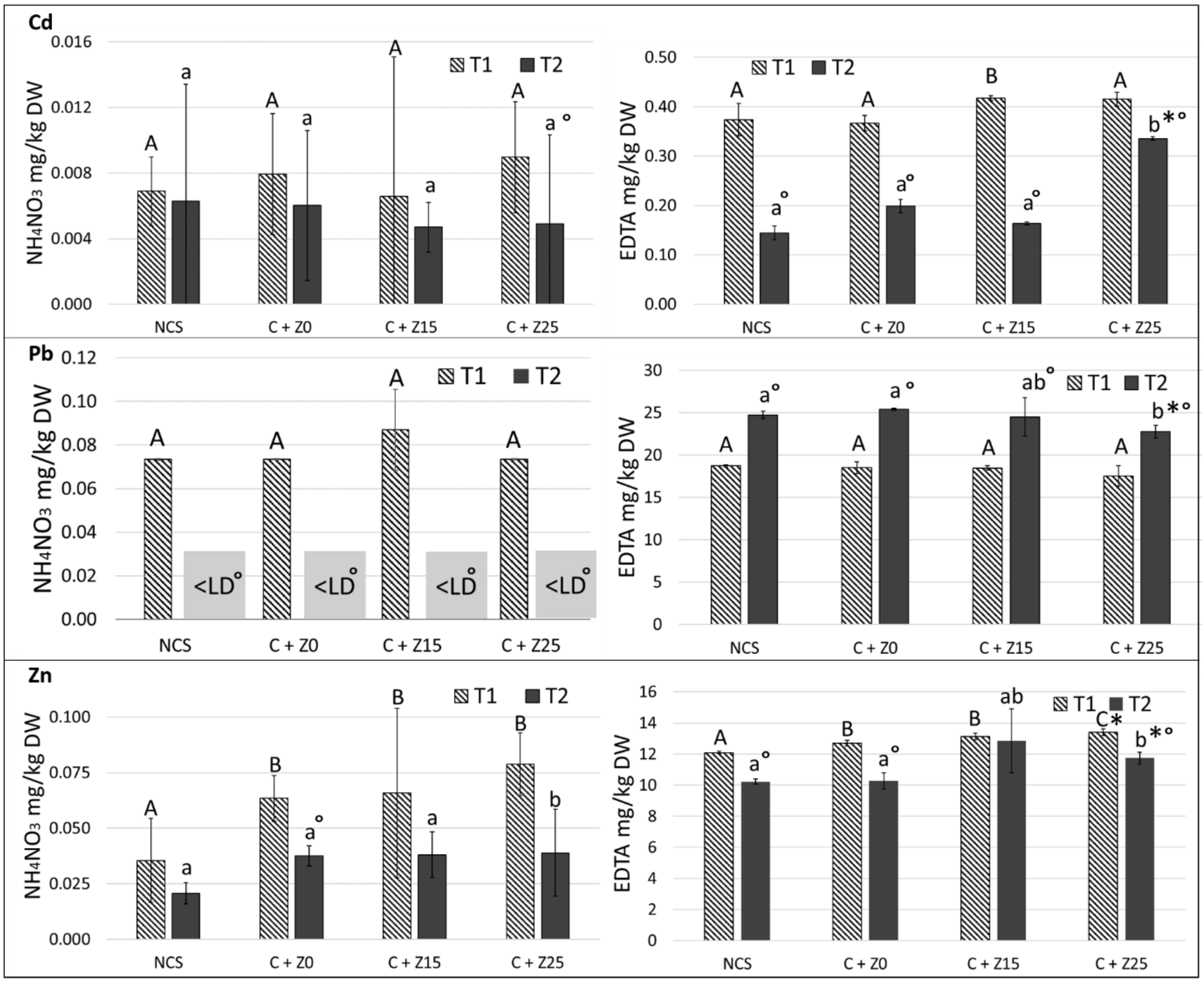

Fig. 4. Extractability of Cd, Pb, and Zn leachates from a compost and its mixes applied to NCS as analyzed by NH4NO3 and EDTA extractions. NCS: non-contaminated soil; C+Z0: no zeolite applied, Z15: 15% of zeolite applied to compost by dry mass, Z25: 25% of zeolite applied to compost (w/w), T1: after 6 weeks of maturation, T2: after 6 weeks of maturation and 4 weeks of rye grass growth in greenhouse. Whereas different letters present significant differences between the control soil and a given condition, * denotes a difference between C+Z0 and other mixes, and ° denotes a difference between T1 and T2 for a given condition.

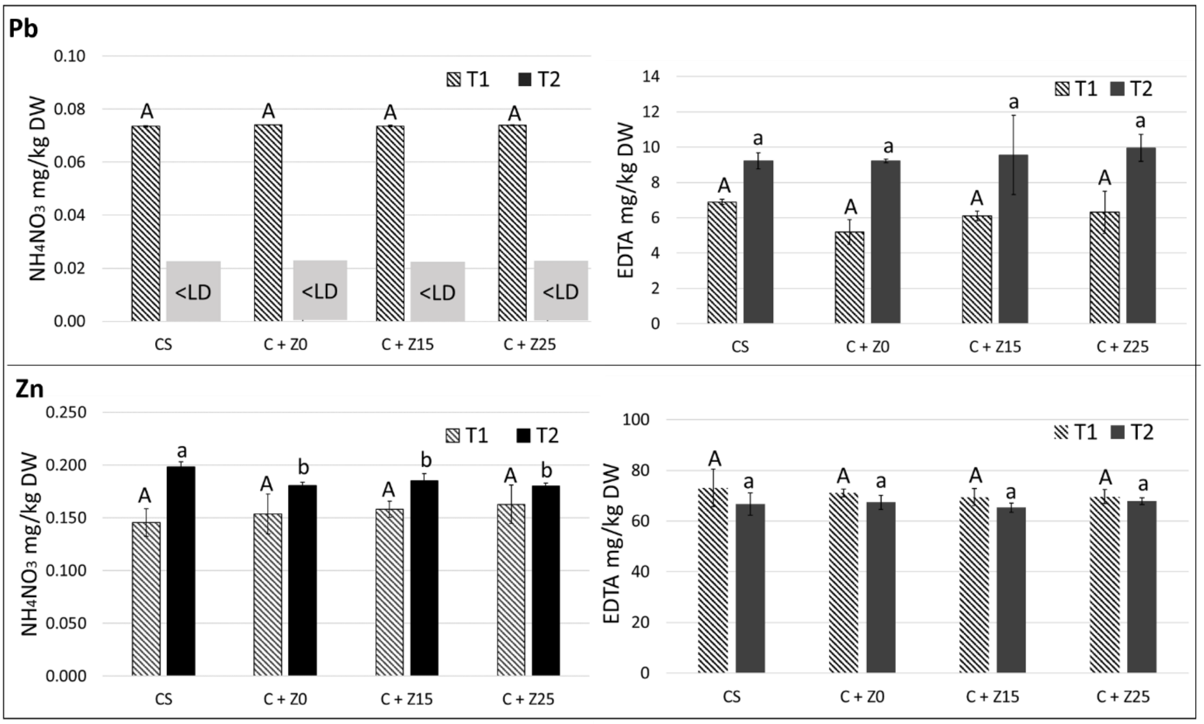

Fig. 5. Part of Pb and Zn extracted by NH4NO3 and EDTA extractions in mg kg−1 of amended or unamended CS. CS: contaminated soil; C: compost applied at 0.6%; Z0: no zeolite applied, Z15: 15% of zeolite applied to compost by dry mass, Z25: 25% of zeolite applied to compost by dry mass, T1: after 6 weeks of maturation, T2: after 6 weeks of maturation and 4 weeks of rye grass growth in greenhouse. Whereas different letters present significant differences ($p < 0.05$) between the control soil and a given condition, * denotes a difference between C+Z0 and other mixes, and ° denotes a difference between T1 and T2 for a given condition.

Differences in behavior among metals can be explained by zeolite's characteristics and soil physico-chemical characteristics. Results showed that the addition of zeolite increased Cd and Zn availability in soil, unlike for Pb. The difference in extractability of Cd and Zn, and Pb for this NCS, could be partially explained by the fact that zeolites can readily uptake metal(loid)s bound to the carbonate and the exchangeable soil fractions with a selectivity of Cu > Cr > Fe > Ni > Mn > Pb > Zn (Singh and Kalamdhad, 2012; Zorpas et al., 2000). Moreover, chabasite is more selective towards Pb^{2+} than Cd^{2+} and Zn^{2+} due to their respective hydration energies (Colella, 1999), and is a less efficient immobilizer when multiple contaminants exist due to competition (Reddy et al., 2014). As seen in Table 1, the addition of zeolite can result in increases in salinity and Cl content, which can mobilize Cd via formation of soluble Cd-chloride complexes (Usman et al., 2005).

This mobilizing effect of zeolite-brought soil salinity increases can be more pronounced in the presence of plant systems because of root exudates (McLaughlin et al., 1997). This mobilizing effect can also be more easily seen on a non-contaminated soil, as it is easier to see changes in metals. As shown by Hamidpour et al. (2017), the presence of root systems influences the metal behavior in zeolite-amended soil alone. This could be linked to the fact that Pb (and Cd) have the tendency to become less available as soil pH increases. However, environment around plant roots tend to be more acidic than surrounding soil, effectively mobilizing metal(loid)s. The soil tested in this section presented a very low degree of contamination in Cd, Pb and Zn and was considered as uncontaminated, but there are quite elevated levels of metal(loid)s present in the tested compost that can be mobilized. However, although an increase of the metal availability was observed in (un-)amended or soil with rye grass, there is very little risk associated with the use of the contaminated self-produced compost studied since it was added at a relatively low rate of 0.6% to the uncontaminated soil.

The CS soil presented a higher degree of contamination than NCS. The study of the metal extractability by NH_4NO_3 in CS before rye grass seeding (T1) showed a slight but significant increase in Pb availability in the soil amended with compost alone (C+Z0) from 0.0735 to 0.0740 mg kg^{-1} (0.065 to 0.067%) in comparison to the control soil, whereas no effect was observed in presence of zeolite (Figure 6). In this condition (C+Z0), a decrease in soil pH from 7.7 to 7.5 was also observed at T1 (Table 3). This difference in availability is nevertheless very small and could be associated with variations. With the EDTA extraction, no variation in Pb extractability was observed, regardless of the amendment conditions. Because of the very small quantity of metal extracted by NH_4NO_3 and EDTA (max. 0.007 and 1.0 mg Pb per pot respectively), it is difficult to determine if zeolite mitigated Pb leaching from compost. Moreover, the Pb amount added by compost (0.6%) represented only 0.34% of the Pb quantity in CS per pot. Thus, these findings showed that the Pb availability in CS is very low. In the presence of rye grass (T2), the concentration of NH_4NO_3-extractable Pb felt below detection limits (0.05 mg kg^{-1} DW). No condition significantly changed EDTA-extractable Pb from the 10 mg kg^{-1} measured in the unamended soil CS (Figure 4). The growth of rye grass decreased the Pb extractability by NH_4NO_3, whereas EDTA-extractable Pb increased in comparison to the unamended CS at T1. However, the percentage of water-soluble and exchangeable Pb (F1) at T2 was higher than at T1 (Figure 3). In the presence of rye grass, Pb might have been transformed into less available form still present in F1 of the soil, consequently reducing NH_4NO_3-extractable Pb while increasing EDTA-extractable Pb (Quenea et al., 2009; Sahuquillo et al., 2003; Vincreanu et al., 2019). Notably, the same trend was observed with the co-application of natural zeolite and vermicompost in soil contaminated in Cd, Pb and Zn by mining activities, which increased Pb availability in the soil. However, this corresponded to a reduction in Pb uptake in corn roots and shoots (Hamidpour et al., 2017).

For Zn in CS, it was seen that the unplanted control soil contained 0.15 mg kg^{-1} (0.04%) of NH_4NO_3-extractable Zn, which did not significantly change with the addition of any amendment. After planting rye grass, Zn availability increased as assessed by this extractant. This is reflected in the sequential extractions, where more Zn by percentage is found in F1 in T2 than in T1. At T2, the unamended control soil CS had the highest quantity of extractable Zn in comparison with the amended soil conditions, at 0.20 mg kg^{-1}. This suggests that Zn was less available with the addition of a Zn-contaminated compost. Regarding the stronger EDTA extraction, there were no significant differences among conditions at either T1 or T2. At T1, 73 mg kg^{-1} (19%) of Zn was extracted, and at T2 this amount slightly decreased to 67 mg kg^{-1} (17%) Zn in CS.

For both the NCS and CS soils, Pb and Zn extractability was relatively low. The amount of Pb added by compost (0.6%) represented a small amount of the Pb quantity in NCS and CS per pot. The addition of compost significantly increased NH_4NO_3- extractable Zn on NCS by 0.028 and 0.017 mg kg^{-1} (80%) at T1 and T2, but the amount of extractable Zn added to CS was not significant and even was associated with a decrease in NH_4NO_3-availability at T2. These findings show that the Pb availability in these soils is low due to Pb's propensity to bind with (hydr)-oxides of Fe, Mn and Al in soil. Zn is highly found in mineralized forms and thus also shows low availability, though not as low as Pb (Figures 2 and 3).

3.2.4 Effect of the co-application of compost and zeolite on accumulation of metals in rye grass

The growth and accumulation of metals in above ground parts of rye grass were examined for the different conditions studied on NCS and CS (Table 4). The NCS was linked to a lower biomass production than CS, and a rye grass uptake of 0.18, 5.35, and 35 mg kg^{-1} Cd, Pb, and Zn, respectively. Though there were no significant differences in metal uptake between the unamended control soil and the amended soils, the addition of C+Z15 was associated with significantly less Pb uptaken in the plant than when amended with compost alone (C+Z0). For the CS, 2.8 g of biomass were produced, which increased significantly with the addition of both compost and zeolite. A maximum amount of 3.3 g DW was collected on the C+Z25 soil. Regarding metals uptaken in the rye grass shoots grown in CS, Pb decreased from 7.39 mg kg^{-1} by more than half with the addition of amendments. There was no change in the amount of uptaken Zn from 85 mg kg^{-1} among conditions.

Table 4. Biomass in g of dry weight (DW) and Cd, Pb and Zn contents in shoots of rye grass (RG) (expressed in mg kg^{-1} DW and in µg per pot) grown on a non-contaminated soil (NCS or CS) amended with compost alone (C+Z0) or in combination with 15% (C+Z15) and 25% (C+Z25) of zeolite (mean values and standard deviation)

	Biomass (g DW)	Cd (mg kg^{-1} RG)	Cd (µg pot^{-1})	Pb (mg kg^{-1} RG)	Pb (µg pot^{-1})	Zn (mg kg^{-1} RG)	Zn (µg pot^{-1})
NCS	1.9 ± 0.2a	0.18 ± 0a	0.36 ± 0.04a	5.35 ± 2.55a	7.52 ± 2.28a	35 ± 2a	67 ± 5a
C+Z0	2.2 ± 0.1a	0.20 ± 0.02a	0.45 ± 0.07a	8.61 ± 1.21a	19.11 ± 1.89b	36 ± 2a	82 ± 7a
C+Z15	2.1 ± 0.1a	0.20 ± 0.02a	0.41 ± 0.04a	5.21 ± 1.23a*	12.11 ± 1.56a	36 ± 0a	75 ± 3a
C+Z25	2.3 ± 0.1a	0.23 ± 0.05a	0.41 ± 0.03a	6.42 ± 1.43a	14.33 ± 2.17a	35 ± 1a	79 ± 6a

	Biomass (g DW)	Pb (mg kg^{-1} RG)	Pb (µg pot^{-1})	Zn (mg kg^{-1} RG)	Zn (µg pot^{-1})
CS	2.8 ± 0.0a	7.39 ± 1.90a	21 ± 1a	85 ± 5a	239 ± 18a
C+Z0	2.9 ± 0.0b	2.74 ± 0.35b	8 ± 1b	76 ± 5a	224 ± 12a
C+Z15	3.0 ± 0.1bc	2.42 ± 0.29b	7 ± 1b	78 ± 6a	234 ± 18a
C+Z25	3.3 ± 0.1c	3.05 ± 1.25a	7 ±1b	80 ± 8a	266 ± 32a

Whereas different letters present significant differences between the control soil and a given condition, * denotes a difference between C+Z0 and other mix

For NCS, all conditions containing compost were associated with a tendency to increase biomass in comparison to the unamended soil (Table 4). Compost with or without zeolite improved the agronomic potential of NCS in particular by the increase in soil CEC (Coppin, 2015). A slight tendency to concentrate and accumulate more Cd per pot in rye grass shoots was observed in compost-amended (C+Z0, C+Z15, C+Z25) pots. This could be because the addition of compost brought Cd to the soil in the pot, and the addition of nutrients to the soil promoted uptake from the soil itself. The addition of C+Z15 significantly reduced Pb's concentration in the vegetal model by 1.7 times when compared to the compost-amended pots without zeolite (C+Z0). Regarding the overall metals studied present in the pots, the addition of compost without zeolite (C+Z0) resulted in the significant increase in shoot accumulation of Pb (19.1 µg vs 7.5 µg in the control). This further supports that rye grass accumulated more Pb when amended with compost alone, as there were no significant differences in biomass among conditions. The addition of zeolite mitigated this uptake (- 37% for C+Z15 and - 25% for C+Z25). This result corresponds to the these of the EDTA extraction at T2, where the addition of 25% of zeolite was associated with a significant decrease in Pb extractability in comparison with the soil amended with compost alone (Figure 4). Moreover, based on the chemical distribution of Pb analyzed by the sequential extraction at T2, zeolite-amended conditions seemed displace Pb to less mobile form in comparison to soil amended with compost alone (Figure 3). There was no difference in the Zn accumulated in the rye grass among all conditions. This metal, however, was accumulated the most of the three metals studied. This is echoed by the sequential extraction, where it was seen that more Zn than Pb was located in F1 (Figure 3).

For CS (Table 4), the phytoavailability of Pb decreased with the amendment. Pb concentration in rye grass shoots decreased from 2.4 to 3.1 times with the addition of compost alone or in mix with zeolite in comparison to the unamended control soil. The quantity of Pb (µg per pot) present in the rye grass in all pots containing compost was also significantly lower than in the control pots (Table 4). As supported by Latifah et al. (2015), zeolite has the propensity to limit metal phytoavailability when added to a compost at a 20% rate because of its absorbent qualities. The results suggest that part of the potentially phytoavailable Pb fraction formed oxides, favored by the presence of zeolite, and/or was complexed with organic compounds released from (i) root exudates and (ii) compost in the form of humic acids (Abbaspour and Golchin, 2011). Additionally, with the addition of compost amendments, and to a lesser extent, zeolite, the biomass of rye grass shoots significantly increased. The addition of 25% zeolite to compost was indeed associated with significantly more rye grass biomass than both the contaminated control soil (CS) and the compost amendment (C+Z0) alone. The tendency for more biomass growth thus increased with increasing doses of zeolite. For this soil, Zn concentration in the plant did not change with amendment, though in comparison to the NCS more than double the Zn was uptaken. Likewise, a study testing the application of the same rate (0.6%) of a Zn-contaminated compost found that its addition did not significantly increase its concentration in the lettuce plant, though 4 times its dose (2.4%) significantly did (Moreno et al., 1997).

Both the NCS and CS soils exhibit either a tendency or statistically significant increase in biomass with the addition of compost and compost mixed with zeolite. Thus, it is suggested that the addition of compost, and furthermore, compost and zeolite, can have a favorable agronomic effect and help increase biomass. These results are supported by the findings of Shi et al. (2009), who reports a reduction in Pb uptake in rape shoots with the co-application of zeolite and humic acids. Similarly, Hamidpour et al. (2017) found that a commercialized vermicompost applied alone or in addition with zeolite resulted in increased shoot and root corn biomass, especially as amounts of both compost and zeolite were increased. This was attributed to the addition of high levels of N and P to the soil added with compost and retained by zeolite (Arancon et al., 2008). This condition was associated with the lowest concentration of Pb in the corn shoots and roots as well, because of surface complexation, coprecipitation, and ion exchange on compost and zeolite (Carrasquero Duran and Flores, 2009; Mozgawa et al., 2009). The contribution of compost and zeolite to soil CEC, typically above 5 and not much higher than 30 cmol+ kg^{-1}, is also linked to decrease in metal phytoavailability for rye grass according to Damian et al. (2013).

3.2.5 Effect of the co-application of compost and zeolite on oral bioaccessibility of Pb in the CS soil

Oral bioaccessibility of Pb and potential exposure for populations in using non-conforming compost in contaminated kitchen gardens was determined. In case of unintentional ingestion of soil particles, the UBM test analyzed the solubilization of metals in the gastric and gastrointestinal phases of digestion, the latter of which can contain metals capable of passing into the bloodstream. Because only CS is predominately contaminated by Pb which is non-essential metal, and because Zn showed marginally elevated environmental availability with the addition of compost, the test was only carried out for Pb. Figure 6 presents both phases of bioaccessibility of Pb on the unamended and amended CS. At T1, on CS, Pb was 71% G- and 3% GI- bioaccessible. At T2, on CS, the metal was 66% and 1% G- and GI- bioaccessible, respectively.

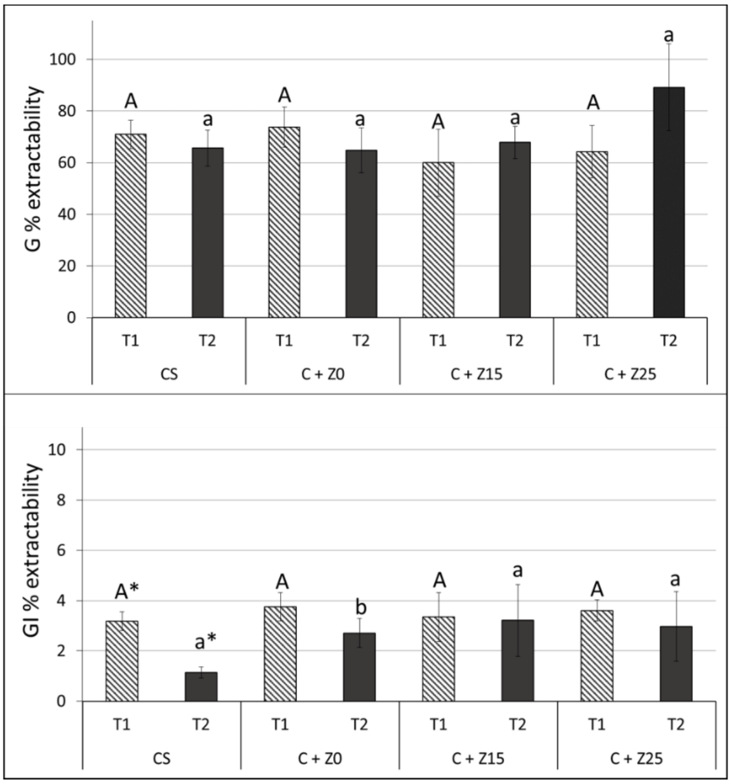

Fig. 6. Part of Pb gastrically (G-) and gastrointestinally (GI-) bioaccessible in % of pseudo-total amended or unamended CS. CS: contaminated soil; C: compost applied at 0.6%; Z0: no zeolite applied, Z15: 15% of zeolite applied to compost by dry mass, Z25: 25% of zeolite applied to compost by dry mass, T1: after 6 weeks of equilibration, T2: after 6 weeks of equilibration and 4 weeks of rye grass growth in greenhouse. Whereas different letters present significant differences ($p < 0.05$) between the control soil and a given condition, * denotes a difference between C+Z0 and other mixes, and ° denotes a difference between T1 and T2 for a given condition.

In the G phase, there was no significant difference at both T1 and T2 in Pb bioaccessibility with the addition of compost alone or in combination with zeolite or in the presence of rye grass. In the GI phase, the bioaccessibility of Pb decreased highly compared to the G phase, due to the change of pH between the gastric and intestinal compartments .Indeed, the pH increased from 1.2 to 6.3, which accompanied the shift from the gastric to the intestinal phase, reasonably favored a decrease of metal cations bioaccessibility, mainly due to their precipitation and/or their partial adsorption to soil components in a carbonate-rich intestinal environment (e.g., clay minerals, and/or organic colloids) (Garau et al., 2019; Pelfrêne et al., 2020). This shift in pH can also lead to the precipitation of Fe as ferrihydrite, which can bind Pb and reduce its GI-bioaccessibility (Smith et al., 2011). In the GI phase, no variation between the control and other conditions were observed at T1 before the rye grass growth. However, after (T2), bioaccessibility of Pb tended to increase with the addition of compost in both the G and GI phases, with a significant increase for C+Z0 in GI (Figure 6). Results also showed that rye grass tended to increase Pb bioaccessibility in G phase when zeolite was added to compost. However, the reverse effect was observed with GI phase. For all conditions, GI Pb measured at T2 was lower than at T1, significantly so for the unamended soil (CS).

One study also found that compost amendments and the presence of plant models effected Pb GI-bioaccessibility marginally, especially in soils with already low Pb bioaccessibility (Attanayake et al., 2017). The ability of compost to reduce bioaccessibility was attributed to it and plant model's ability to shift Pb into the organic soil fraction F3 in solution, and increasing the stability of the soil fraction F2 in the acidic gastrointestinal environment (Attanayake et al., 2017). This does not mean that the addition of organic matter in the form of compost is risk-free, however. As shown by Florido et al. (2011), repeated (2) additions of 0.6% of a organic-matter and Pb- rich (184 mg kg^{-1}) biosolid in the same order as the compost tested in this study (213 mg kg^{-1}) is linked to increased Pb bioaccessibility (by using the SBET method) over time in field conditions.

4. Conclusion

Compost is seen as a green way to dispose of household and garden waste all while improving soil quality. Many self-produced composts contain various metals at varying concentrations, which could potentially contaminate plants grown on soils amended with these composts. To attempt to mitigate metal displacement and prevent metal transfer to plants, zeolite was added to metal contaminated mature compost to be mix into soil. Its effects on Cd, Pb and Zn availability, phytoavailability and oral bioaccessibility in soils contaminated by various degrees were assessed to analyze potential metal leaching trends and risks of using contaminated compost in gardening.

The addition of increasing amounts of zeolite to compost tends to decrease Cd and Zn extractability. On NCS all amendments reduced NH_4NO_3-extractable Zn. For Pb, this effect was observed until 15% in EDTA extracts; above, Pb availability increased. There were no differences in extractable Pb before rye grass seeding. However, the addition of zeolite (15%) successfully offset the compost effect on Pb uptake by rye grass. For the contaminated soil, all amendments were efficient in reducing Pb content in rye grass shoots while no effect on environmental availability was observed. However, Pb tends to be more bioaccessible with the addition of 25% of zeolite in G phase as well as in GI phase from the addition of compost and with the zeolite amount increase. For both soils, it seems that, with rye grass, the exchangeable fraction might be transformed into less available form and consequently reduced NH_4NO_3-extractable Pb (the easily exchangeable metal fraction), and Pb concentration in plant as well as increased EDTA-extractable Pb which assess the pool of metals absorbed both by organic matter, (hydr-)oxides and carbonates.

The experimentation showed that a typical French compost possessing a relatively high level of Cd, Pb, and Zn can and will indeed leach Pb or enhance its uptake from soil, and this mobilization can be limited by the addition of 15% and 25% of zeolite the compost in question. The addition of compost, and furthermore compost and zeolite, can also increase biomass output. However, realistically one application of such a compost applied at the recommended dose of 0.6% poses little environmental or human risk. Less is known about the effects of a contaminated compost with a more typical pH on soil metal speciation, and the potential effects on an acidic soil. Additionally, though in this study one application of compost posed little risk, repeated application risks harming soils quality, leaching metals into the soil solution, and leading to further plant uptake, particularly for specific metal(loid)s and specific plants. This in turn could imply environmental and human risk and would need to be studied further.

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Supplementary Material

Table S1. Sequential extraction of Cd, Pb, and Zn expressed in percentage of pseudo-total metal present in the unamended and amended contaminated soil (CS) and non-contaminated soil (NCS) before (T1) and after (T2) seeding with rye grass

			Cd %				Pb%				Zn%			
			F1	F2	F3	F4	F1	F2	F3	F4	F1	F2	F3	F4
CS	T1	CS	23	34.5	27.1	15.4	1.2	73.5	4.2	21.1	25.6a	47.1	16.1	8.4
		C+Z0	19.3	40.1	25.9	14.7	1.1	79.5	4.0	15.4	24.8a	47.5	16.5	7.6
		C+Z15	26	30.1	27.9	15.9	1.1	75.9	3.6	19.5	24.4b	47.3	16	8.7
		C+Z25	34	26.9	24.9	14.2	1.5	77.1	3.9	17.5	24.6ab	48.6	16.7	7.2
	T2	CS	50.5*	20.2*	18.7	10.7	3.7*	75.9	3.6	16.8	25.5	52.8*	8.2*	10
		C+Z0	41.9*	23.7	22	12.5	4.3*	71.5	4.8	19.4	23.5	55.1*	8.5*	8.5
		C+Z15	47.2*	22.1*	19.6*	11.2*	3.2*	72.3	3.4	21.1	23.1	55.2*	8.8*	9.2
		C+Z25	39.4	30.2*	19.5*	10.8*	2.8*	70.2	4.4	22.6	24	54.7*	8.7*	8.6
NCS	T1	NCS	19.3	32.9	30.5	17.4	4.0	78.1	7.1	10.8	27.4	34.8	9.8	15.6
		C+Z0	19.8	26.1	40.4	13.8	3.9	76.9	7.9	11.3	28.6	35.6	11.3	13.3
		C+Z15	22.3	30.7	28.5	16.2	4.1	76.4	8.3	11.1	30.3	34.7	10.5	13.7
		C+Z25	35.3	27.7	23.6	13.5	4.0	76.7	6.9	12.3	19	24.3	7.1	13.7
	T2	NCS	35.8*	26.1*	24.2*	13.8*	3.7	77.8	7.6	10.8	28.9	40.0*	3.0*	17.2
		C+Z0	33.4*	25.9	27	13.7	3.7	76.8	8.6	10.8	30.5	42.2*	3.2*	13.9
		C+Z15	32.4*	29.4	24.3*	13.9*	4.6	77.7	7.6	10.0	29.5	40.6	2.8*	16.1
		C+Z25	38.4	25.1	23.3	13.3	3.8	70.4	7.6	18.3	29.1	39.2	3.7	15.6

Whereas different letters present significant differences between the control soil and a given condition, * denotes a difference between T1 and T2 for a given condition. F1: Fraction 1, the exchangeable fraction; F2: Fraction 2, the reducible fraction; F3: Fraction 3, the oxidizable fraction; F4: Fraction 4; the residual fraction.

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Chapter takeaways

Chapter 6 shows that a self-produced compost containing non-negligible levels of Cd, Pb, and Zn in comparison to amendment regulations has little impact on their environmental availability after one dose at the recommended rate of 20 tons ha^{-1}. Self-produced compost can decrease phytoavailable Pb in rye grass grown on a contaminated kitchen garden soil (CKG-L). When this compost is mixed with zeolite, the little metal mobilization that occurs with compost addition can be mitigated with the addition of 15% and 25% of zeolite added by mass. The addition of compost, and furthermore, compost and increasing proportions of zeolite, is linked with increases in rye grass biomass.

Chapter 7: General discussion and perspectives

Chapter 7: General discussion and perspectives

Throughout the chapters of this thesis, the main objective was to explore if **“culturally-relevant doses of soil amendments can reduce metal(loid) mobility, (bio)availability and oral bioaccessibility in multi-contaminated soils”**. This question was gradually approached by evaluating:

- The effects of several soil amendments on physico-chemical soil parameters and on environmental availability of metal(loid)s (Chapter 3);
- The influence of the establishment of a crop in combination with amendments on the environmental availability and phytoavailability of metal(loid)s (Chapter 4);
- The use of soil amendments as a management technique for moderately contaminated soils to reduce population exposure (Chapter 5); and
- The management of vegetable garden soils with contaminated self-produced compost and the environmental and toxicological interest of the co-application of such compost and a natural zeolite to manage a metal-contaminated soil (Chapter 6).

This manuscript examines the effect of 14 amendments as analyzed by different experiments. The results obtained during these experiments allowed for the selection of six amendments to apply to each of the three kitchen garden soils. This discussion focuses on the evaluation of these six amendments tested during in Experiment 1a and Experiment 2 by way of results analyzed for significant statistic differences ($p < 0.05$) in comparison to an unamended control. This allows for the determination of amendments that significantly change a given property (*e.g.,* environmental availability, soil agronomic potential, and possible human toxicological impact) by assessing their efficiency factors (EF), calculated as a ratio between a given amended condition and the unamended control. These cumulative results were then used to calculate overall scores for each given amendment and soil in order to better classify the tested amendments. This general discussion synthesizes the answers to the questions above provided in the context of this thesis, in order to identify effective amendments for contaminated soil management and propose recommendations and perspectives for three moderately contaminated garden soils.

1. General discussion

1.1 Efficiency of amendments at lowering metal(loid) environmental availability

In both Experiment 1a (unplanted soils) and Experiment 2 (planted soils), simple extractions were performed on amendments: an NH_4NO_3 extraction indicating short-term environmental bioavailability, and an EDTA extraction allowing for the determination of a less extractable, organic matter-, (hydr-) oxide-, or carbonate-bound, and potentially toxicologically bioavailable, pool of metal(loid)s accessible over time. Figure 7-1 shows the efficiency factors of these amendments, based upon the NH_4NO_3 extraction, whereas any amendment under a ratio of 1 is efficient and decreased metal(loid) NH_4NO_3-extractability.

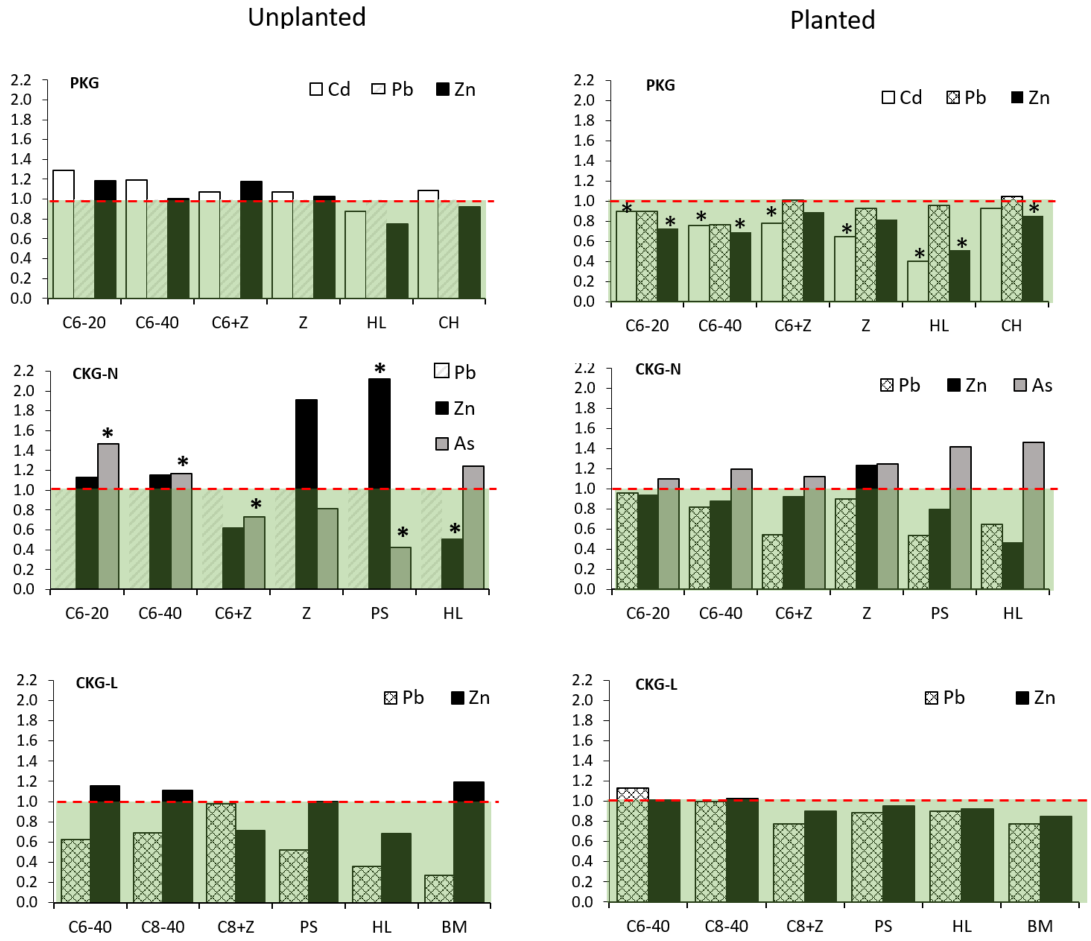

Figure 7-1. Efficiency factors of amendments in comparison to their respective Experiment 1a unplanted (U1) and Experiment 2 planted (U2) controls as evaluated by a NH_4NO_3 extraction. C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. * denotes a significant difference ($p < 0.05$) in extractability in comparison to the control as evaluated by a Student test. Green frame shows amendments falling within effective range.

Figure 7-2 shows the efficiency factors of the amendments tested both without plant and in the presence of lettuce, based upon the ratio between that which was extracted by EDTA on the control and the amended soil.

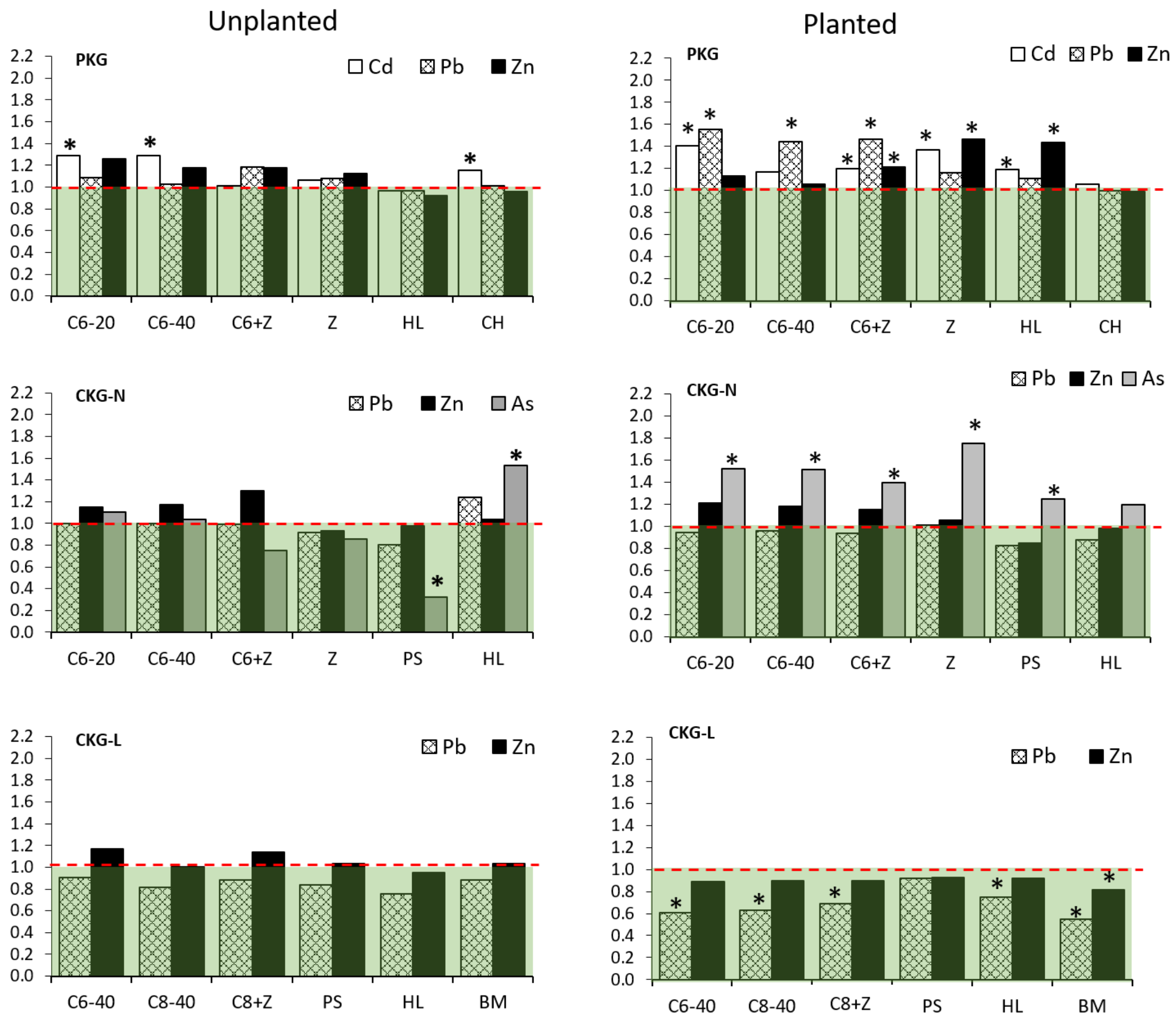

Figure 7-2. Efficiency factors of amendments in comparison to their respective Experiment 1a unplanted and Experiment 2 planted controls as evaluated by an EDTA extraction. U: unamended control; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. * denotes a significant difference ($p < 0.05$) in extractability in comparison to the control as evaluated by a Student test. Green frame shows amendments falling within effective range.

➢ *Before planting*

For PKG, HL was the only amendment that reduced both Cd and Zn short-term extractability as analyzed by NH_4NO_3. The extracted Pb was below the limit of detection. In the long-term, as evaluated by EDTA, only HL reduced extractable Cd, Pb, and Zn as well. For CKG-N, before the addition of lettuce, C6+Z was the only amendment to reduce both short-term Zn and As extractability; As significantly. In the long-term, both Z and PS were effective for Pb, Zn, and As. Concerning CKG-L, before planting, C8+Z, PS, and HL reduced short-term extractable Pb and Zn. In the long-term, all amendments reduced Pb availability, and HL also reduced Zn availability. Thus:

- For PKG, considering short- and long- term, **HL** is the most effective amendment;
- For CKG-N, **C6+Z** is efficient in the short-term and **Z and PS** are effective in the long-term; and
- For CKG-L, considering short-and long-term, **C8+Z, PS, and HL** are the most effective amendments.

➢ *After planting*

On PKG, in the short-term, C6-20, C6-40, Z, and HL were effective for Cd, Pb, and Zn. For Cd, HL was the most efficient amendment, reducing Cd accessibility by 60%. For Pb, C6-40 was the most efficient amendment, whereas for Zn HL was the most efficient amendment. However, no amendment reduced long-term extractable Cd, Pb, or Zn. For CKG-N, in the short-term, all amendments reduced Pb extractability, which was under the limit of detection before planting, but all amendments increased As availability. Thus no amendment was effective for all metal(loid)s on this soil, but C6-20, C6-40, C6+Z, PS, and HL were effective for Pb and Zn. For Pb, PS and C6+Z were the most efficient amendments. For Zn, HL was the most efficient. In the long-term, C6-20, C6-40, C6+Z, Z, and PS significantly increased As extractability by EDTA. PS was nevertheless the most effective amendment, reducing two out of the three present metal(loid)s despite increasing long-term As availability. Concerning CKG-L, C8+Z, PS, HL, and BM reduced both Pb and Zn short-term availability in comparison to the control, with C8+Z being the most efficient amendment for both metals. In the long-term, all amendments decreased Pb and Zn extractability. BM was the most effective amendment in the long-term as it produced significant results on both Pb and Zn and showed the lowest EF. Thus:

- For PKG, considering short-term, **C6-20, C6-40, Z, and HL** are the most effective amendments;
- For CKG-N, in the short-term, **C6-20, C6-40, C6+Z, PS, and HL** are the most efficient, and in the long-term, PS is the most efficient; and
- For CKG-L, considering short-term, **C8+Z** is the most efficient amendment, whereas in the long-term BM is the most efficient.

➢ *Effective amendment evolutions with the addition of a crop system*

Regarding both short-term (NH_4NO_3) and long-term (EDTA) efficiency of amendments to reduce extractability of Cd, As, Pb, and Zn before and after planting, several trends arise. Notably:

- For PKG, though **HL** is globally the most effective amendment, no amendment reduced extractable Cd, Pb, or Zn in the long-term on the planted soil. The addition of lettuce on this soil was associated with a significant increase in pH, decrease in $CaCO_3$, EC, and available P which potentially influenced long-term metal behavior.
- For CKG-N, before the addition of lettuce, **C6+Z** and **PS** were the most effective amendments at reducing As short-term extractability, and after planting these same two amendments reduced short-term extractable Pb. Regarding long-term extractability, before planting, PS was again effective for Pb, Zn, and As. After planting, **PS** and **HL** were the most effective amendments despite increasing long-term As availability. Interestingly, PS reduces As availability in both the short- and long-term before planting, but not after the introduction of a lettuce model despite a lack of significant physico-chemical changes with its addition.
- For CKG-L, results before and after planting showed more concurrence. Before and after the addition of a lettuce model, **C8+Z, PS,** and **HL** reduced short-term and long-term extractable Pb and Zn, and the addition of the lettuce model did not significantly change physico-chemical soil characteristics.

1.2 Efficiency of amendments at increasing agronomic potential of soils

As shown by these extractions, in the presence of the plant, various amendments successfully reduce the extractability of several metal(loid)s as evaluated by two simple extractions. These effects, however, do not necessarily translate to a healthier, more productive plant. Figure 7-3 examines the biomass grown on the three different soils, whereas an amendment is considered efficient when it is linked to more biomass production than the control (EF > 1). For PKG, the addition of **C6+Z** was associated with 18% more lettuce biomass grown. This amendment also reduced short-term available Cd in the presence of the plant. The highly effective HL amendment, however, was associated with a biomass decrease. For CKG-N, the addition of **C6-40, Z,** and **HL** were associated with biomass increases of 35%, 64% and 29%, respectively. These amendments also reduced short-term available Pb after lettuce addition. Additionally, Z reduced long-term available As, Pb, and Zn before planting, and C6-40 and HL reduced long-term available Pb after planting. For CKG-L, **C6-40, C8+Z,** and **PS** increased biomass, by 27%, 7%, and 4%, respectively. Before planting, in the short-term, C6-40 and PS reduced extractable Pb, and C8+Z and PS reduced extractable Pb and Zn after planting. In the long-term, these amendments all reduced extractable Pb before and after planting.

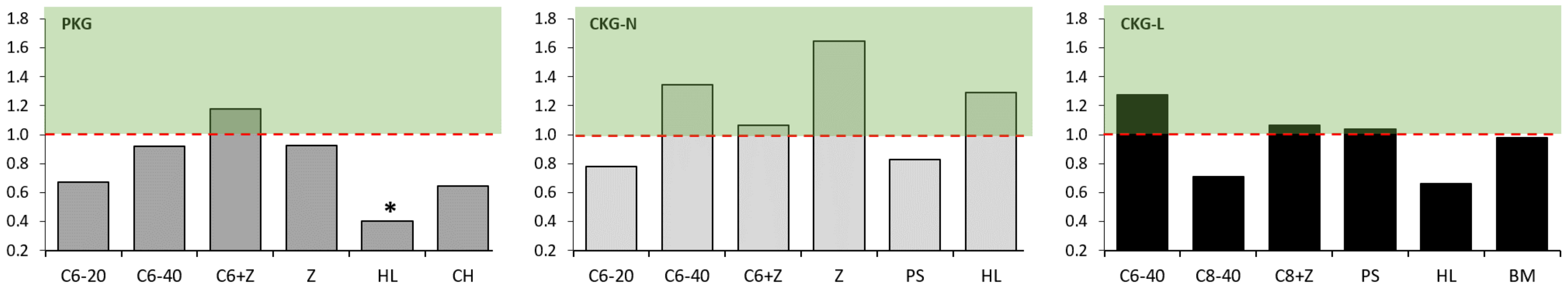

Figure 7-3. Efficiency factors of amendments in comparison to their respective Experiment 2 planted control (U2) as evaluated by an analysis of biomass.; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. * denotes a significant difference ($p < 0.05$) in extractability in comparison to the control as evaluated by a Student test. Green frame indicates an EF > 1 and a relative increase in biomass.

1.3 Efficiency of amendments at improving human exposure

Specifically concerning Experiment 2, which was planted and a stronger representative of possible field conditions than Experiment 1, efficiency factors (EF) were also calculated concerning potential human exposure, whereas an EF < 1 indicates less exposure. These comparisons concern the accumulation of metal(loid)s in lettuce as calculated by their BCF and the oral G- and GI- bioaccessibility of the same metal(loid)s. Figure 7-4 shows the BCF of Cd, Pb, Zn, and As in aerial parts of lettuce grown during 6 weeks. For PKG, **C6-20, C6-40, Z, and HL** were effective for all tested metals, with HL being significantly effective for each metal. For CKG-N, **C6-20, C6-40, C6+Z, and HL** were effective at reducing the BCF of As, Pb, and Zn. For CKG-L, **C6-40, C8-40, C8+Z, PS, and BM** successfully decreased the concentration of Pb and Zn in this soil.

Figure 7-5 shows the G- and GI- oral bioaccessibility of the metal(loid)s that pose the greatest human exposure, Cd, Pb, and As, on the three amendment kitchen garden soils. An EF was calculated for both phases of the oral bioaccessibility test. G-phase bioaccessibility is seen as a more conservative measure of assessing potential risk for Cd and Pb, as this phase extracts more metal and does not necessarily correspond to that which can pass into the bloodstream and be bioavailable. GI-phase Cd and Pb bioaccessibility can be considered as a more physiologically relevant marker for recommendations, as this fraction better represents that which can become bioavailable. For As, there is globally little difference between the two phases.

For PKG, both Z and HL reduced the G- bioaccessibility of both metals present on this soil, and C6-20, C6-40, C6+Z, and HL reduced the GI- bioaccessibility of both Cd and Pb. Thus **HL** was efficient for both phases and metals. Concerning just the GI-phase, **C6-40 and HL** were the most efficient amendments, with C6-40 decreasing Cd GI-bioaccessibility by 24% and Pb GI-bioaccessibility by 22%, and HL reducing Cd GI-bioaccessibility by 35% and Pb GI-bioaccessibility by 21%. For CKG-N, C6-20, C6-40, C6+Z, and PS reduced the G- and GI- bioaccessibility of both Pb and As. For Pb, C6-40, C6+Z, HL, and PS all reduced GI-bioaccessibility of Pb over 20%. For GI-bioaccessible As, C6-40, C6+Z, and PS were the most effective amendments. Thus **C6-40, C6+Z**, and **PS** were the most effective amendments to reduce GI-phase oral bioaccessibility for this planted soil. For CKG-L, **C6-40, C8-40, and HL** were effective amendments on Pb for both phases of this test. C6-40 was the most effective amendment in the GI-phase, reducing orally bioaccessible Pb by 42%. Overall, HL reduced oral bioaccessibility in both phases for all metal(loid)s tested in the gardens in PKG and CKG-L, whereas C6-40 was effective for both of the community gardens, CKG-N and CKG-L.

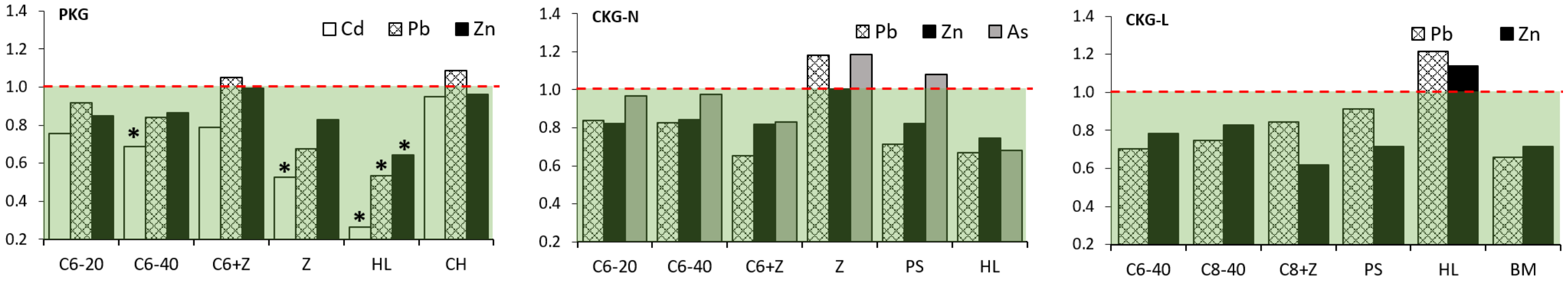

Figure 7-4. Efficiency factors of amendments in comparison to their respective Experiment 2 planted control (U2) as evaluated by an analysis of bioconcentration factors (BCF).C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. * denotes a significant difference ($p < 0.05$) in extractability in comparison to the control as evaluated by a Student test. Green frame indicates an EF < 1 and a relative decrease in BCF.

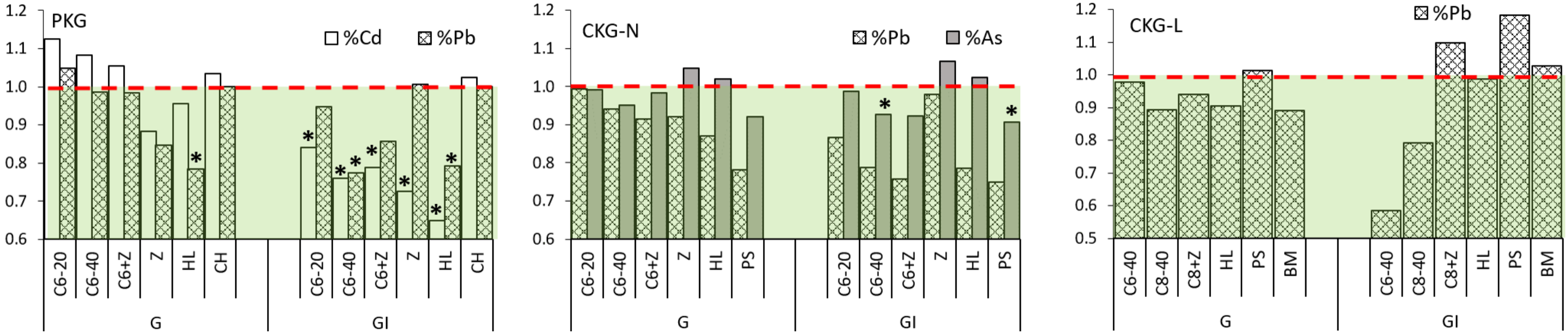

Figure 7-5. Efficiency factors of amendments in comparison to their respective Experiment 2 planted controls as evaluated by an analysis of *in vitro* gastric (G) and gastrointestinal (GI) oral bioaccessibility as measured by the Unified Barge method (UBM). C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. * denotes a significant difference ($p < 0.05$) in extractability in comparison to the control as evaluated by a Student test. Green frame indicates an EF < 1 and a relative decrease in bioaccessibility.

1.4 Determination of most effective amendments for each planted soil

As seen previously, considering the tested culturally-relevant doses of soil amendments tested, certain were able to reduce metal(loid) mobility, (bio)availability, and oral bioaccessibility in multi-contaminated soils. Amendment impacts on (i) environmental metal(loid) availability as analyzed by NH_4NO_3 and EDTA extractions, (ii) agronomic merit determined by biomass, and (iii) human exposure as analyzed by the BCF and GI-bioaccessibility in the presence of a plant system are reviewed and resumed in Figure 7-6. In this figure, only the amendment effects in the presence of a plant system are used in order to more closely approach possible field condition responses. GI-phase bioaccessibility was used over G-phase bioaccessibility in this interpretation, as it can be considered as a more physiologically-relevant marker which better represents that which can become bioavailable.

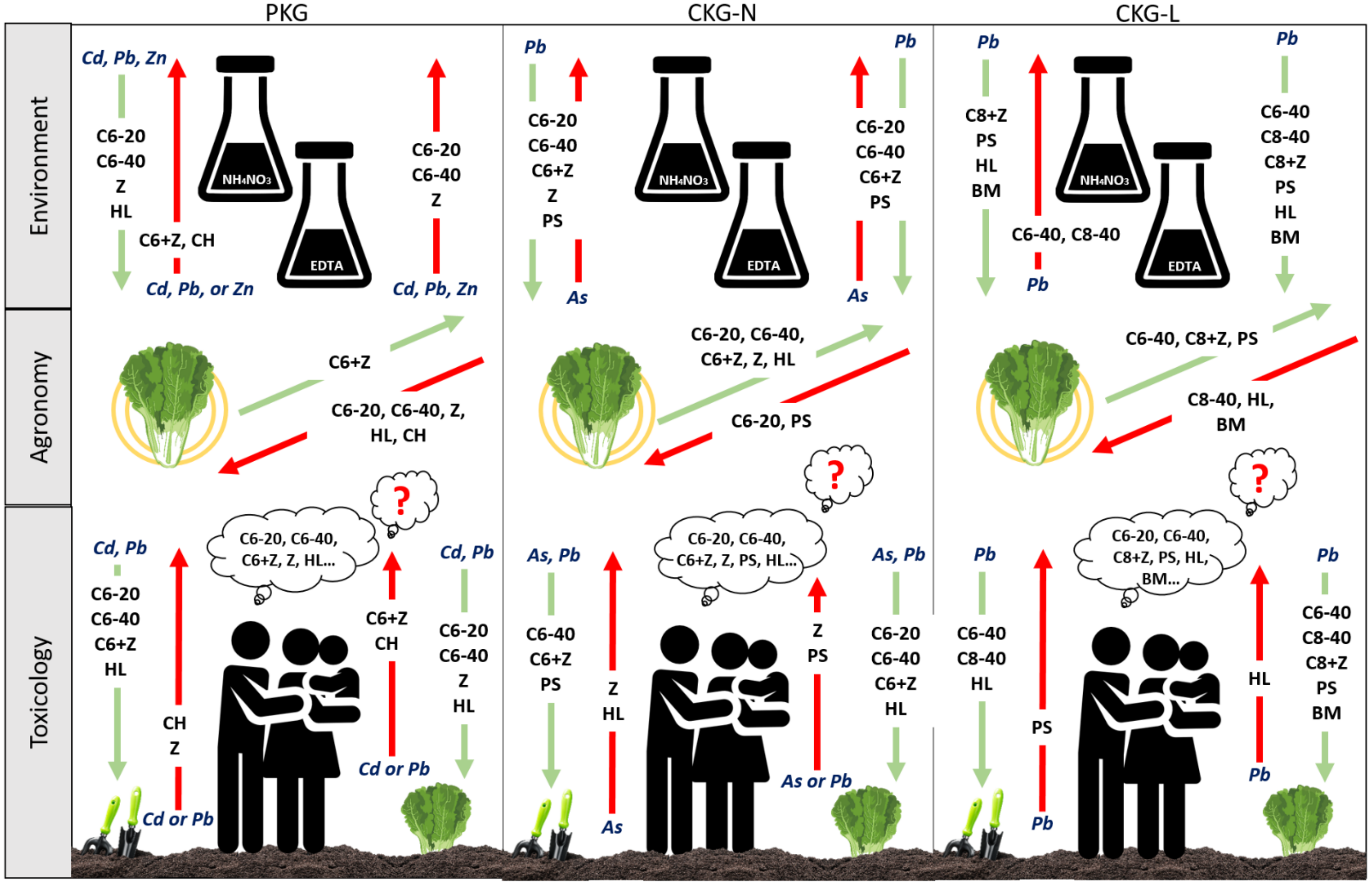

Figure 7-6. Illustration of the short-term and long-term environmental (as evaluated by NH$_4$NO$_3$ and EDTA), agronomic (as evaluated by biomass), and toxicological impact (as evaluated by GI-oral bioaccessibility and BCF in lettuce) of amendments in comparison to their respective Experiment 2 planted controls. C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. Green arrow indicates a favorable amendment-led response. Red arrow indicates an unfavorable amendment-led response.

- ***Scores***

In order to more concretely determine the overall interest of using certain amendments in the presence of a plant system and potential in field conditions, their impacts on (i) environmental metal(loid) availability as analyzed by NH_4NO_3 and EDTA extractions, (ii) agronomic merit determined by biomass, and (iii) human exposure as analyzed by the BCF and GI-bioaccessibility attributed to scores. Based on these results, one point was attributed to amendments that decreased metal(loid) availability for a given element, or increased biomass, and 3 points to amendments that significantly did so. Likewise, 1 point was removed for amendments that increased availability, and 3 for those which significantly did so. Thus, for a given amendment, a score may be comprised each analysis, metal(loid), and impact category, as seen in the example in Table 7-1, where it is seen that concerning environmental impact, Amendment 3 is the most efficient amendment, regarding agronomic impact, Amendment 1 is the most efficient, and regarding human impact, Amendment 2 is the most efficient.

Table 7-1. **Example of score building based on environmental, agronomic, and human impact**

	Environmental impact				**Agronomic impact**	**Human impact**			
	NH_4NO_3		EDTA			GI		BCF	
	Cd	Pb	Cd	Pb	Biomass	Cd	Pb	Cd	Pb
Amendment 1	-1	-3	3	1	3	1	1	1	1
Amendment 2	-1	-1	1	1	-1	1	3	3	1
Amendment 3	3	1	3	-1	1	1	-1	1	-1

The sum of each of the three impact categories was then divided by the number of variables (*i.e.*, metal(loid)s) present, and impact categories were given weights, in order to devise an overall score for a given amendment considering all metal(loid)s and impact categories. The category environmental metal(loid) availability was given a weight of 1, agricultural merit a weight of 0.5, and human health impacts were given a weight of 2. The weights were determined so to prefer lettuce quality (BCF) over production quantity (biomass), and because human impact is considered as a more pressing concern in kitchen gardens than environmental impact. This culminates in the formulas:

$$Metal(loid)\ score = \text{Environmental impact} + \frac{\text{Agronomic impact}}{2} + \text{Human impact} \times 2$$

$$Sum\ of\ scores\ = \Sigma(\text{Metal(loid)score})$$

$$Overall\ score\ = \frac{\text{Sum of scores}}{\text{\# of measured metal(loid)s}}$$

Using the example illustrated in Table 7-1, according to this cumulative formula, Amendment 2 would be the best amendment for the example soil. The individual results of the additions of the extractions, biomass, BCF, and GI bioaccessibility results for PKG, CKG-N, and CKG-L are seen in Table 7-2. The scores analyzed by metal(loid) indicate the most effective amendments for a given soil with higher, the most positive results banded in increasingly dark green, and negative results in red. Their cumulative efficacy is taken into account in the overall score, or the sum of the metals' scores divided by the number of metals analyzed. Based upon the cumulative scores for all metal(loid)s for each kitchen garden soil, and with customized score tables taking into account the most pressing issues for each kitchen garden, the most effective amendments were determined.

Table 7-2. Scores of amendments in comparison to their respective Experiment 2 planted control.

		Cd	Pb	Zn	As	*Sum*	*Overall score*
PKG	**C6-20**	3.5	1.5	2.5	nd	*7.5*	**2.5**
	C6-40	6.5	3.5	2.5	nd	*12.5*	**4.2**
	C6+Z	4.5	-2.5	1.5	nd	*3.5*	**1.2**
	Z	5.5	0.5	0.5	nd	*6.5*	**2.2**
	HL	4.5	7.5	4.5	nd	*16.5*	**5.5**
	CH	-0.5	-4.5	3.5	nd	*-1.5*	**-0.5**
CKG-N	**C6-20**	nd	2.5	1.5	-0.5	*3.5*	**1.2**
	C6-40	nd	3.5	5.5	2.5	*11.5*	**3.8**
	C6+Z	nd	3.5	3.5	0.5	*7.5*	**2.5**
	Z	nd	0.5	0.5	-3.5	*-2.5*	**-0.8**
	PS	nd	2.5	5.5	-0.5	*7.5*	**2.5**
	HL	nd	3.5	2.5	-0.5	*5.5*	**1.8**
CKG-L	**C6-40**	nd	3.5	2.5	nd	*6.0*	**3.0**
	C8-40	nd	2.5	1.5	nd	*4.0*	**2.0**
	C8+Z	nd	4.5	3.5	nd	*8.0*	**4.0**
	PS	nd	1.5	3.5	nd	*5.0*	**2.5**
	HL	nd	1.5	-1.5	nd	*0.0*	**0.0**
	BM	nd	3.5	3.5	nd	*7.0*	**3.5**

C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn; nd: Non-determined. Color gradient indicates the strength of the score whereas dark green is the most suitable, highest scoring amendment and red indicates a negatively-scoring amendment.

For PKG, **C6-20, C6-40, C6+Z, Z, and HL** are globally effective, with **HL** scoring the highest due to its polyvalent ability to reduce available Cd, Pb, and Zn. Regarding overall amendment efficiency, HL is the most effective for this soil. C6-40 is also a toxicologically-interesting amendment. On this soil, CH was clearly an amendment to avoid, as it invokes negative responses for both Cd and Pb. For CKG-N, **C6-20, C6-40, C6+Z, PS, and HL** were globally effective, with **C6-40** having the highest score due to its efficacy on Pb, Zn, and As. For CKG-L, no amendment was inefficient. The compost mixed with zeolite (**C8+Z**) had the highest overall score because of its Pb- and Zn- reduction abilities, and BM was a suitable amendment because of its toxicological interests

However, it is important to note that this score must be used as a key. Depending on preferred impact categories, illustrated in the Annexes 7-1, 7-2, and 7-3, different amendments may be chosen. Notably, considering PKG's highly mobile Cd which hyperaccumulated in lettuce, and Pb's presence in this soil, it is most pertinent to focus on the scores regarding these two elements. Environmentally, C6-20, C6-40, Z, and HL were the most efficient amendments for this condition, whereas toxicologically, C6-40 and HL were the most efficient. Overall, HL is the most effective amendment for Pb, whereas C6-40 was more efficient for Cd (Annex 7-1). For CKG-N, the main concern on this soil is reducing Pb and As mobility and their human impact. Amendments using C6 were the only ones that earned a positive score for both As and Pb. However, PS' significant decrease of human impact as analyzed by GI-bioaccessible As is not negligible. Concerning the most effective amendments on human impact reduction, C6-20, C6-40, C6+Z, and PS were the most effective amendments for this soil, with their overall toxicological impacts determining C6-40 to be the most efficient (Annex 7-2). For CKG-L, Pb is the most problematic element. Environmentally, C8+Z, HL, and BM were the most efficient amendments for this soil. Agronomically, C6-40, C8+Z, and PS were the most efficient amendments. Toxicologically, C6-40, C8-40, C8+Z, and BM were the most efficient amendments. Overall, C8+Z and BM were the most effective amendments for this element (Annex 7-3).

Additionally, these scores are based upon a lettuce model, which is a leafy vegetable not necessarily representative of all kitchen garden plants. This model was chosen because of its high prevalence as a crop grown in kitchen gardens, with 51% of gardeners choosing to grow a variety of this crop (Bidar et al., 2017). This study was also carried out in controlled greenhouse conditions which are not necessarily representative of field conditions. Thus this score and its components are useful for the PKG, CKG-N, and CKG-L soils, but the practical in-field application of the studied amendments may pose some potential for gardeners.

1.5 Amendment limitations

Gardeners typically use soil amendments to improve their soil and crop quality. However, amendments can invoke different responses in soil flora, fauna, and metal(oid) fractionation depending on their doses. Chemical fertilizers can burn plants with too much nutrients if applied at high doses, and this may also impact metal(loid) mobility and plant uptake. The question of the durability of organic amendments is also raised, as their reapplication is required. Current protocols suggest compost reapplication every 2 years, but this is not necessarily followed by gardeners, who may apply more often. The amendments studied were thus applied at culturally-relevant, “low” doses. Though all of the tested amendments were chosen to be affordable, easily applicable, and accessible, natural preferences may exist. Of the most effective amendments tested during this thesis, commercialized compost (C), compost mixed with zeolite (C+Z), potting soil (PS), bone meal (BM), and hydrated lime (HL) at different rates of application were used.

Whereas compost was applied at either 0.6% or 1.2%, PS was applied at 3%, BM at 0.05%, and HL at either 0.05 or 0.1%. Typically, organic matter-rich amendments are more expensive than mineral amendments like HL, so it may be economically preferable for a gardener to apply a 0.05% dose of HL than 3% of PS, for example. Specifically regarding PS applied at 3% to CKG-N, Experiment 1b found no significant differences in efficacy on As in its active components, peat and perlite, applied at 1.2%. Potting soil typically costs 1.6€ L^{-1}, perlite costs 0.42€ L^{-1}, and peat costs 0.45€ L^{-1}. The two latter products are approximately 1/3 of the density of PS, making their addition to soil instead of PS approximately 1/3 of the price. Thus economically, gardeners may prefer to use either perlite or peat.

Concerning the compost and zeolite mix, this was seen to be an effective amendment. However, mixing the products together at the right doses may be time-intensive for gardeners treating a large surface area. Additionally, it may be difficult for gardeners to measure doses of their amendments, and this may alter their affects, as with the contaminated compost mixed with zeolite. Additionally, gardeners are likely to produce their own compost instead of buying the commercialized, non-contaminated product, as compost is seen as a green way to dispose of household and garden waste all while improving soil quality. These auto-produced composts, however, can show variable quality and be contaminated by metal(loid)s present in the amendment’s parent material (*e.g.,* green garden waste, garden soil, homegrown vegetable peelings). On average, composts produced near a smelter in northern France (*n* = 52) exceeded the legislation concentration limits of Cd and Pb (3.0 and 180 mg kg^{-1}, respectively) for organic amendments (Pelfrêne et al., 2019) and self-produced composts hailing from Nantes showed that up to 85% exceeded organic farming thresholds for Pb and Zn (Kohli et al., 2022). As Pb-contaminated composts have been shown to increase its soil mobility (Hamidpour et al., 2017; Kohli et al., 2022), this could be problematic. In this study, in a contaminated kitchen garden soil (CKG-L), the addition of a contaminated compost added at 0.6% had no impact on Pb extractability as examined by NH_4NO_3 or EDTA, however.

Furthermore, in comparison to an unamended control soil, transfer of Pb to vegetables can be reduced with auto-produced compost addition (Kohli et al., 2022; Hiller et al., 2022) because urban soils rich in organic matter with near-neutral pH can limit Pb transfer into vegetables (Sauvé et al., 1998; McBride et al., 2013; Paltseva et al., 2018). This phenomenon happens because the fraction of Pb in the SPW is mainly complexed with dissolved organic matter (Sauvé et al., 1998; McBride et al., 2013; Paltseva et al., 2018; Attanayake et al., 2017). In this study, for CKG-L, contaminated compost indeed reduced Pb content in rye grass shoots, but in a non-contaminated soil the same compost increased Pb's plant uptake. The addition of zeolite (15%) successfully offset this uptake. Compared to the unplanted soil, the addition of a plant model likely promoted the conversion of Pb to a less available form, reducing NH_4NO_3-extractable Pb. Globally, this experimentation showed that a French compost produced in typical ways but having a typically low pH, and possessing a relatively high level of Cd, Pb, and Zn, can indeed enhance Pb's uptake from soil. This mobilization can be limited by the addition of 15% and 25% of zeolite the compost in question. The addition of compost, and furthermore compost and zeolite, can also increase biomass output. Realistically, one application of such a compost applied at the recommended dose of 0.6% poses little environmental or human risk. Repeated application, however, could imply environmental and human risk and would need to be studied further. Less is known about the effects of a contaminated compost with a more typical pH on soil metal speciation, and the potential effects on an acidic soil. Though in this study one application of compost posed little risk, repeated application risks harming soil quality, leaching metals into the soil solution, and leading to further plant uptake, particularly for specific metal(loid)s and specific plants. This in turn could imply environmental and human risk and would need to be studied further, with additional plant species other than rye grass.

2. Perspectives

The logical next step of testing these amendments would be to do so in *in situ* conditions. This would allow for the interpretation of metal(loid) behavior in field conditions, where the gardens located throughout France are subjected to different climatic conditions. Natural variations in soil temperature, humidity, rainfall and splash, soil compaction, and flora and fauna site interactions can change metal(loid) behavior between *ex situ* and *in situ* conditions (McBride et al., 2013). Currently, a planted experiment testing the effects of HL on plants grown on the PKG soil is in place, as well as an experiment testing the effects of C-40 (commercialized compost applied at 40 t ha^{-1}), HL, and PS on

CKG-N and one testing the effects of C-40, C+Z, HL, and BM on CKG-L. As seen in Figure 7-7, for each site, multiple plots were amended in randomly-spaced replicates before plantation.


Plot preparation
Plot amendment
Plant growth

Figure 7-7. ***In situ*** **experimentation set up example**

Biological activity of the studied soils was measured in terms of global bacterial activity and fungal biomass during this thesis. However, some results found that changes in metal(loid) availabilities had little connection to the physico-chemical characteristics and global biological activity measured. Certain species of soil flora, represented by bacteria, actinomyces, archaea, fungi, and algae may be interesting to identify and study further. The potential presence and/or influence of soil fauna such as earthworms, ants, termites, and *Collembola* on soil structure and metal(loid) fractionation, as well as their uptake of metal(loid)s, would also be an interesting indicator of soil health and metal(loid) bioavailability in the garden soils.

Experiment 2 studied the impact of amendment on a lettuce model. Further experimentation could study the impact of amendments on other plant species with different metal(oid) uptake mechanisms (varied cropping), plant species grown at the same time on the same plot of soil (coupled cropping), and successively planted crops (Figure 7-8). As lettuce is a leafy vegetable, it would be interesting to also test the impact of amendments on metal(loid) uptake in a root vegetable like the carrot, a root vegetable with edible aerial parts, like a radish, an aromatic plant, or a flowering plant like squash. Other experiments could also test two or multiple different plant species grown at the same time in the same plot, as is often done in field conditions (*e.g.,* corn, beans, and squash). Further studies could also examine the impact of successive cropping. An experimental set up could compare the impact of seeding an aerial plant followed by another species, whereas an experiment ran in parallel could just test amendment impact on the second species grown directly. For example, after lettuce harvest, a new species such as an aromatic plant could be sown on the same soil. At the same time the lettuce is seeded, a radish or aromatic plant could be seeded on other pots. This could elucidate how successive cropping may change or minimize metal(loid) risk in moderately contaminated gardens.

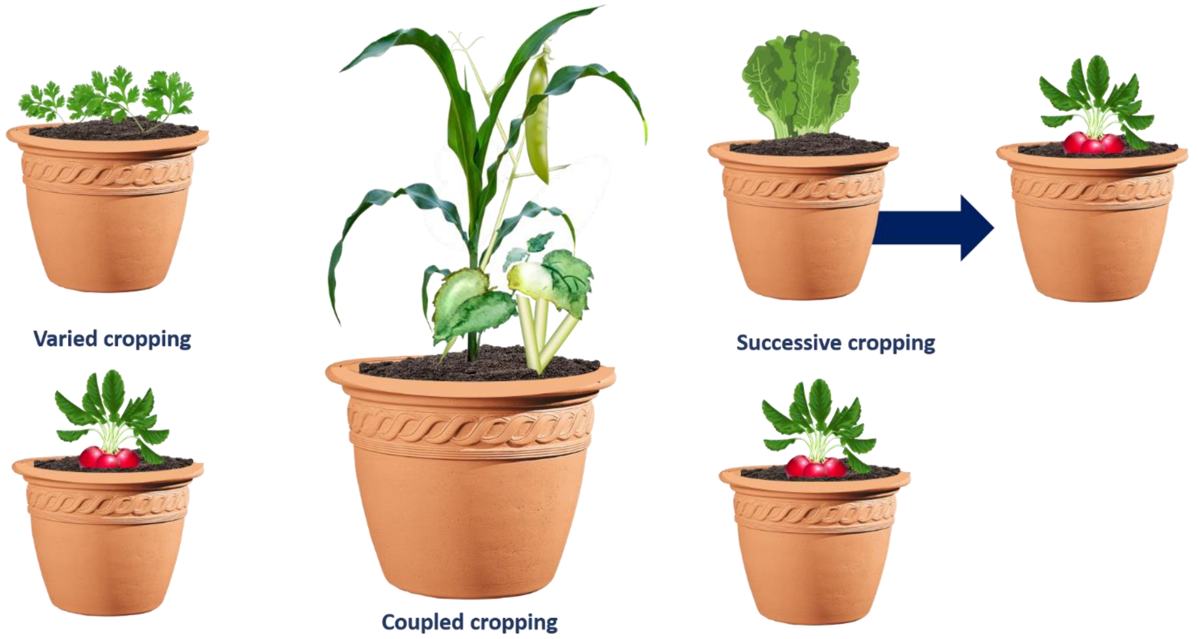

Figure 7-8. **Illustration of possible future experiments on the impact of amendments on varied, coupled, and successive plant cropping models.**

Interpretations of the influence of amendments in metal(loid) environmental and toxicological results and soil physico-chemical properties suggested that metal(loid)s, specifically in the case of the geogenously contaminated soil CKG-N, may bind to Fe- hydroxides because of a presence of arsenopyrite in the parent soil (Le Guern et al., 2013). A Mehra and Jackson evaluated of iron oxides may further elucidate these potential interactions. Additionally, success with the mixing of compost and zeolite was seen on metal(loid) immobilization. A better idea of the chemical structures potentially formed with this amendment mixes' influence may better be understood with X-ray crystallography methods.

3. Conclusion

The main objective of the thesis explored if **"culturally-relevant doses of soil amendments can reduce metal(loid) mobility, (bio)availability and oral bioaccessibility in multi-contaminated soils."** The six most pertinent amendments studied for each soil were compared to an unamended control in order to evaluate their impacts on soil physico-chemical characteristics, environmental extractability of metal(loid)s, biomass, and toxicological availability of metal(loid)s. This allowed for the determination of the most efficient amendments for each soil. As illustrated in Figure 7-9, amendments C6-40 and HL were determined to be the most efficient for PKG; C6-20, C6-40, C6+Z, and PS were determined to be the most pertinent for CKG-N, especially C6-40; and C8+Z and BM the most pertinent for CKG-L. However, there is no one amendment that can produce favorable impacts on all three soils for all of the impact categories discussed. Amendments must specifically be chosen according to soil properties, contamination nature, and experimental trials.

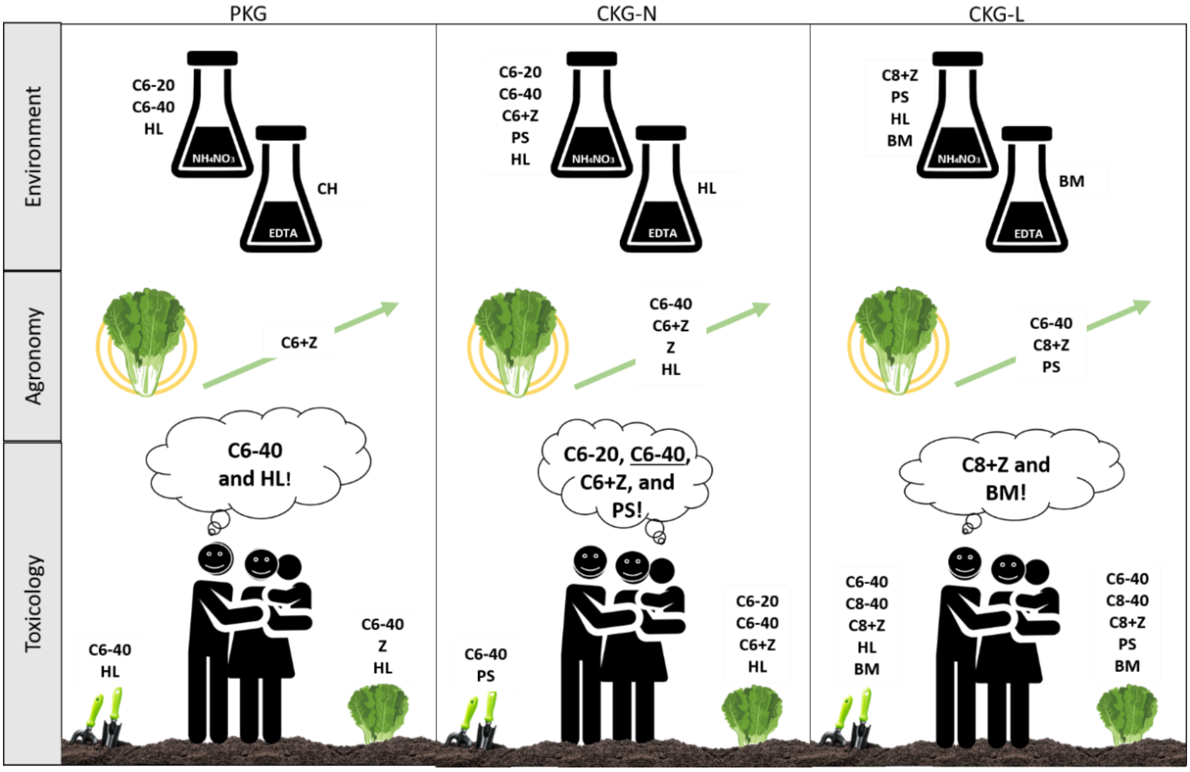

Figure 7-9. Illustration of the highest-scoring amendments evaluated by short-term and long-term environmental (as evaluated by NH_4NO_3 and EDTA), agronomic (as evaluated by biomass), and toxicological impacts (as evaluated by GI-oral bioaccessibility and BCF in lettuce) in comparison to their respective Experiment 2 planted controls. C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn.

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Annexes

Annex 4-1. Significant differences in physico-chemical properties among PKG conditions in Experiment 2

Physico-chemical	pH	$CaCO_3$ g kg^{-1}	P_2O_5 g kg^{-1}	EC µS cm^{-1}	Soluble C_{org}
U	6.27 bc	1.1 d	0.46 cd	887 bc	6.1 d
C6-20	**6.41 a**	1.5 cd	0.46 cd	859 c	5.7 d
C6-40	6.34 ab	**2.1 bc**	0.53 bcd	1081 bc	**7.6 c**
C6+Z	6.17 c	**2.1 bc**	0.56 bc	1249 abc	**8.5 bc**
Z	6.18 c	**2.6 b**	**0.62 b**	1311 ab	**9.6 b**
HL	6.28 abc	**3.6 a**	**0.79 a**	**1589 a**	**10.9 a**
CH	6.29 abc	**1.9 c**	0.44 d	823 c	5.3 d
Pr > F	***0.021***	***<0.0001***	***0.000***	***0.017***	***<0.0001***

C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. As analysed by a Fisher test and treated by an ANOVA with a Tukey post-hoc test, whereas letters denote significant differences among conditions and letters in bold denote a significant difference in comparison to the control soil.

Annex 4-2. Significant differences in physico-chemical properties among CKG-N conditions in Experiment 2

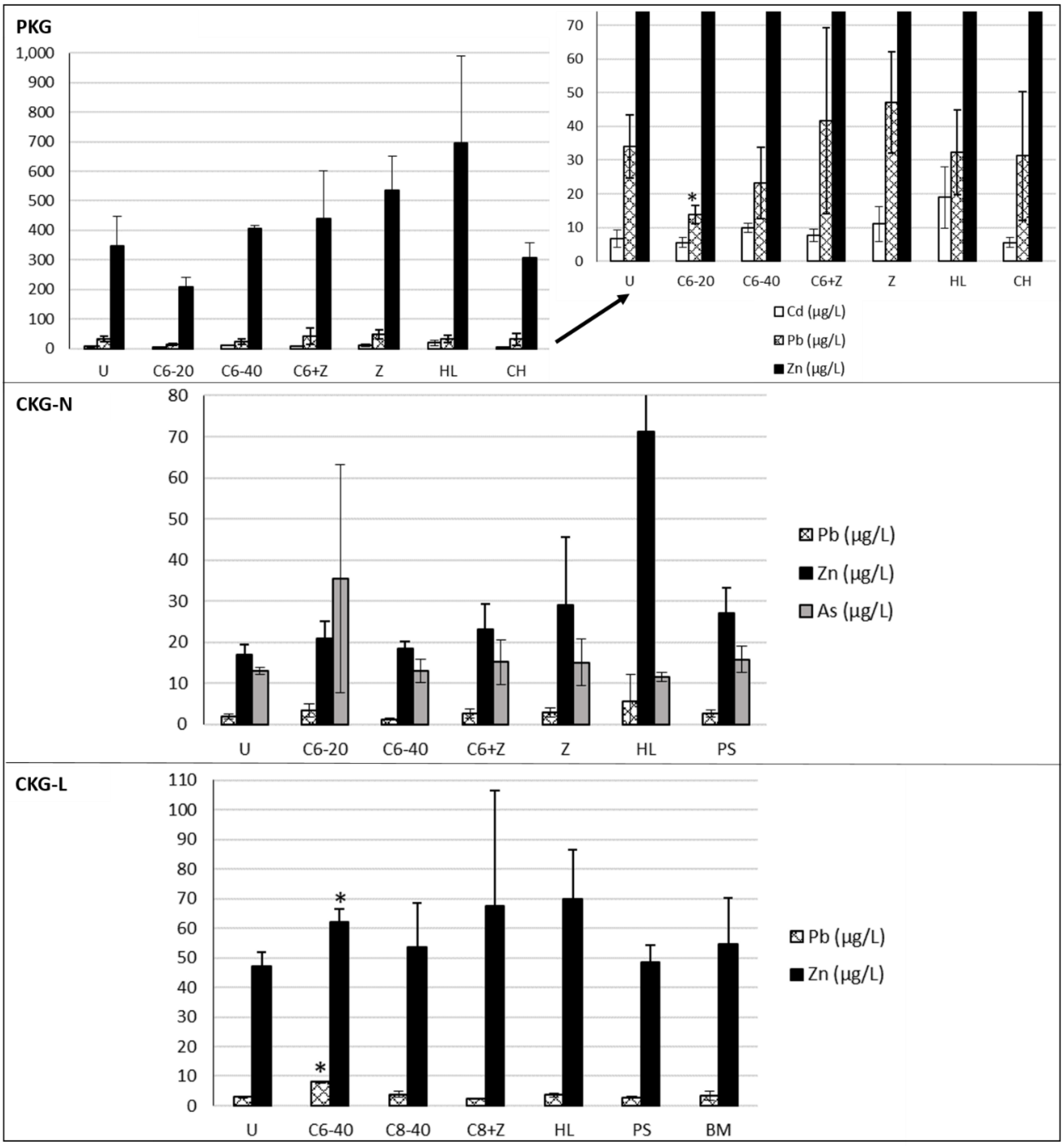
	pH	$CaCO_3$ g kg^{-1}	P_2O_5 g kg^{-1}	EDTA As %	NH_4NO_3 Zn %	Zn% F2
U	7.12 b	0.9 d	0.35 c	0.02 c	0.00016 ab	17 a
C6-20	7.10 bc	2.0 a	0.47 a	0.04 ab	0.00014 ab	12 b
C6-40	7.10 bc	2.1 a	0.47 a	0.04 ab	0.00014 ab	12 b
C6+Z	7.01 d	1.7 b	0.43 ab	0.04 ab	0.00015 ab	12 b
Z	7.04 cd	1.2 c	0.35 c	0.05 a	0.00019 ab	12 b
PS	7.17 b	1.5 b	0.37 c	0.03 bc	0.00013 ab	14 ab
HL	7.34 a	1.7 b	0.40 bc	0.03 bc	0.00007 ab	15 ab
Pr > F	***<0.0001***	***<0.0001***	***0.001***	***0.018***	***0.048***	***0.033***

C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. As analysed by a Fisher test and treated by an ANOVA with a Tukey post-hoc test, whereas letters denote significant differences among conditions and letters in bold denote a significant difference in comparison to the control soil.

Annex 4-3. Significant differences in physico-chemical properties among CKG-L conditions in Experiment 2

	pH	$CaCO_3$ g kg^{-1}	P_2O_5 g kg^{-1}	FDA	Cd mg kg^{-1} in lettuce	Pb mg kg^{-1} in lettuce	Pb in soil solution (µg/L)	EDTA Pb %
U	7.77 e	72 b	0.41 bc	1.95 abc	0.97 b	0.74 bc	2.9 b	42 a
C6-40	7.84 d	83 a	0.44 ab	1.96 ab	0.85 bc	0.58 c	8.0 a	25 c
C8-40	8.10 a	77 c	0.48 a	1.63 cd	0.97 b	0.70 bc	3.7 b	26 c
C8+Z	7.88 cd	78 c	0.47 a	2.15 a	0.71 bc	0.70 bc	2.4 b	29 bc
PS	7.87 cd	76 c	0.40 bc	1.62 d	0.66 c	0.75 bc	2.7 b	38 ab
HL	8.02 b	76 c	0.38 c	1.74 bcd	1.30 a	1.10 a	3.5 b	31 abc
BM	7.94 c	78 c	0.42 bc	1.76 bcd	0.87 bc	0.84 b	3.4 b	23 c
Pr > F	***<0.0001***	***0.001***	***0.003***	***0.029***	***0.004***	***0.015***	***0.000***	***0.026***

C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. As analysed by a Fisher test and treated by an ANOVA with a Tukey post-hoc test, whereas letters denote significant differences among conditions and letters in bold denote a significant difference in comparison to the control soil.



Annex 4-4. Concentrations of metal(loid)s in soil pore water (mean and standard deviation values expressed in µg L^{-1}) in the three kitchen garden soils (PKG, CKG-N, CKG-L) 6 weeks after lettuce seeding. U2: unamended planted control; C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. * denotes a significant difference ($p < 0.05$) between the unamended planted control U2 and a given condition for a given soil as evaluated by a Student test.

Annex 4-5. Pearson correlation matrix of variable relationships in PKG soil. Numbers in bold represent a significant correlation between two variables ($p < 0.05$).

	Cd BCF	Cd % NH$_4$	Cd% F2	C$_{org}$	Pb% F3	P$_2$0$_5$	[Cd]	Cd% F1	CaCO$_3$
Cd BCF	**1**								
Cd % NH$_4$	**0.92**	**1**							
Cd% F2	**-0.79**	**-0.90**	**1**						
C$_{org}$	**-0.76**	**-0.86**	**0.96**	**1**					
Pb% F3	**-0.83**	**-0.87**	**0.88**	**0.91**	**1**				
P$_2$0$_5$	**-0.80**	**-0.90**	**0.92**	**0.90**	**0.86**	**1**			
[Cd]	**-0.88**	**-0.96**	**0.95**	**0.91**	**0.87**	**0.94**	**1**		
Cd% F1	**0.77**	**0.86**	**-0.96**	**-0.92**	**-0.79**	**-0.89**	**-0.94**	**1**	
CaCO$_3$	**-0.79**	**-0.87**	**0.87**	**0.82**	**0.77**	**0.83**	**0.89**	**-0.84**	**1**

Annex 4-6. Significant differences in Cd extractability among PKG conditions in Experiment 2

Cd	Cd BCF	EDTA Cd %	NH$_4$NO$_3$ Cd %	F1 Cd %	F2 Cd %
U	3.5 a	47 c	2.0 a	36.1 b	46.7 de
C6-20	**2.6 b**	**66 a**	1.8 ab	**38.2 a**	45.1e
C6-40	**2.5 bc**	**62 ab**	**1.5 bc**	36.9 ab	**51.3 c**
C6+Z	2.8 ab	**56 b**	**1.5 b**	**33.7 c**	**54.5 c**
Z	**1.8 c**	**64 a**	**1.3 c**	**27.2 d**	**59.6 b**
HL	**0.9 d**	**56 b**	**0.8 d**	**23.3 e**	**65.2 a**
CH	3.3 ab	50 c	1.8 a	36.6 ab	47.9 d
Pr > F	***<0.0001***	***<0.0001***	***<0.0001***	***<0.0001***	***<0.0001***

C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. As analysed by a Fisher test and treated by an ANOVA with a Tukey post-hoc test, whereas letters denote significant differences among conditions and letters in bold denote a significant difference in comparison to the control soil.

Annex 4-7. Significant differences in Pb extractability among PKG conditions in Experiment 2

Pb	EDTA Pb %	F1 Pb %	F2 Pb %	F3 Pb%
U	46 c	5.1 ab	80.6 a	9.1 d
C6-20	**71 a**	4.7 b	**77.7 bc**	**11.8 c**
C6-40	**65 a**	4.8 ab	**76.2 cd**	**14.1 bc**
C6+Z	**67 a**	**3.8 c**	**74.0 de**	**13.9 c**
Z	**53 b**	**3.5 cd**	**72.8 e**	**16.5 ab**
HL	51 bc	**2.9 d**	**72.3 e**	**17.2 a**
CH	45 c	**5.5 a**	79.6 ab	9.3 d
Pr > F	***<0.0001***	***<0.0001***	***<0.0001***	***<0.0001***

C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. As analysed by a Fisher test and treated by an ANOVA with a Tukey post-hoc test, whereas letters denote significant differences among conditions and letters in bold denote a significant difference in comparison to the control soil.

Annex 4-8. Pearson correlation matrix of variable relationships in CKG-N soil. Whereas numbers in bold represent a significant correlation between two variables ($p < 0.05$).

CKG-N	**Pb % EDTA**	**$[Zn]_{soil}$**	**Zn BCF**	**Pb BCF**	**$[Pb]_{lettuce}$**	**$[Zn]_{lettuce}$**	**As BCF**	**$[As]_{lettuce}$**
Pb % EDTA	**1**							
$[Zn]_{soil}$	**-0.77**	**1**						
Zn BCF	**0.63**	**-0.73**	**1**					
Pb BCF	**0.56**	**-0.54**	**0.90**	**1**				
$[Pb]_{lettuce}$	0.25	-0.24	**0.76**	**0.92**	**1**			
$[Zn]_{lettuce}$	0.30	-0.30	**0.86**	**0.85**	**0.88**	**1**		
As BCF	0.41	-0.37	**0.79**	**0.81**	**0.83**	**0.84**	**1**	
$[As]_{lettuce}$	0.20	-0.14	**0.67**	**0.72**	**0.83**	**0.84**	**0.96**	**1**

soil: concentration in soil; lettuce: concentration in lettuce; BCF: bioconcentration factor

Annex 4-9. Pearson correlation matrix of variable relationships in CKG-L soil. Whereas numbers in bold represent a significant correlation between two variables ($p < 0.05$)

CKG-L	**Pb% F4**	**Zn BCF**	**$[Pb]_{soil}$**	**Pb BCF**
Pb% F4	**1**			
Zn BCF	-0.22	**1**		
$[Pb]_{soil}$	**-0.48**	**0.65**	**1**	
Pb BCF	-0.05	**0.62**	**0.74**	**1**

F4: Fraction R; soil: concentration in soil; BCF: bioconcentration factor

Annex 4-10. Metal(loid) extractability ratio (based on NH_4NO_3- and EDTA-extractants) calculated between Experiment 2 compared to the unamended unplanted control soils (U1) in Experiment 1a

		NH_4NO_3					EDTA			
Soil	*Amendment*	U1	**Cd**	**As**	**Pb**	**Zn**	**Cd**	**As**	**Pb**	**Zn**
PKG	C6-20	**NH_4NO_3:** Cd = 1.8% Zn = 1.3% **EDTA** Cd = 70% Pb = 66% Zn = 50%	0.96	nd	**0.23**	**0.13**	**0.67**	nd	0.89	**0.67**
	C6-40		**0.81**	nd	**0.20**	**0.12**	**0.56**	nd	**0.83**	**0.62**
	C6+Z		0.83	nd	**0.26**	**0.16**	**0.57**	nd	0.84	**0.71**
	Z		**0.69**	nd	**0.24**	**0.15**	**0.65**	nd	**0.67**	**0.86**
	HL		**0.43**	nd	**0.25**	**0.09**	**0.57**	nd	**0.64**	**0.84**
	CH		0.98	nd	**0.27**	**0.15**	**0.50**	nd	**0.57**	**0.58**
CKG-N	C6-20	**NH_4NO_3:** Zn = 0.68% As = 0.23% **EDTA** Pb = 14% Zn = 17% As = 7.4%	nd	**0.52**	**0.15**	**0.02**	nd	**0.54**	**0.82**	**0.66**
	C6-40		nd	**0.56**	**0.13**	**0.02**	nd	**0.54**	**0.84**	**0.64**
	C6+Z		nd	**0.53**	**0.09**	**0.02**	nd	**0.49**	**0.82**	**0.63**
	Z		nd	**0.59**	**0.14**	**0.03**	nd	**0.62**	0.88	**0.58**
	PS		nd	**0.69**	**0.10**	**0.01**	nd	**0.42**	**0.77**	**0.53**
	HL		nd	0.67	**0.08**	**0.02**	nd	**0.44**	**0.72**	**0.46**
CKG-L	C6-40	**NH_4NO_3:** Pb = 0.04% Zn = 0.01% **EDTA** Pb = 48% Zn = 14%	nd	nd	0.82	1.40	nd	nd	**0.54**	**1.43**
	C8-40		nd	nd	0.72	1.42	nd	nd	0.56	**1.44**
	C8+Z		nd	nd	0.56	1.25	nd	nd	**0.61**	**1.44**
	PS		nd	nd	0.65	1.28	nd	nd	0.66	**1.48**
	HL		nd	nd	0.64	1.32	nd	nd	0.82	**1.48**
	BM		nd	nd	0.56	1.17	nd	nd	**0.48**	**1.31**

C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. Whereas red denotes a significant increase, and green denotes a significant decrease ($p < 0.05$) as evaluated by a Student test and nd means non-determined.

Annex 5-1. Pearson correlation matrix of variable relationships in CKG-N soil. Whereas numbers in bold represent a significant correlation between two variables (p < 0.05).

	%Pb GI	Pb% F3	Pb% F1	Pb% F4	Pb% F2
%Pb GI	**1**	**0.981**	**0.863**	-0.355	0.245
Pb% F3	**0.981**	**1**	**0.886**	-0.444	0.336
Pb% F1	**0.863**	**0.886**	**1**	-0.622	0.529
Pb% F4	-0.355	-0.444	-0.622	**1**	**-0.993**
Pb% F2	0.245	0.336	0.529	**-0.993**	**1**

GI: gastro-intestinally bioaccessible; F1: Fraction A; F2: Fraction B; F3: Fraction D; F4: Fraction R

Annex 5-2. **Metal(loid) bioaccessibility ratio calculated between Experiment 2 amended (U2), planted soils and the unamended unplanted control soils in Experiment 1a (U1)**

		G			GI		
Soil	*Amendment*	**Cd**	**As**	**Pb**	**Cd**	**As**	**Pb**
PKG	C6-20	**1.13**	nd	**0.85**	1.91	nd	1.15
	C6-40	**1.08**	nd	**0.80**	1.72	nd	0.94
	C6+Z	**1.06**	nd	**0.80**	1.79	nd	1.04
	Z	**0.89**	nd	**0.69**	1.65	nd	1.22
	HL	**0.96**	nd	**0.63**	1.47	nd	0.96
	CH	**1.04**	nd	**0.81**	2.32	nd	1.21
CKG-N	C6-20	nd	**0.59**	**0.60**	nd	**0.67**	**5.25**
	C6-40	nd	**0.57**	**0.57**	nd	**0.63**	**4.77**
	C6+Z	nd	**0.59**	**0.55**	nd	**0.63**	**4.59**
	Z	nd	**0.63**	**0.56**	nd	**0.72**	**5.94**
	PS	nd	**0.61**	**0.53**	nd	**0.70**	**4.76**
	HL	nd	**0.55**	**0.47**	nd	**0.62**	**4.54**
CKG-L	C6-40	nd	nd	0.89	nd	nd	1.35
	C8-40	nd	nd	0.82	nd	nd	1.83
	C8+Z	nd	nd	0.86	nd	nd	2.54
	PS	nd	nd	0.83	nd	nd	2.28
	HL	nd	nd	0.93	nd	nd	2.73
	BM	nd	nd	0.81	nd	nd	2.37

C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 10%; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 10% ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. Whereas red denotes a significant increase, and green denotes a significant decrease ($p < 0.05$) compared to U1 values as evaluated by a Student test. nd means non-determined.

Annex 7-1. Score building based on environmental, agronomic, and human impact on PKG

	Environmental impact						Agronomic impact	Human impact				
	NH_4NO_3			EDTA				GI			BCF	
	Cd	Pb	Zn	Cd	Pb	Zn	Biomass	Cd	Pb	Zn	Pb	Zn
C6-20	3	1	3	-3	-3	-1	-1	3	1	1	1	1
C6-40	3	1	3	-1	-3	-1	-1	3	3	3	1	1
C6+Z	3	-1	1	-3	-3	-3	1	3	1	1	-1	1
Z	3	1	1	-3	-1	-3	-1	3	-1	3	1	1
HL	3	1	3	-3	-1	-3	-3	3	3	3	3	3
CH	1	-1	3	-1	-1	1	-1	-1	-1	1	-1	1

C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. Color gradient indicates the strength of the score whereas dark green is the most suitable, highest scoring amendment and red indicates a negatively-scoring amendment.

Annex 7-2. Score building based on environmental, agronomic, and human impact on CKG-N

	Environmental impact						Agronomic impact	Human impact				
	NH_4NO_3			EDTA				GI		BCF		
	Pb	Zn	As	Pb	Zn	As	Mass	Pb	As	Pb	Zn	As
C6-20	1	1	-1	1	-1	-3	-1	1	1	1	1	1
C6-40	1	1	-1	1	-1	-3	1	1	3	1	1	1
C6+Z	1	1	-1	1	-1	-3	1	1	1	1	1	1
Z	1	-1	-1	-1	-1	-3	1	1	-1	-1	1	-1
PS	1	1	-1	1	1	-3	-1	1	3	1	1	-1
HL	1	1	-1	1	1	-1	1	1	-1	1	1	1

C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. Color gradient indicates the strength of the score whereas dark green is the most suitable, highest scoring amendment and red indicates a negatively-scoring amendment.

Annex 7-3. **Score building based on environmental, agronomic, and human impact on CKG-L**

	Environmental impact				Agronomic impact	Human impact		
	NH_4NO_3		EDTA			GI	BCF	
	Pb	Zn	Pb	Zn	Mass	Pb	Pb	Zn
C6-40	-1	-1	3	1	1	1	1	1
C8-40	-1	-1	3	1	-1	1	1	1
C8+Z	1	1	3	1	1	1	1	1
PS	1	1	1	1	1	-1	1	1
HL	1	1	3	1	-1	1	-1	-1
BM	1	1	3	3	-1	1	1	1

C6-20: young compost (6 months) at 20 t ha^{-1}; C6-40: young compost (6 months) at 40 t ha^{-1}; C6+Z: young compost (6 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8+Z: mature compost (8 months) at 20 t ha^{-1} mixed with zeolite at 2 t ha^{-1} ; C8-40: mature compost (8 months) at 40 t ha^{-1}; Z: chabazite zeolite; HL: hydrated lime; PS: potting soil; BM: bone meal; CH: crushed horn. Color gradient indicates the strength of the score whereas dark green is the most suitable, highest scoring amendment and red indicates a negatively-scoring amendment.

Title: Effects of soil amendments on the functionality of urban vegetable garden soils contaminated with metallic elements and on the reduction of environmental and health hazards

Key words: soil, metallic pollutants, amendments, human exposure

Abstract: The need for nature in the city, the craze for "healthy eating" and difficult socio-economic contexts contribute to the development of gardening in (peri-)urban areas. Communities are regularly solicited for the creation of collective gardens. However, due to their environmental and historical contexts, the soils of vegetable gardens are complex environments, still little known; their functioning can be strongly disturbed by physical, chemical and biological degradation. Their contamination can even present health hazards, particularly in connection with the ingestion of soil particles or vegetables. Among the techniques that can improve the functioning of soils and influence the behavior of pollutants, especially metallic ones, the addition of amendments such as green waste compost, phosphate and carbonate products, natural or synthetic zeolites, or industrial by-products (red mud, iron shot, iron oxy-hydroxides) are cited as being able to reduce the mobility and bioavailability of metallic elements. However, the effectiveness of these amendments and their durability are still in question. The management of amendments, whether organic or mineral, raises questions since they may contain metallic and/or organic contaminants. However, the use of soil amendments as a method of managing vegetable garden soils and the health risks on amended soils are still relatively unstudied.

The subject of this thesis is to study the interest of organic and mineral amendments to manage urban vegetable garden soils with moderate anthropogenic contamination. The aim is to evaluate the potential of these amendments (used alone or in mixtures) to reduce in a sustainable way the phyto-availability of metallic pollutants as well as the exposure of gardeners and their families. In situ experiments will be carried out in different environmental and urban contexts and will be based on ex situ experiments aimed at selecting the choice of the studied amendments.

Titre : Les effets d'amendements sur la fonctionnalité des sols de potagers contaminés par les éléments métalliques et sur la réduction des dangers environnementaux et sanitaires

Mots clés : sol, polluants métalliques, amendements, expositions des populations

Résumé : Le besoin de nature en ville, l'engouement pour le « manger sain » et le contexte socio-économique difficile contribuent au développement du jardinage en milieu (péri)-urbain. Les collectivités sont régulièrement sollicitées pour la création de jardins collectifs. Or, de par leurs contextes environnementaux et historiques, les sols de potagers sont des milieux complexes, encore peu connus ; leurs fonctionnements peuvent être fortement perturbés par des dégradations physiques, chimiques et biologiques. Leur contamination peut même présenter un danger sanitaire notamment, en lien avec l'ingestion de particules de terre ou de légumes. Parmi les techniques pouvant améliorer le fonctionnement des sols et influer sur le comportement des polluants, notamment métalliques, l'ajout d'amendements tels que le compost de déchets verts, les produits phosphatés et carbonatés, les zéolites naturelles ou synthétiques, ou les sous-produits industriels (boues rouges, grenailles de fer, oxy-hydroxydes de fer) sont cités comme pouvant réduire la mobilité et la biodisponibilité des éléments métalliques. Se posent néanmoins les questions de l'efficacité de ces amendements et sa pérennité. La gestion des amendements, qu'ils soient organiques ou minéraux, pose toutefois question puisque ces derniers peuvent présenter des contaminants métalliques et/ou organiques. Or, le recours aux amendements comme méthode de gestion des sols de potagers et les risques sanitaires sur sols amendés restent encore assez peu étudiés.

Le sujet de la thèse vise à étudier l'intérêt d'amendements organique et minéraux, pour gérer des sols de potagers urbains présentant des contaminations anthropiques modérées. Il s'agit d'évaluer le potentiel de ces amendements (utilisés seuls ou en mélange) pour réduire de façon durable la phytodisponibilité des polluants métalliques ainsi que l'exposition des jardiniers et de leur famille. Des expérimentations *in situ* seront réalisées dans différents contextes environnementaux et urbains et s'appuieront en amont sur des expérimentations *ex situ* visant à sélectionner le choix des amendements étudiés.