Effect of Organic Amendments on Heavy Metal Distribution and Uptake in Vegetable Gardens in Senegal

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THESIS ABSTRACT

The major constraints to food production in West Africa are related to the lack of suitable lands. Consequently, farmers incorporate organic amendments and wastewater to improve their yields. Within some limits, such wastes enhance soil fertility and can improve its physical properties. However, the advantages of using organic waste as fertilizer and soil amendment should be assessed with possible environmental and toxicological impacts due to the potential presence of heavy metals. The objective of this study was to assess the effect of organic amendments on heavy metal distribution in soils and vegetables in market gardens in Senegal. Organic amendments and soils samples were collected from four sites in eastern and southern Senegal. Samples were analyzed for physicochemical properties including particle size, total heavy metals, carbon content, nutrients and pH. A sequential extraction procedure was conducted to determine heavy metal sinks. Results showed that sites were sandy in nature, low to medium in organic carbon content (8300 to 36600 mg kg^{-1}), and had pH ranging from 5 to 7.9. The sequential extraction procedure showed that metals were distributed in the more stable soil fractions: Fe-Mn oxide, organic and residual. The highest soil metal concentrations in soils were

found in Pikine and Rufisque sites. Plant samples were collected from these two sites and analyzed for total metal content. Results showed that all metal concentrations in soils, organic amendments, and vegetables were within the safe limits proposed by the World Health Organization, with the exception of Cd, Pb and Zn levels in vegetables.

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GENERAL AUDIENCE ABSTRACT

Application of composted organic wastes and untreated wastewater to urban vegetable garden soils is raising serious concerns about possible health risks associated with the consumption of these vegetables particularly with regard to the concentrations of heavy metals in their edible portions. Therefore, this study focused on the evaluation of heavy metal concentrations in soils, organic amendments and vegetables from local gardens of Senegal and also, the determination of metal sinks in soil phases via a sequential extraction procedure (SEP). Soils, organic matter and vegetable concentrations of cadmium, cobalt, chromium, copper, manganese, nickel, lead and zinc were analyzed for total metals. Results from the SEP showed that metals in soils were located on the stable soil phases and would not be easily released unless environmental conditions changed (e.g. more acidic pH or anoxic conditions). Data from total metal analyses revealed that all metal concentrations in soil, organic amendments, and vegetables were within the safe limits proposed by the World Health Organization (WHO) with the exception of Cd, Pb and Zn levels in vegetables.

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TABLE OF CONTENT

Chapter I: Literature Review 1
INTRODUCTION 1
OBJECTIVES 2
HEAVY METALS 3
Cadmium (Cd) 4
Cobalt (Co) 5
Copper (Cu) 6
Chromium (Cr) 7
Lead (Pb) 8
Manganese (Mn) 9
Nickel (Ni) 10
Zinc (Zn) 11
BIOAVAILABILITY OF HEAVY METALS 12
PLANT UPTAKE 12
SOURCE OF HEAVY METALS IN AFRICAN SOILS 13
Sewage Sludge or Biosolids 14
Animal Manure 14
Wastewater 15
Pesticides and Fertilizers 17
Mining 18
Atmospheric Depositions 19
HEAVY METALS IN GARDENS 20
STRATEGIES TO REDUCE METALS LEVELS IN GARDENS 20
SUMMARY 21
REFERENCES 22
Chapter II: Heavy Metals in Organic Amendments, Soils and Vegetables 40
ABSTRACT 40
INTRODUCTION 41
METHODS AND MATERIALS 42
Study Sites and Farming Practices 42
Soil and Organic Matter Sampling Protocol 43
Soil and Organic Matter Characterization & Procedures 44
Vegetables Sampling Protocol 49

Metal Analyses in Vegetables 49
STATISTICAL ANALYSIS 50
RESULTS AND DISCUSSION 50
Soil and Organic Matter pH 51
Soil Total Carbon Content 52
Soluble Salts 53
The Estimated Cation Exchange Capacity (CEC) 54
Soil Nutrient Contents 54
Sequential Extraction 55
Chromium (Cr) 55
Cadmium (Cd) and Cobalt (Co) 56
Copper (Cu) 56
Manganese (Mn) and Zinc (Zn) 57
Nickel (Ni) 57
Lead (Pb) 58
Total metals 58
Cadmium (Cd) 59
Cobalt (Co) 60
Chromium (Cr) 61
Copper (Cu) 62
Manganese (Mn) 63
Nickel (Ni) 64
Lead (Pb) 65
Zinc (Zn) 66
Summary 67
CONCLUSION 68
REFERENCES 70

LIST OF TABLES

Table1: Source of heavy metals in the Environment (Calamari and Naeve, 1994)..... 39

Table 2.1. Tessier's sequential extraction procedures of heavy metals in soil (Tessier et al., 1979) 88

Table 2.2: Soil physiochemical parameters in all sites. Control 1: Uncultivated soil from Niayes region site and control 2: Uncultivated soil from Essyl site. Particle size and total carbon (TC) (mg kg^{-1}), estimated CEC (cmol (+) kg^{-1}), electrical conductivity (EC) (dS m^{-1}), nutrient contents (P, K, Ca Mg) (kg ha^{-1})..... 89

Table 2.3: Organic matter physiochemical parameters. PM: Composted animal manure and slaughterhouse waste collected from Pikine. RM: Composted animal manure and slaughterhouse waste collected from Rufisque. Total carbon (mg kg^{-1}), estimated CEC (cmol (+) kg^{-1}), nutrient contents (P, K, Ca Mg) (kg ha^{-1})..... 90

Tables 2.4: Total heavy metal concentration (mg kg^{-1}) ± SD in controls and amended soils. Control 1: Uncultivated soil from the Niayes region. Pikine, Rufisque and Rao: amended soils from the Niayes region. Control 2: Uncultivated soil from Essyl site. Essyl: amended soil from Essyl site nd: not detected 91

Tables 2.5: Total heavy metal concentration (mg kg^{-1}) ± SD in the organic amendments and the Pollutant Concentration Limits (PCL) for land-applied biosolids (USEPA, 1994). PM: Composted animal manure and slaughterhouse waste collected from Pikine. RM: Composted animal manure and slaughterhouse waste from Rufisque. 92

Table 2.6: Heavy metal concentration (mg kg^{-1}) ± SD in vegetables grown in Pikine site and the World Health Organization (WHO) Permissible level of metals (PLM) in vegetables (Organization, 2014). nd: not detected 93

Table 2.7: Heavy metal concentration (mg kg^{-1}) ± SD in vegetables grown in Rufisque site and the World Health Organization (WHO) Maximum Permissible Level of metals (MPL) in vegetables (Organization, 2014). nd: not detected 94

Table 2.8. The Maximum Permissible Level Limits (MPL) of heavy metals (mg kg^{-1}) in irrigation water, soils and vegetables established by the World Health Organization (WHO) (Organization, 2014) 95

Tables 2.9: Highest heavy metal concentration (mg kg^{-1}) in vegetable garden soils from this study, other African studies and the World Health Organization (WHO) Maximum Permitted Level (MPL) of metals in soils (Organization, 2014)..... 96

LIST OF FIGURES

Figure 2.1: Map of Senegal, the Niayes region sites and Essyl site. http://www.memoireonline.com/08/10/3840/m_Limpact-du-maraichage-dans-la-degradation-des-ressources-naturelles-dans-les-niayes-de-la-bordur1.html ……..……..97

Figure 2.2: Vegetable gardens in Pikine site, Dakar, April 2015 98

Figure 2.3: Wastewater and animal manure used in Pikine gardens, Dakar, April 2015 98

Figure 2.5: Animal manure used in Rufisque gardens, Dakar, April 2015 99

Figure 2.6: Vegetable gardens in Rao site, St. Louis, April 2015 100

Figure 2.7: Vegetable gardens in Essyl, Ziguinchor, April 2015 100

Figure 2.8: Chromium distribution in market garden soils of the Niayes region and Essyl..... 101

Figure 2.9: Cadmium distribution in market garden soils of the Niayes region and Essyl 102

Figure 2.10: Cobalt distribution in market garden soils of the Niayes region and Essyl 103

Figure 2.11: Copper distribution in market garden soils of the Niayes region and Essyl 104

Figure 2.12: Manganese distribution in market garden soils of the Niayes region and Essyl.... 105

Figure 2.13: Zinc distribution in market garden soils of the Niayes region and Essyl..... 106

Figure 2.14: Nickel distribution in market garden soils of the Niayes region and Essyl 107

Figure 2.15: Lead distribution in market garden soils of the Niayes region and Essyl 108

Chapter I: Literature Review

INTRODUCTION

Soil pollution by heavy metals is a significant environmental problem worldwide (Hu et al., 2013). In particular, metal pollution may occur naturally, as a result of mineral weathering, or anthropogenically, due to industrial activities, including mining, smelting and agricultural practices (e.g. application of metal contaminated fertilizers, sewage sludges and other biosolids) (You et al., 2015). The dumping of wastes from metalliferous mining and processing activities, is usually the main cause of anthropogenic heavy metal release into the environment (Baker et al., 1994). Other operations such as smelting, effluent and waste disposal, play a large part in introducing metals into the environment (Micó et al., 2006; Elekes, 2014). Previous studies have shown that in agricultural soils, the presence of metals such as Cd, Cr, Co, Zn, Ni, Mn, Cu and Pb, is of increasing concern because of their high potential of persistence and toxicity (He et al., 2005; Ali and Fishar, 2005; Wuana and Okieimen, 2011; Kelepertzis, 2014). For instance, they can be transferred from the soil system to other ecosystem components, such as the groundwater or crops, and therefore, may affect human health through the water supply and the food web (Micó et al., 2006). Although some trace elements (Mn, Zn, Fe, Cu, etc.) are essential plant micronutrients, they can have very toxic effects at high concentrations (Rahman et al., 2012). In addition, plants are primary producers, and thus, become a potential threat to human and animal health when grown on metal polluted soils (Efremova and Izosimova, 2012). In many African farmlands, qualitative and quantitative information about heavy metal concentrations and fluxes is lacking (Olatunji et al., 2013). Hence, the aim of this study is the assessment of heavy metal concentrations such as Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in organic waste, soil and vegetable in

some Senegalese gardens. This information would help to achieve sustainable use and preservation of the soil resources against heavy metal build-up, in the long-term (Towett et al., 2015).

OBJECTIVES

Organic amendments can substantially increase the fertility of soils in the Sahel region of Africa. However, many of these amendments may contain significant levels of heavy metals and may potentially pose a threat to human health and the environment. Accordingly, the objectives of this research are:

1) To assess the concentrations of the heavy metals in organic amendments and soils.

2) To determine the heavy metals sinks in soils.

3) To evaluate the heavy metal concentrations in vegetables grown on these soils

HEAVY METALS

Heavy metals are defined "as elements in the periodic table having atomic numbers more than 20 or densities more than 5 g cm^{-3}, generally excluding alkali and alkaline earth metals" (Sherene, 2010). They are often referred to as toxic elements because of their noxious effects in plants, animals and humans (Abdu, 2010). Heavy metals exist in different forms and are associated with a range of soil components which determine their bioavailability and potential toxicity (Rieuwerts et al., 1998). Metals may be occluded in soil minerals as well as bound to different phases of soil particles by chemisorption, ion exchange, co-precipitation, and complexation (Orroño and Lavado, 2009). Soil properties such as organic matter content, mineralogy, pH and redox potential influence trace metal solubility and potential bioavailability (Ashraf et al., 2012). Some heavy metals including cobalt (Co), copper (Cu), zinc (Zn), nickel (Ni) and manganese (Mn) are micronutrients essential for plant growth, while others such as selenium (Se), arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg) and chromium (Cr) have undetermined biological functions (Gaur and Adholeya, 2004). Olade (1987) has shown that the major sources of anthropogenic heavy metal pollution in Africa are fossil fuels, coal combustion, industrial effluents, solid waste disposal, fertilizers, mining and metal processing. Particularly, mining activities were found to be the most important causes of metal pollution in the environment. This was the case in Algeria with Hg, As in Namibia and South Africa, tin in Nigeria and Zaire and Cu in Zambia (Calamari and Naeve, 1994). Currently, the impact of these pollutants is exhibited mostly in the urban areas with large populations, high traffic density and consumer-oriented industries (Simeonov et al., 2010). Table 1 presents examples of potential sources for metals in the environment (Calamari and Naeve, 1994). In the following sections some of the most common heavy metals occurring in the environment and their toxicity will be discussed.

Cadmium (Cd)

Cadmium has an atomic number 48, atomic weight 112.4, density 8.65 g cm^{-3}, melting point 320.9°C, and boiling point 765°C. It is ranked 67th in abundance among the 90 naturally existing elements on Earth. Cd is considered one of the most toxic substances in the environment, occurs in the earth's crust at a concentration of 0.1-0.5 ppm and is commonly associated with Zn, Pb, and Cu ores (Judd et al., 2002). Natural sources of Cd include underlying bedrock or transported parent material such as glacial till and alluvium (Tran and Popova, 2013). However, anthropogenic inputs occur by atmospheric deposition, biosolids, manure and phosphate fertilizers application (Faroon et al., 2012). Concentrations of Cd in surface soils depend on factors such as pH, organic matter, clay and oxide content, natural geochemistry and magnitude of contamination (Capleton et al., 2006). In the environment, Cd exists in only one oxidation state (2^+) and does not undergo oxidation-reduction reactions (Mohamed, 2008). Cadmium is a non-essential element that is readily taken up by plant roots and efficiently transported to the above ground tissues of plants (Melo et al., 2014). This efficient transfer of Cd from soil to plants poses a potential threat to human health through the food chain (Satarug et al., 2003). The major sources of Cd in farm lands and especially in rice paddy fields are contaminated irrigation water, mining and industrial processes (Lai et al., 2010). For example, Street et al. (2009) have shown that Cd contamination of agricultural soils in South Africa is due to an increase in application of fertilizers, sewage disposal and mining activities. However, visible toxicity symptoms of the presence of Cd in plants have only been reported in a few studies due to its low concentration (Cosio et al., 2006). Regarding the impact on human health, long-term exposure to Cd has been shown to cause health problems including cancer and the Itai-Itai disease (Horiguchi et al., 1994). Cadmium is considered a human carcinogen by the International Agency for Research on Cancer and the National

Toxicology Program (Hu et al., 2014). Cadmium exerts toxic effects on human and animal organs through the formation of kidney stones, pneumonitis with pulmonary oedema and can also impact the skeletal system (Organization, 2010).

Cobalt (Co)

Cobalt has an atomic number 27, atomic weight 58.93, density 8.9 g cm^{-3}, melting point 1495°C, and boiling point 2,870°C. It is the 33rd most abundant element found in the Earth's crust and is usually combined with other elements. Cobalt is a component of more than 70 naturally occurring minerals, including various sulfides, arsenides, and oxides (Kim et al., 2006). Cobalt has many industrial uses in cutting tools, super alloys, surface coatings, high speed steels, cement carbides, ceramics and pigments (Gál et al., 2008). Therefore, it is mined in 17 countries, with the most significant deposits being associated with Ni/Cu production in the Democratic Republic of Congo and from arsenide ores in Canada and Morocco (Banza et al., 2009). Cobalt may enter the environment from both natural sources and human activities. It can occur in small amounts in rock, soil, air, water, and plants (Kabata-Pendias, 2010). However, elevated concentrations may result from anthropogenic activities such as mining, ore smelting facilities, application of phosphate fertilizers and Co-containing sludge (Bordean et al., 2012). Cobalt exits in the 0, 2^+, and 3^+ valence states, with Co^{2+} more stable than Co^{3+}, which is an excellent oxidizing agent (Pierpont and Lange, 2007). A biochemically important Co compound is vitamin B_{12} or cyanocobalamin, which is essential to good health for animals and humans (Zhang et al., 2009). According to Pilon-Smits et al. (2009), Co has been recognized as an essential element for animals and microorganisms. However, it is not needed for plant growth and may have toxic effects on plants at high concentrations. So far, the only physiological role ascribed to Co is in the fixation of molecular nitrogen in root nodules of leguminous plants (Palit et al., 1994). Moreover, studies have

demonstrated that inhalation of Co oxide particles can Pb to adverse negative effects on humans and animals (Ortega et al., 2014; Dick et al., 2003; Jomova and Valko, 2011). For instance, Karovic et al., (2007) have reported that toxic effects of Co include cardiomyopathy, pulmonary failures, carcinogenicity, neurotoxicity, and memory deficiency (Karovic et al., 2007).

Copper (Cu)

Copper was one of the first metals ever extracted and used by humans. It has an atomic number 29, atomic weight 63.5, density 8.96 g cm^{-3}, melting point 1083°C and boiling point 2595°C. Copper is the earth's 25th most abundant element and occurs as a soft reddish metal that can be found native as large boulders or as sulphide ores (Karlin and Tyeklár, 2012). The latter are complex mixtures of Cu, iron and sulphur in combination with other metals such as As, Zn and silver (Davis, 2001). Copper conducts heat and electricity efficiently (Mathews, 2014). As a result, Cu was important to early humans and continues to be a material of choice for power generation and transmission, electronic product manufacturing (Ashby, 2012), production of industrial machinery and transportation vehicles and high-technology applications (Doebrich, 2009). Copper ions can exist in both, oxidized, cupric (Cu^{2+}), or reduced, cuprous (Cu^{+}), but is predominantly exists in the (Cu^{2+}) state and most of it is complexed or tightly bound to organic matter (Williams et al., 2004). Natural discharges of Cu to air and water, can occur from windblown dust, volcanic eruptions, native soils, volcanoes, and decaying vegetation (Frederiksen et al., 2009). Anthropogenic sources are from the mining and factories that make or use Cu metal or Cu compounds (Graedel et al., 2004). Copper can also enter the environment through domestic waste water, combustion of fossil fuels and wastes, wood production and phosphate fertilizer production (Balabanova et al., 2011). A study in East Africa, has shown that the repeated use of Cu fungicides to control coffee berry disease can result in increased Cu content in soils and vegetation and thus

raising the pollution levels and human health risks (Loland and Singh, 2004). Copper plays an important role in organisms such as plants, bacteria, and mammals because it is involved in a number of vital bioenergetic processes (ATP synthesis) required for growth, development, and maintenance (Karlin and Tyeklár, 2012). However, in excess, Cu is a toxic heavy metal that primarily affects the liver, since it is the first site of Cu deposition after it enters the blood circulation system (Gaetke and Chow, 2003). Excess of Cu in soil plays a phytotoxic role, induces stress, plant growth retardation and leaf chlorosis (Boojar and Goodarzi, 2007). For humans and animals, Cu toxicity is manifested by the development of liver cirrhosis, damage of renal tubules, the brain and other organs (Leise et al., 2014).

Chromium (Cr)

Chromium has an atomic number 24, atomic mass 52, density 7.19 g cm^{-3}, melting point 1875°C, and boiling point 2665°C. It is the 17th most abundant nongaseous elements in the earth's crust occurring naturally from soils and rocks, almost always in the trivalent state (Ljung and Vahter, 2007). It exists in two major stable oxidation states, hexavalent chromium, $Cr^{6+,}$ and trivalent chromium, Cr^{3+}. Elemental Cr is never found in nature. Chromite ($FeOCr_2O_3$) is the only major commercial Cr mineral and mostly found in South Africa, Soviet Union, Philippines, and Rhodesia (Pacyna and Nriagu, 1988). Because of the multifarious uses of Cr in industrial activities such as leather tanning, pigments and paints, fungicides, ceramic and glass and in photography, its environmental contamination is widespread (Shanker et al., 2005). The trivalent reduced form of chromium, Cr^{3+} is an important component in human and animal balanced diet, while the hexavalent oxidized form, Cr^{6+}, is highly harmful even in small quantities (Zayed and Terry, 2003). Hexavalent Cr is detrimental to plants because it causes a decrease of growth and development

and is a human carcinogen that provokes pneumonia and other respiratory illness in humans and animals (Guertin, 2005; Karar et al., 2006).

Lead (Pb)

Lead has an atomic number 82, atomic mass 207.2, density 11.4 g cm^{-3}, melting point 327.4◦C, and boiling point 1725°C. It is the 50th most abundant element and is initially found at low concentrations in the Earth's crust predominantly as Pb sulfide. Lead is a nonessential and highly toxic heavy metal that has deleterious effects on biological systems (Pattee and Pain, 2003). Pb exists in two states, Pb^{2+}, more common and, Pb^{6+} the least frequent form (Ahmad et al., 1980). The widespread occurrence of Pb in the environment is largely due to anthropogenic sources such as the application of chemical fertilizers and agro-chemicals in agricultural lands (Pandey and Pandey, 2009), pipes and plumbing, pigments and paints, gasoline additives, construction materials and Pb-acid batteries (Llopis et al., 2006). In addition, its utilization increased with industrialization and rose dramatically with its use in automobile industries (Callender and Rice, 2000). Consequently, plants growing near highways are usually exposed to more Pb than other localities (Nabulo et al., 2006). Also, some sewage sludges containing large quantities of Pb and are frequently applied as organic amendments on fields and garden soils (Sharma and Dubey, 2005). Thus, increasing levels of Pb in agricultural lands can inhibit germination of seeds and exert a wide range of negative effects on plant growth and metabolism (Verma and Dubey, 2003). Lead is a toxic trace metal that can affect the human body through inhalation and ingestion of contaminated air, water, soil, and food (Mudgal et al., 2010). For instance, Cheng and Hu (2010) have shown that Pb poisoning impacts the peripheral and central nervous systems, kidneys and blood pressure. In Africa, children are the most vulnerable to Pb toxicity because they are frequently in contact with the contaminated soils. Lead pollution is increased due to the

unrestricted use of leaded gasoline, Pb-acid batteries in automobiles and more importantly, unregulated cottage industries associated with electronic waste recycling (Ogunseitan and Smith, 2007). For example, in a Senegalese study, Diouf et al. (2006) concluded that urban children from the Dakar region have higher blood Pb levels than rural children from Khombole, due to soil contamination from leaded-gasoline.

Manganese (Mn)

Manganese is the 10th most abundant element in the Earth's crust and the second most common heavy metal after iron (Förstner and Wittmann, 2012). Geochemically, Mn behaves like Mg, Fe, Ni, and Co and is readily depleted from igneous and metamorphic rocks by interactions with surface and groundwater (Doe, 1997). It occurs in natural systems in three different oxidation states: 2^+, 3^+, and 4^+ and is highly mobile as Mn^{2+} in acidic aqueous systems (Post, 1999). Manganese is an essential constituent of the human diet at low concentrations and is required for normal metabolism of amino acids, lipids, proteins and carbohydrates (Davidsson et al., 1991). Anthropogenic activities such as mining, ore transformation, application of agrochemicals containing Mn and other industrial processes are generally sources of Mn in the environment (Mergler, 1999). Much of the Mn in natural water bodies is found in the sediment (Novotny, 1995). Therefore, Mn is less toxic than most other metals in aquatic systems (Sanders et al., 1998). The principal pathway of Mn into human and animal systems is via food (rice, grain, nuts and tea) consumption. Human exposures are associated with neurologic and neuropsychiatric disorders with Mn deposition in the brain (Bouchard et al., 2011). Shi and Zhu (2008) have reported that excess Mn in plants may cause deficiency of Fe, Mg and Ca and induce inhibition of photosynthesis.

Nickel (Ni)

Nickel is an element with atomic number 28, atomic weight 58.69, density 8.9 g cm^{-3}, melting point 1455 °C, and boiling point 2730 °C. It is the 24th most abundant element in the Earth's crust and is usually combined with other elements. Nickel is found in all soils and is also emitted from volcanoes (Irwin et al., 1997). In the environment, Ni is primarily found combined with oxygen or sulfur as oxides or sulfides (Das et al., 2008). Although it can exist in several different oxidation states, the only important oxidation state under environmental conditions is Ni^{2+} (Haber et al., 2000). Some metals such as iron, Cu, Cr, and Zn are generally alloyed with Ni to make metal coins, jewelry, stainless steel and other industrial products (Das and Büchner, 2007). The progress of industrialization of Ni and Ni compounds has led to increased emission of pollutants into ecosystems (Barceloux and Barceloux, 1999). Even though Ni is essential for many living organisms, high concentrations in some areas from both anthropogenic and natural release may be toxic (Cempel and Nikel, 2006). The harmful impacts of higher concentrations of Ni on plants include inhibition of mitotic activities, reduction in plant growth, water content, photosynthesis and inhibition of enzymatic activities as well as nitrogen metabolism (Yusuf et al., 2011). For humans, inhalation exposure in occupational settings is a primary route for Ni-induced toxicity, and may cause lung cancer and respiratory tract disorder (Zhao et al., 2009).

Zinc (Zn)

Zinc has an atomic number 30, atomic mass 65.4, density 7.14 g cm^{-3}, melting point 419.5°C, and boiling point 906°C. It is the 27th most abundant element in the Earth's crust. Zinc is found in the air, soil, water and in all foods (Roney, 2005). Zinc occurs in small quantities in almost all igneous rocks and in sulfides, sphalerite and wurzite minerals (Silvera and Rohan, 2007). Due to its unique properties, Zn is used in a wide range of consumer, infrastructure, agricultural and industrial products (Callender and Rice, 2000). Therefore, the largest anthropogenic sources of Zn to the environment include metal production, waste incineration, fossil fuel consumption, phosphate fertilizers, herbicides and cement production (Councell et al., 2004). More importantly, Zn is an essential micronutrient, playing an important role in biological processes, specifically in the proper functioning of proteins in all living organisms (Andreini et al., 2006). Zinc is crucial for cell division, nitrogen regulation, photosynthesis and growth. Zinc is considered to be relatively non-toxic to humans because, according to the Toxnet database of the U.S. National Library of Medicine, the oral lethal dose (LD_{50}) for Zn is close to 3 g kg^{-1} body weight. This dose is 10 and 50 times greater than that of Cd and mercury, respectively (Plum et al., 2010). However, excess Zn is toxic to plants, causing disturbance of a wide range of biochemical and physiological processes, inducing iron (Fe) deficiency in plants resulting in leaf defoliation. Soil thresholds for Zn potential toxicity were 175.6, 74.9, and 101.0 mg kg^{-1} for Chinese cabbage, pak choi, and celery (stem), respectively (Long et al., 2003).

BIOAVAILABILITY OF HEAVY METALS

The fraction of heavy metals that can be readily mobilized in the soil environment and taken up by plant roots is considered bioavailable (Intawongse and Dean, 2006). Similarly, the term ‘‘bioavailability’’ has been defined as the proportion of total metals that is available for incorporation into biota (bioaccumulation) (John and Leventhal, 1995). Generally, metals occur in soils in the following fractions; soil solution, exchangeable, carbonate, organically bound, sorbed and occluded onto oxides and within the primary lattice phase of minerals (Black, 2010). Of these metal fractions, the most readily taken up by plants are metals present in the soil solution, with other metal fractions being less available (Peijnenburg et al., 2007). Bioavailability of trace elements in metal-contaminated soils depends on physicochemical conditions that give the framework in which biological factors can modify the metal availability (Ernst, 1996). Specially, the availability of elements to plants is controlled by metal speciation in soil, which in turn is influenced by management conditions such as pH, cation exchange, redox potential, texture, and organic matter content (Chojnacka et al., 2005).

PLANT UPTAKE

Heavy metals available for plant uptake are those present in soluble forms in the soil solution or easily solubilized by root exudates (Kuiters and Mulder, 1993). Even though plants require certain heavy metals for their growth, excessive amounts of these metals can become harmful (Chibuike and Obiora, 2014). Metal uptake into plants is affected by several factors such as type of metals, plant species, pH, organic matter and soil texture (Legind et al., 2012). Plant uptake represents a critical pathway by which potentially toxic metals released into the environment from anthropogenic sources can enter the food chain (Sukkariyah, 2003). Plant roots exude organic acids such as citrate and oxalate that affect the bioavailability of metals (Seuntjens

et al., 2004). However, the effectiveness of root exudates vary among plant species (Dhir, 2013). Chaudhry et al. (1998) reported that plants act as both “accumulators” and “indicators or excluders” in the way they take up and translocate trace metals to above ground biomass. Similarly, Tangahu et al. (2011) stated that plant accumulators survive despite concentrating contaminants in their tissues by biotransforming them into inert forms. On the other hand, plant excluders are plants that limit concentrations of metal translocation in their tissues and contain relatively small quantities in their biomass.

SOURCE OF HEAVY METALS IN AFRICAN SOILS

The major sources of heavy metal pollution in Africa are from anthropogenic sources including those associated with fossil fuel and coal combustion, industrial effluents, solid waste disposal, fertilizers, mining and metal processing. Presently, the impact of these pollutants is confined mostly to urban areas, which have the largest populations, high traffic density and manufacturing industries (Olade, 1987; Micó et al., 2006; Wuana and Okieimen, 2011). Heavy metals contamination in the environment may be detrimental to both plants and animals including humans (Duruibe et al., 2007). Whereas food crops may be exposed to heavy metal through contaminated soil or atmospheric dispersal, human beings may be exposed through consumption of contaminated foods (Biney et al., 1994). Therefore, the problem of metal contamination has arisen in Africa as a result of rapid population growth, increased urbanization and expansion of industrial activities (Tchounwou et al., 2012).

Sewage Sludge or Biosolids

Sewage sludge or biosolid are waste products generated via municipal and industrial wastewater treatment processes and is being produced in very large volumes due to growing population and increasing urbanization (Tiruneh et al., 2014). In agricultural lands, biosolids are used as a soil conditioner for improving physical and chemical properties such as soil structure, water holding capacity, CEC and increasing nitrogen and phosphorus content (Sterritt and Lester, 1980; De-Bashan and Bashan, 2004; Dolgen et al., 2007). In Africa, domestic and industrial wastes are generally not separated during the treatment processes (Baker et al., 1994). Therefore, the final product of biosolids obtained can be highly enriched in heavy metals such as Zn, Cd, Pb, Cu, Ni and Cr. For example, Shamuyarira and Gumbo (2014) have conducted a study in Limpopo province of South Africa, where biosolids from wastewater treatment plants were collected for metal analyses. The authors found that the average concentration of Cd and Pb in the biosolids were 3.10 and 171.87 mg kg^{-1} respectively. Long term application of biosolids in agricultural areas can therefore, increase heavy metal loadings in soil (Hodomihou et al., 2015).

Animal Manure

Concerns about the effects of heavy metals present in animal manure on the environment and human health has gained attention in recent years (Shamuyarira and Gumbo, 2014). When appropriately managed, animal manure can be a good source of important plant nutrients (Singh, 2015). Certain animal wastes such as poultry, cattle, and pig manures are commonly applied to soils as amendments. Although most manures are seen as valuable fertilizers, their long term application in agricultural lands may Pb to elevated levels of metals in the soil and possible risk of eutrophication of surface water bodies (Wuana and Okieimen, 2011). Currently, heavy metals are added to animal diet at low concentration due to improvements in our knowledge of animal

nutritional requirements (Petersen et al., 2007). For example, Cu is added in livestock diets to enhance performance, while Zn is thought to act as an anti-bacterial agent in the animal gut (Nicholson et al., 2003). To determine metal content in animal feeds and manures in northeast China, Zhang et al. (2012) have collected and analyzed livestock feeds and animal manure samples. Results showed that the highest Cu and Cd contents were respectively 137.1 mg kg^{-1} and 31.65 mg kg^{-1} in pig feeds and 98.08 mg Cu kg^{-1} and 8.00 mg Cd kg^{-1} of dry matter in both poultry and cattle feeds. In pig manures, Cu and Cd concentrations were 642.1 and 15.1 mg kg^{-1}, in poultry manures, 65.6 and 1.6 mg kg^{-1} and in cattle manures, 31.1 and 0.5 mg kg^{-1}. This suggests that animal manure can represent an important source of heavy metals to the environment. The authors indicated that Cd was not added as feed additives for animal growth, however, it was often present in mineral supplements such as phosphates, Zn sulfate and Zn oxide as an impurity. Odoemelam and Ajunwa (2008) conducted a study to estimate short-term heavy metal build up in arable soils in Nigeria amended with animal manure. Results indicated that heavy metal concentrations were higher in the amended soils compared to the background soils. Zinc was the most abundant metal with the highest concentration of 159 mg kg^{-1}, while Cd had the lowest concentration of 2.26 mg kg^{-1}. The greatest concentration for Pb and Cr was 16.89 and 26.33 mg kg^{-1} respectively.

Wastewater

As a result of increasing population, horticulture and specifically market gardening has become an important sector for economic growth in Africa (Mapanda et al., 2005). In many African urban areas, farmers use wastewater (industrial, municipal and domestic) as an alternative resource in vegetable gardens to face the growing demand for irrigation water (Tom et al., 2014). In fact, wastewater reuse for irrigation has several advantages including: reduction of effluent disposal in receiving water bodies, supply of nutrients as fertilizer and improvement in yield

production during the dry season (Kallel et al., 2012) . However, soils irrigated with wastewater can accumulate heavy metals, which may be transferred in the food chain through plant uptake (Khan et al., 2008; Singh et al., 2010). In Nairobi, Kenya, Mutune et al. (2014) have investigated the concentrations of some heavy metals in various vegetables irrigated with wastewater. They found that the highest concentration of Pb, Cu, Zn, Cd and Cr in the vegetables were 2.4, 21.34, 89.85, 3.02 and 1.24 mg kg^{-1}, respectively. These results suggested that some metals were higher than the recommended norms by the World Health Organization and the Food and Agriculture Organization (WHO/FAO). Permissible limits recommended by WHO for metal concentration in vegetables are 73, 0.3, 0.1, 67, 0.1, 2.3, 425.5, 500, 99.4 and 0.43 mg kg^{-1} for Cu, Pb, Cd, Ni, Co, Cr, Fe, Mn, Zn and As, respectively (Bambara et al., 2015; Asdeo and Loonker, 2011). In another study conducted in Burkina Fasso to evaluate the concentrations of heavy metals in wastewater, results showed that the average concentrations of Cr (0.116 mg l^{-1}), Mn (0.462 mg l^{-1}), Ni (0.451 mg l^{-1}) and Hg (0.034 mg l^{-1}) observed in the irrigation water were below the guideline values proposed by WHO (Lente et al., 2014). The maximum permissible level in irrigation water proposed by WHO/FAO for Cr, Mn and Ni are 0.55, 0.20 and 1.4 mg l^{-1}, respectively (Organization, 2014). However, it is critical to encourage future studies as heavy metal contamination is expected to be a challenge in developing countries in the near future (Lente et al., 2014).

Pesticides and Fertilizers

The long term application of chemicals such as phosphate fertilizers and pesticides on agricultural lands may result in the increase of heavy metals in soils (Nicholson et al., 2003; Abdu, 2010). Phosphate rocks are natural mineral deposits of phosphorus and calcium, but can be contaminated with trace metals depending on their geological origins (Al-Shawi and Dahl, 1999). For example, it was reported that the average Cu, Cd, Ni, Zn, Co, Pb and Mn concentrations in phosphate rocks deposits in a Morocco site were 16, 40, 32, 490, 1, 22 and 20 mg kg^{-1}, respectively; whereas, in South Africa, the concentration of the same metals found in the phosphate rocks were 130, 0.15, 35, 6, 1.5, 35 and 145 mg kg^{-1}, respectively (Al-Shawi and Dahl, 1999). Semu and Singh (1995) assessed the accumulation of some metals in soils under phosphate fertilizers and Cu fungicide applications and found that all trace element concentrations were higher in the amended soils compared to their background controls. Additionally, Gray et al. (1999) have reported that soil Cd content may be correlated to the amount of superphosphate fertilizers added to soils. They confirmed this in a long-term study of superphosphate fertilizers application in agricultural lands in New Zealand. Results from the study indicated high Cd accumulation rate of 7.8 g ha^{-1} yr^{-1} in the soils amended with a fertilizer treatment of 376 kg superphosphate ha^{-1} yr^{-1}. In Kermanshah, Iran, due to the over application of agrichemicals (pesticides, triple super phosphate and sulfate fertilizer) in wheat-cultivated soils during a one year study the concentrations of Cd, Pb and As increased (Atafar et al., 2010).

Mining

Mining activities generate a huge quantity of waste rocks and tailings that may represent sources of heavy metals (Wong, 2003). Enhanced industrial and mining activities have been reported to contribute to the increasing concentration of metals like Cu in ecosystems (Yadav, 2010). Operations such as smelting and waste disposal have widely disseminated metal contaminants from their sources of generation to other environmental ecosystems (Baker et al., 1994; Wuana and Okieimen, 2011). In addition, it has been reported that pyrite bearing mine tailings at neutral or slightly alkaline conditions can weather within months or few years to produce extreme acidity and Pb to acid mine drainage (AMD). These acidic soils usually contain high levels of heavy metals and may impact water quality and natural ecosystems (Shu et al., 2001). Moreover, acid mine drainage at inactive mines, has long term effects including degradation of water quality and inhibition of plant growth (Singo, 2013). For example, in South Africa high concentrations of heavy metals were found in soils of the Rustenburg area that is well known for its important mining activities. Results from an investigation showed that metal contamination of soils was high and dominated by Cr and Ni, which are extracted in the mines near agricultural lands (Gzik et al., 2003). In a study evaluating the spatial distribution of heavy metals in mining areas of Zambia (Kabwe), Ikenaka et al. (2010) found that metal pollution of soils nearby mines is increasing. The average Cr, Co, Ni, Cu, Zn, As, Sr, Cd, Hg and Pb concentration detected in soil samples from Kabwe, at the most polluted site, was 39, 46, 47, 572, 17, 32, 13, 7.12, 0.1 and 7.08 mg kg^{-1} respectively. Cobbina et al. (2013) have reported that in Ghana, contamination of drinking water sources have particularly been impacted in gold mining communities. Iron, Cd, As and Zn maximum concentrations were found to be 3.35, 0.008, 0.007 and 0.004 mg l^{-1} respectively. Except for Zn, all metal concentrations were higher than the WHO recommended limits for drinking water

quality. The maximum admissible limits set by WHO for the same metals are reported to be 0.3, 0.003, 0.001 and 5 mg l^{-1} (Mebrahtu and Zerabruk, 2011).

Atmospheric Depositions

Atmospheric deposition is ubiquitous, especially in soils in close proximity to sources of pollution such as industries of energy production, mining, metal smelting and refining, manufacturing processes and waste incineration (Nicholson et al., 2003). It has been reported that atmospheric inputs of heavy metals to agricultural systems can be a significant contributor to Pb, Zn, Cu, and As loading (Huang et al., 2007). In addition, Micó et al. (2006) have suggested that atmospheric deposition of Pb could occur in soils near roads with heavy traffic, from solid particles and toxic fumes. In a study assessing trace metal contamination of soil and vegetables in farming sites along major highways around Kampala (Uganda), Nabulo et al. (2006) found that the highest metal concentration in soils for Pb, Zn, and Cd were 76.3, 328.8, and 1.56 mg kg^{-1} respectively. The authors indicated that soil trace metal contents decreased with distance up to 30 m from the road, where they reached background concentrations. They also concluded that Pb and Cd concentrations of both washed and unwashed Amaranthus leaves were above the recommended maximum limit for vegetables, set at 0.3 and 0.2 mg kg^{-1}, respectively. Similarly, it has been found that the maximum soil metal concentration due to aerial deposition from gasoline exhaust in Annaba, Algeria were 0.45, 30.9, 65.8, 54.5, 93.9, and 462.2 mg kg^{-1} for Cd, Cr, Cu, Pb, Zn, and Mn, respectively (Maas et al., 2010). These values were within the safe limits proposed by WHO/FAO, which are 3, 100, 100, 100, 300 and 2000 mg kg^{-1}, respectively.

HEAVY METALS IN GARDENS

In Africa, vegetables constitute essential components of the diet, by contributing protein, vitamins and nutrients which are usually supplied in small amount. They also act as buffering agents for acid substances obtained during the digestion process (Bahemuka and Mubofu, 1999). However, the use of untreated wastewater to irrigate urban vegetable gardens and the application of organic amendments, are raising serious concern due to their trace elements content (Abdu et al., 2011; Hodomihou et al., 2015). Atayese et al. (2008) found in a study carried out in two major highways in Lagos, Nigeria, that levels of Pb and Cd in soil ranged from 47 to 151 mg kg^{-1} and 0.30 to 1.33 mg kg^{-1} respectively, while concentrations in vegetable leaves ranged from 68 to 152 mg kg^{-1} and 0.5 to 4.9 mg kg^{-1} for Pb and Cd, respectively. It has been reported that people eating vegetables grown in six Tanzanian localities, were consuming Pb and Zn at concentration levels potentially hazardous to their health due to an increasing growth of the population and the industries. The highest concentration of Pb, Cd, Cr, Ni, Zn and Cu in vegetables were 6.1, 0.4, 7.9, 0.8, 64.7 and 7.9 mg kg^{-1} respectively (Othman, 2004). These results showed that metal concentration in the vegetables were above the maximum permitted values of WHO/FAO.

STRATEGIES TO REDUCE METALS LEVELS IN GARDENS

In many cities, gardens are located on old, abandoned landfills and dumping sites. Cities have expanded by filling up spaces around the city with garbage, rubble and earth. Normal garbage and rubble in landfills does not present a problem, however industrial and chemical waste can present a health hazard, especially when concentrations of contaminants are above acceptable limits (Organization, 1999). A number of alternative methods to address soil Pb risk have been investigated to determine if less expensive methods including sandboxes, shrubs as barriers, and raised beds with clean soil could be used by gardeners to reduce community soil Pb risks (Farfel

et al., 2005). Raised beds for instance has been defined by Food (2000) as a wooden frame that is filled with about half a meter of clean soil, with a special mesh placed at the bottom. This will help the plants to avoid contamination with the underlying soil and also allow both rainwater and worms through. Mitchell et al. (2014) have indicated that raised beds tend to have lower metal levels than gardens where crops are sown directly into the preexisting soil. Gorospe (2012) examined the effectiveness of raised beds to reduce soil Pb levels over a four year period, and found that the raised beds reduced Pb from 950 mg $kg^{-1}$to 336 mg kg^{-1}. This suggested that raised beds may be effective at reducing Pb contamination in garden soils even if the Pb level is still above the threshold value proposed by WHO (100 mg kg^{-1}). Additionally, Clark et al. (2008) indicated that raised beds may allow gardeners to continue growing produce and introduce education and awareness into the community, which can have an important impact on exposure reduction.

SUMMARY

Over the last decades, many researchers have been involved in investigating the contamination of heavy metals such as Cd, Co, Cu, Cr, Zn, Mn, Ni, and Pb in crops and soils. Through this literature review, it has been possible to assess the range of concentration reflecting different degrees of soil metal contamination throughout many African countries. Sources of trace metals in agricultural or garden soils are mostly related to atmospheric depositions, mining activities, and the application of animal manure, wastewater, sewage sludge and biosolids used as organic amendments, phosphate fertilizers and pesticides. A studied alternative to reduce metal uptake is the raised bed methods, but further investigation needs to be done.

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Table1: Source of heavy metals in the Environment (Calamari and Naeve, 1994)

Use	Metal
Batteries and other electronics	Cd, Hg, Pb, Zn, Mn, Ni
Pigments and paints	Ti, Cd, Hg, Zn, Mn, Ni, Sn, As, Cu, Fe, Al
Alloys and solders	Cd, As, Pb, Zn, Mn, Sn, Ni, Cu
Biocides (pesticides, herbicides)	As, Hg, Pb, Cu, Sn, Zn, Mn
Glass	As, Sn, Mn
Fertilizers	Cd, Hg, Pb, Al, As, Cr, Cu, Mn, Ni, Zn
Plastics	Cd, Sn, Pb
Dental and cosmetics	Sn, Hg
Textiles	Cr, Fe, Al
Refineries	Ni, V, Pb, Fe, Mn, Zn
Fuel	Ni, Hg, Cu, Fe, Mn, Pb, Cd

Chapter II: Heavy Metals in Organic Amendments, Soils and Vegetables

ABSTRACT

In Senegal, urban agriculture plays an increasingly important role in food security for its high supply of vegetables. However, production is still low because soils are very infertile and low in organic matter. Consequently, farmers apply organic amendments, such as animal manure from feedlots, wastewater and composted slaughterhouse waste to improve their production. Even though their benefits on improving soil fertility are recognized, many of these organic amendments are thought to contain elevated levels of heavy metals. The objective of this study was to assess the effect of organic amendments on the distribution of the heavy metals Cd, Co, Cr, Cu, Ni, Mn, Pb and Zn in local soils and vegetables from Senegal. Composted wastes and soil samples were collected from four sites (Pikine, Rufisque, Rao and Essyl) and vegetables from two sites (Pikine and Rufisque) in Eastern and southern Senegal. The physicochemical analyses showed that all sites were sandy in nature, low to medium in total carbon (0.83 - 3.66 %) with pH ranging from 5 to 7.9. A sequential extraction procedure (SEP) conducted on the soil samples revealed that the metals were mostly associated with the amorphous Fe-Mn oxide, organic and residual fractions which represent the more stable phases. The highest total metal concentrations for Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn were 0.4, 1.9, 20.9, 23.7, 166.5, 7.3, 10.3 and 107.2 mg kg^{-1} in the organic wastes, 0.8, 6.23, 57, 20.2, 202.8, 21.5, 16.2 and 65.3 mg kg^{-1} in the soil and 4.02, 0.4, 2.1, 21, 80, 8.1, 13, and 115 mg kg^{-1} in the vegetables. These metal concentrations were within the prescribed safety limits proposed by WHO except for Cd, Pb and Zn in vegetables.

INTRODUCTION

The major constraints to food production in West Africa are related to the lack of suitable land, fresh irrigation water, low rainfall and rising temperatures. Numerous studies have shown that soil degradation is threatening food security in many developing countries (Scherr, 2003; Stocking, 2003; Godfray et al., 2010). As a result, urban agriculture, defined as the cultivation and distribution of crops and livestock in and around cities, plays an increasing role in the food security of poor regions (Armar-Klemesu, 2000). In Senegal, the population in the cities exceed that of the rural areas and Dakar, the capital, accounts for one-fourth of the Senegalese's total population (Daouk et al., 2015). In this context, truck farming has rapidly developed in towns such as Dakar and St. Louis. Despite the fact that vegetable gardening is very beneficial for the supply of vegetables, the production is still low because the soils are very infertile (Anh et al., 2004). In Senegal, most soils are sandy and consequently low in organic carbon content. This is mainly due to climatic variability (recurring drought and irregular rainfall) and excessive deep tillage (Jones et al., 2011). Degraded, low quality soils are not fertile and thus cannot maintain sustainable production (Francis et al., 2005). At the same time, the production of urban and industrial organic waste materials is widespread because of the growing population (Diacono and Montemurro, 2011). Therefore, methods for utilizing such organic wastes in agriculture should be developed (Burton and Turner, 2003). This may be advantageous because organic matter improves soil physical, chemical and biological properties. It also reduces the processes of erosion and runoff and the use of chemical fertilizers (Tella et al., 2013). However, the application of organic waste as fertilizer and soil amendment should be examined for environmental impacts due to the possible presence of heavy metals (HMs) (Diacono and Montemurro, 2010). Their solubility is low in circumneutral soils due to their adsorption on minerals and organic matter and co-

precipitation as solid phases (e.g., oxides, carbonates, and sulfides) (Audry et al., 2006) . Still, at high concentrations and acidic pH values these metals may become soluble. Since metals are not biodegradable, as concentrations increase they can have toxic effects on soil organisms, plants and animals (Mulligan et al., 2001). Additionally, when transferred to the food chain, at elevated concentrations, they also present a risk to human health (Sherene, 2010). In urban areas, soils represent a major sink for metals released into the environment from a variety of anthropogenic activities. As a result, heavy metals are present in composted organic materials and obviously in the amended soils (Lopes et al., 2011; Hodomihou et al., 2015). Accordingly, the overall objective of this research is to evaluate the effect of organic amendments on the distribution of heavy metals in market garden soils and vegetables in Senegal.

METHODS AND MATERIALS

Study Sites and Farming Practices

This study was conducted in urban areas of Senegal, specifically in Dakar, Saint Louis and Ziguinchor. Sites in Dakar (Pikine and Rufisque) and Saint Louis (Rao) are located in the Niayes region, which is a 185 km long area, made of littoral dunes and depressions, extending along the Atlantic Ocean from Dakar to Saint-Louis. The Niayes region is an urban agricultural area providing more than 70% of fresh vegetables to the local markets of Dakar (Mbaye and Moustier, 2000). The Niayes area is semi-arid with a high water table, dominated by parallel sand dunes and depressions. Those geological formations originated from ferruginous and sandy soils are poor in organic matter due to rapid mineralization (Daouk et al., 2015). Soils in Pikine and Saint Louis are characterized as Arenosols (Entisols), related to the sandy. Rufisque on the other hand, is dominat8HIJed by sandy loam Fluvisols associated with the Inceptisol and Entisol orders (Hodomihou et al., 2015). The fourth site is in Essyl-Thionck, a rural area located in Ziguinchor

region, southern Senegal. The climate is tropical with wet and dry seasons and loamy sandy soil that are low in organic matter. Because of the low soil organic matter content in those localities, farmers have used organic material as soil amendments to improve soil physicochemical properties and increase yield production (Hodomihou et al., 2015). Composted wastes such as animal (poultry, sheep, cow, pig and horse) manure and slaughterhouse wastes have been applied in Pikine and Rufisque. Sewage sludge was also used in Pikine, while raw animal manure (from free-ranging animal) was applied in Rao (Saint Louis) and Essyl (Ziguinchor). For irrigation, farmers in Pikine use groundwater from deep pits called "céanes" and wastewater from industrial and municipal sources. In Rufisque, only tap water is used and outside of Dakar, in Rao and Essyl, mainly well water is mainly used for irrigation.

Soil and Organic Matter Sampling Protocol

Soil samples were collected once in April 2015. To obtain a representative average sample for each site, a total of 3 composite samples (consisting of 10 subsamples each) were collected in 3 plots randomly chosen at each site. Two natural uncultivated reference/control soils were selected for comparison of heavy metals contamination in the Niayes region (Control 1) and in Essyl Thionck site (Control 2). All samples were taken at an average depth of 15 cm using a shovel. This shovel was thoroughly rinsed with deionized water following each sample. Composted wastes were also sampled from Pikine and Rufisque, but not for Rao and Essyl since the organic waste was not composted and was directly added to the soil. Soils and organic material samples were air dried and crushed to pass through a 2 mm sieve, homogenized and stored in plastic bags prior to laboratory analysis. Each sample was analyzed in triplicate.

Soil and Organic Matter Characterization & Procedures

Soil and Organic Matter pH

Soil and organic matter pH were determined using a pH-meter equipped with a combination glass and reference electrode. The pH-meter was calibrated with standards of pH 4 and 7. After that, 10 grams of air-dried soil or compost were weighed into a beaker with 10 ml or 20 ml of deionized water and shaken (soil-water ratio of 1:1 and water-OM ratio of 2:1). Samples were equilibrated for 10 min and then the suspension was swirled and an electrode inserted into the clear supernatant. The pH values were recorded, and the electrodes rinsed in between readings (Thomas et al., 1996).

Particle size analysis

Particle size was determined using the hydrometer method. The sample was pretreated to enhance separation of aggregates and remove particle coatings. It was ground to obtain 2-mm sized fraction. Forty grams of air-dried soil was added to a dialysis membrane to remove carbonates using a 1 M sodium acetate ($NaC_2H_3O_2$) and acetic acid (CH_3COOH) buffer adjusted to pH 5 (Bouyoucos, 1962). Once dissolution of the carbonates ceased (as determined by lack of effervescence), the sample was transferred to a separate container and desalted under tap water flowing continuously until the water became clear. Next, the sample was centrifuged for 10 minutes at 1500 rpm until a clear supernatant was observed. The supernatant was then decanted and the soil washed two or more times (clear supernatant) by shaking with 50 ml of di-ionized water. Following pretreatment, the sample was air dried and 10 grams was used to determine hygroscopic moisture content. The 10 grams were dried at 105˚C over night (13 hours), cooled and then weighed again and the difference was recorded. The hydrometer was calibrated as follows: 100 ml of calgon solution (HMP) was added to a cylinder and the volume brought to 1 L

with room temperature distilled water. It was mixed thoroughly with a plunger and the temperature recorded. Correction of hydrometer readings for other temperatures and for solution viscosity and density effects were made by taking a hydrometer reading, R_L, in the blank (no soil) solution. Following the blank reading 40 g of soil were weighed into a 600 ml beaker, 250 ml of distilled water and 100 ml of HMP solution were added, and the sample was allowed to soak over-night. The suspension was mixed for 5 minutes with a mechanical mixer, transferred into the sedimentation cylinder and distilled water added to bring the volume to 1 L. Next the sedimentation cylinders containing the suspension were placed in a sedimentation cabinet, allowing temperature to equilibrate (approximately 2 hours). When the temperature became constant, the plunger was inserted and moved up and down to mix the content thoroughly (avoid spilling). As soon as the mixing was completed, time was recorded. After exactly 60 seconds, the hydrometer was lowered into the suspension and the value at the top of the meniscus was recorded as R_{60}. The hydrometer was carefully removed, rinsed and wiped to dry. Without remixing the suspension, the hydrometer was reinserted carefully into the solution about 10 seconds before each measurement and readings taken at 1 (R_1), 10 (R_{10}), 60 (R_{60}), 90 (R_{90}), 120 (R_{120}) and 1440 (R_{1440}) minutes. The reading blank R_L was taken immediately after the uncorrected reading, R, was recorded. The corrected concentration of soil in suspension at any specified time was $C = R - R_L$, where C is expressed in g L^{-1}. Additionally, the sand fractions were separated after the last hydrometer reading. The suspension from the sedimentation cylinders was transferred into a 270-mesh (53µm) sieve using a water bottle. Then, the sand was transferred to a weighted beaker, dried at 105˚C and weighed again. The dried sand was transferred and sieved through nest of 18, 35, 60, 140 and 270 sieves and shaken for 3 minutes. Then, the weight of each fraction of sand and the residual silt and clay that has passed through the 270-mesh was recorded (Burt, 2004).

Soil total carbon (TC)

Soil total carbon was analyzed via an Elementar Vario MAX total CN carbon analyzer (Mt. Laurel, NJ). Prior to analysis, soils were pretreated for carbonates using 0.5 M Na-acetate adjusted to pH 5 with acetic acid (Nelson et al., 1996). An untreated sample was also analyzed and the difference between the treated and untreated samples was inorganic carbon.

Soil soluble salts and nutrients

Extractable nutrient (P, K, Ca, Mg, Fe, Zn, Cu, Mn, and B) contents were determined at the Virginia Tech Soil Testing Laboratory. For the soluble salt determination, 20 grams of prepared soil was measured into a 50 ml beaker, and 40 ml of distilled water were added for a soil/water ratio of 1:2 (vol/vol). At least one internal soil reference ("test") sample was included per batch of unknown soil samples. The solution was stirred and the suspension allowed to settle for at least 1 hour. The electrical conductivity (EC) was then determined using a Fill Cell (YSI 3254 Pyrex 5-ml). The concentration of soluble salts in the soil were calculated from the following equation: ppm soluble salts in soil = EC x 6.4 x 2. In this equation, EC represents the conductivity reading in mhos x 10-5, 6.4 is the factor for converting the conductivity measurement to ppm soluble salts, and 2 represents the water volume dilution factor. Nutrients were extracted using a Mehlich 1 (0.05N HCl in 0.025N H_2SO_4) solution. A four gram scoop of prepared soil was measured into a 60 ml straight-walled plastic extracting beaker and 20 ml of the Mehlich 1 extracting solution was added with an automatic pipetting machine. The samples were shaken on a reciprocating shaker with a stroke length of 3.8 cm for 5 minutes at 180 oscillations per minute and filtered through Whatman No. 2 (or equivalent), 11-cm filter paper soon after the shaking stopped. All elements were analyzed in the same extract by an ICP-AES (Inductively Coupled Plasma-Atomic Emission

Spectrometer), CirOS VISION model with a CETAC ASX520-HS autosampler (Rhoades et al., 1996).

Estimation of Cation Exchange Capacity by Summation (CEC)

Cation exchange capacity was also determined at the Virginia Tech Soil Testing Laboratory by summation of the Mehlich 1 extractable bases, or non-acid generating cations (Ca, Mg and K), plus the acidity estimated from the Mehlich soil-buffer pH after conversion of all analytical results to meq/100 g or cmol (+)/kg (Hajek et al., 1972). Sodium is not included in the equations since it is not routinely determined in the Mehlich 1 extract in routine analysis. Since exchangeable Na is usually at a very low concentration, its omission is not considered to be a cause of error in the calculated CEC.

Sequential Extraction Procedure (SEP)

Metal concentration in soil was determined through the sequential extraction procedure of Tessier et al. (1979). The theory behind the extraction procedures is that the most labile metals are removed in the first extraction and continue in order of decreasing lability (Zimmerman and Weindorf, 2010). Based on Tessier et al. (1979) the operational definition of the fractions are as follows: exchangeable, carbonate bound, Fe and Mn oxide bound, organic matter bound and residual. Typically metals of anthropogenic origin tend to reside in the first four fractions depending on soil chemical and mineralogical composition, while metals found in the residual fraction are generally of natural occurrence in the parent rock (Ratuzny et al., 2009). Soil samples were oven-dried at 105 ˚C, homogenized and stored at 4 ˚C until analysis. One gram of sample was placed in a 50 ml tube, exposed to reagents and shaken. Each fraction was separated from the supernatant by centrifugation at 10,000 rpm for 30 min and the supernatant was collected for lab analysis. The soil was rinsed with 8 ml of deionized water and centrifuged again between steps (Table 2.1) (Tessier et al., 1979).

Total heavy metals

Total metals were determined by digesting samples using HNO_3, H_2O_2 and HCl. The nitric acid destroys the organic matter and oxidizes the sulfide material. It reacts with concentrated hydrochloric acid to generate aqua regia: $3HCl + HNO_3 \rightarrow 2\ H_2O + NOCl + Cl_2$. Aqua regia is considered adequate for dissolving most base element sulfate, sulfide, oxides and carbonates. Hydrogen peroxide is also a strong oxidizing agent that is used to enhance the destruction of the organic matter in the soil. One gram of soil or organic matter was added to a 125 mL conical beaker with 10 ml HNO_3. The mixture was covered with a watch glass and heated to 95°C and refluxed for 15 min. This was subsequently cooled, and 5 ml concentrated HNO_3 were added. This solution was covered with a watch glass, refluxed for 30 min, and repeated again. It was then evaporated to 5 ml without boiling. The solution was cooled, followed by the addition of 2 ml of deionized water with 3 ml H_2O_2 (30%) and covered with a watch glass. The mixture was heated until the reaction subsided and then cooled. To degrade all the organic matter, hydrogen peroxide (1 ml) was continually added until its reaction with the sample was minimal. Concentrated HCl (5 ml) was added with 10 ml deionized water, covered, and refluxed for 15 min. This was cooled and filtered through acid-washed filter paper into a 50 ml volumetric flask. The beaker and filter paper were rinsed with 1:100 HCl (Hossner et al., 1996). Following digestion, the total heavy metal concentrations were determined using the Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), CirOS VISION model with a CETAC ASX520-HS autosampler at the Virginia Tech Soil Testing Laboratory. Acid digestion blanks were prepared and analyzed by the same means as the soil. The element concentration values obtained from these blanks were subtracted from the soil sample values.

Vegetables Sampling Protocol

In May 2016, four different types of common vegetables (onion: Allium cepa, lettuce: Lactuca sativa, carrot: Daucus carota and tomato: Solanum lycopersicum) were sampled from Pikine and Rufisque sites. Plants were separated from their roots and washed in a 0.50% Sodium Laurel Sulfate solution. Then, they were washed in a 0.10 M HCl solution and thoroughly rinsed with de-ionized water (DI). This washing procedure was determined to be effective at removing surface contamination based on the analysis of titanium, since this latter is very insoluble and not easily taken up by plants. Each plant sample was placed in a separate glass beaker, covered with aluminum foil, and placed in a 70 ^{o}C drying oven for 48 hours. Once the plant samples were dried, they were ground and passed through a 2 mm sieve to ensure uniformity (Klassen, 1998).

Metal Analyses in Vegetables

Samples for total metal analysis were digested in nitric acid and hydrogen peroxide following standard procedures (EPA, 1996). The sample extracts were analyzed using Inductively Coupled Mass Spectrometer (ICP) (CirOS VISION model with a CETAC ASX520-HS autosampler). The plant samples were digested using the following procedure: 0.5g of sample was placed in a 100 ml digestion tube, 8 ml concentrated HNO_3 were added and the tubes were allowed to sit overnight. The tubes were placed in a 106 ^{o}C digestion block and heated for 2 hours. Then, they were removed from the heat and allowed to cool. A total of 10 ml of 30% hydrogen peroxide was added in 2 ml and 4 ml aliquots with the tube placed back on the digestion block for 30 mins and cooled after each H_2O_2 addition (EPA, 1996). Samples were diluted to 25 ml and sent at the Virginia Tech Soil Testing Laboratory for analysis of heavy metals (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn and Ti). All reagents were trace metal grade and reagent blanks were run using the same procedure without plant samples to determine potential metal contamination from reagents.

STATISTICAL ANALYSIS

Metal partitioning in soils was performed using Excel (Microsoft office) and an Analysis Of Variance (ANOVA) from JMP was used to determine whether there were any significant differences among the mean values of the physicochemical parameters, the heavy metals (Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn) distribution in the five soil fractions, the different sites and in the organic wastes. Tukey's Honest Significant Difference was used second to determine means that were significantly different at a level of significance (α) of 0.05, with a sample size of 42 for the soil samples and 6 for the organic wastes. For the vegetables analysis, a one-way ANOVA was performed to determine the mean values of the metal concentrations and their standard deviations. All raw sample data were reported in ppm (mg L^{-1}) and then were transformed to mg kg^{-1} based on the sample mass and the extract volume (mg kg^{-1} = (mg L^{-1} * volume) / weight).

RESULTS AND DISCUSSION

Particle Size Analysis

The soil texture was sandy in Pikine and Rao (Table 2.2). Similar, Sy et al. (2014) found that soils in this part of the Niayes Region are mainly sandy because they are located in littoral sand dunes and depressions that formed from Aeolian parent materials. Daouk et al. (2015) reported that the depressional areas of the Niayes region are rich in carbonate and saturated by the groundwater for long enough periods to develop "gleyic color patterns". Therefore, the higher silt and clay content in the sandy loam soil of Rufisque can be associated with its location in those depressions. In Essyl, the loamy sand nature of the soil is related to its water- deposited parent material.

Soil and Organic Matter pH

In the Niayes region, the soil pH ranged from 5 to 7.9 in the cultivated soils and was 5.9 in the control uncultivated soil (Table 2.2). At the Pikine site, the pH decreased from 5.9 in the control to 5.0 in the amended soil. This increase of the soil acidity may be associated with the use of wastewater for irrigation in this site. It has been reported that some of the drawbacks of using wastewater in agricultural lands are the increase of soil acidity, salinity and metal content in the long term (Jiménez, 2006). The slightly alkaline soil pH of 7.9 observed in Rufisque may be related to the addition of compost, agrichemicals and the deposition of carbonate at the soil surface due to a Senegalese cement factory adjacent to the site. In Rao, the neutral pH of 7.2 measured in the amended soil, suggests that the application of raw animal manure increases the soil pH. Many studies have showed that manure application increases soil pH (Whalen et al., 2000; Walker et al., 2004; Beesley et al., 2010). In Essyl, the slightly acidic pH of 5.1 and 6.5 in both the control and the amended soil may be explained by the high rainfall in this humid southern part of the country. Generally, in environment conditions with sandy soils, high rainfall and warm temperature, there is an excessive drainage and intensive leaching of base cations, resulting in acidic pH (Bolan et al., 2003). Consequently, due to a direct effect of the soil pH, a lower metal bioavailability can be expected in Rufisque and Rao compare to Pikine and Essyl. Table 2.3 also showed that the mixture of composted animal manure and slaughterhouse waste used in Pikine (PM) exhibited a slightly alkaline pH of 7.6, while that from Rufisque (RM) was neutral.

Soil Total Carbon Content

In the Niayes region, the total carbon content was 0.16% (1600 mg kg^{-1}) in the control and 0.83, 1.6 and 3.66% (8300, 16000 and 36600 mg kg^{-1}) in the amended soils from Rao, Pikine and Rufisque respectively (Table 2.2). In Essyl, soil total carbon varied between 0.28 (2800 mg kg^{-1}) in the control to 1.41% (14100 mg kg^{-1}) in amended soil. The increase of total carbon in the amended soils in all sites over their controls suggests that the application of organic waste as fertilizer also increase soil carbon content. A large number of studies have shown increased soil carbon concentrations when manures, composts or municipal biosolids are land applied (Goyal et al., 1999; Brown and Cotton, 2011; Youngquist et al., 2014). Although the soil total carbon increased from the control to the amended soils, it was still very low in Pikine, Rao and Essyl. This may be related to the intensive cropping systems and the rapid mineralization of the organic matter under hot, semiarid conditions and sandy soils (Daouk et al., 2015). On the other hand, the highest carbon content was detected in Rufisque and can be associated with the finer soil texture in this site. Sherene (2010) has reported that organic matter is important for metals retention by soil solids, thus decreasing mobility and bioavailability. Consequently, high clay and organic carbon content combined with alkaline pH may decrease the mobility of heavy metals in Rufisque site. Table 2.3 indicated that total carbon content was low in the organic amendments and ranged from 16.4 to 17.9% (164000 to 179000 mg kg^{-1}) in PM and RM respectively. It has been shown that during composting of animal manures, organic carbon losses can reach 67% (670000 mg kg^{-1}) in cattle manure and 52% (520000 mg kg^{-1}) in poultry manure. This was related to the characteristics of the bedding material, the bulking agent added and the effect of environmental conditions on the mineralization of the organic matter during composting (Bernal et al., 2009)

Soluble Salts

Soil salinity ranged between 0.04 in the control soil to 1.77 dS m^{-1} in the amended soil of the Niayes region (Table 2.2). In Essyl, the soil salinity was around 0.2 dS m^{-1} in both the control and the amended soils. Based on Kissel et al. (2012), soils with low organic matter and electrical conductivity (EC) between 0.15-0.50, 0.51-1.25 or 1.26-1.75 dS m^{-1} are ranked as low, medium or high, respectively. Therefore, salinity was rated high in Pikine (1.77 dS m^{-1}), medium in Rao (0.64 dS m^{-1}) and low in Rufisque and Essyl (0.4 and 0. 2 dS m^{-1}). The increase of the soil salinity from the control to the amended soil of the Niayes region may be associated with the addition of agricultural products. Additionally, the highest soil acidity and salinity observed in Pikine may be a result of the application of wastewater for irrigation in this site. It has been well documented that wastewater irrigation increases soil salinity and decreases soil pH (Kiziloglu et al., 2008; Toze, 2006). Table 2.3 showed an extremely high soluble salt of 9.5 and 13.5 dS m^{-1} recorded in PM and RM organic amendments, respectively. Epstein et al. (1976) have reported that both sewage sludge and compost can increase soil salinity, potentially to a level that may affect salt-sensitive plants.

The Estimated Cation Exchange Capacity (CEC)

In the Niayes region, the CEC ranged between 1.5 in the control to 9.13, 10.83 and 26.4 cmol kg^{-1} in the amended soils of Rao, Pikine and Rufisque, respectively. In Essyl, the CEC was 1.6 in the control and 7.06 cmol kg^{-1} in the amended soil (Table 2.2). Generally, soil organic matter and clay content are responsible for the bulk of soil CEC (Ashraf et al., 2012). Consequently, the highest CEC found in Rufisque may be explained by the occurrence of finer soil texture and greater total carbon content in this site. In contrast, the lower CEC observed in Pikine, Rao and Essyl sites can be related to their sandy nature and low organic matter content. As expected both organic materials RM and PM exhibited high CECs of 24 and 32 cmol kg^{-1} respectively (Table 2.3).

Soil Nutrient Contents

Results showed that the soil nutrient concentrations were sufficient and high in all sites with an increase from the controls to the amended soils (Table 2.4). With the exception of calcium and magnesium, which were more abundant in Rufisque, all the nutrient (P, K, Ca, Mn, Fe, Zn, Cu, Fe and B) contents decreased in the following order: Pikine > Rao > Essyl > Rufisque. The high nutrient abundance in the amended soils of all sites is associated with the continual application of organic waste amendments (Cooperband, 2002; Hue and Silva, 2000; Doran and Parkin, 1994). Table 2.5 showed also sufficient micronutrient and very high macronutrient contents in both organic amendments.

Sequential Extraction

The statistical analysis (ANOVA) performed on the results obtained from the sequential extraction procedure showed that metal concentrations in soil were significantly different ($P < 0.05$) from each other. In general, the metal concentrations follow the decreasing order of: bound to oxides > bound to organic matter > bound to residual > bound to carbonate > exchangeable fraction. This indicates that metals were mostly associated with more stable soil fractions and should be less available to growing plants.

Chromium (Cr)

In general, Cr was held in the following fractions in decreasing abundance: bound to the organic matter > bound to oxides > bound to residual fraction. Figure 2.8 shows that Cr was primarily held in the organic fraction, ranging from 65 to 70% in all sites. It has been reported that organic matter may constitute an important sink for Cr in the environment, due to its strong interaction with Cr^{3+}, and its ability to reduce Cr^{6+} to Cr^{3+} (Balasoiu et al., 2001; Gustafsson et al., 2014). Chromium abundance varied between 20 to 30% in the oxides fraction and less than 10% in the residual phase. Generally, this predominance of Cr in the last three fractions (oxides, organic matter and residual) suggests that it would be less available to plants.

Cadmium (Cd) and Cobalt (Co)

Cadmium and Co exhibited similar partitioning and were strongly bound to the oxide fraction (with the exception of Essyl) with concentrations ranging from 60 to 80% and 60 to 75 % respectively in Pikine, Rufisque and Rao (Figure 2.9 and 2.10). This result is similar to that of Wong et al. (2002) who reported that in soils, Co was strongly associated with Fe-Mn oxides fraction. Manganese oxides were found to play a significant role in the fixation of Cd and Co due to their strong affinity (Backes et al., 1995). The second greatest proportion of both metals was associated with the organic matter fraction. In Essyl, all the Cd was found in the organic matter fraction, suggesting that its presence may be related to the addition organic matter. Less than 15% of Cd and Co were found in the carbonate and exchangeable phases, making them more available to plants.

Copper (Cu)

A significant amount of Cu was found associated with the organic fraction in Essyl and Pikine with the highest concentrations ranging from 67 to 87%, respectively (Figure 2.11). This is not surprising because organic matter is well known to have high affinity for Cu, forming strong and stable Cu-organic matter complexes (Hickey and Kittrick, 1984; Fernandes, 1997; Ma and Rao, 1997). In contrast, in Rao and Rufisque, Cu was found in the residual phase ranging between 75 and 78%, respectively. In Pikine and Essyl, Cu held in the residual phase was between 10 and 30%, respectively. Elevated Cu concentration in the residual fractions at Rao and Rufisque suggests its natural occurrence in those sites. Very little Cu was associated with the exchangeable fraction, suggesting that Cu was not very available to plants.

Manganese (Mn) and Zinc (Zn)

The chemical partitioning of Mn and Zn showed that they were mainly associated with the oxides and carbonate fractions. Manganese concentrations ranged from 50 to 75% and 10 to 30% in the oxides and carbonate phases respectively (Figure 2.12 and 2.13); whereas, the majority of the Zn ranged from 50 to 70% in the oxides and from 5 to 25% in the carbonate phase. These results agree with the observations of Li et al. (2001) and Karar et al. (2006) who found that in urban garden soils from Kolkata, India, the predominant fractions for Zn are the oxides and carbonate phases. In addition to the significant occurrence of Mn and Zn in the carbonate phase, 5 to 25% of the Mn was also found in the exchangeable fraction of all sites, making it more available.

Nickel (Ni)

The oxides fraction was by far the most important fraction for Ni with concentrations ranging from 45 to 70 % (Figure 2.14). It has been suggested that Ni adsorption by Mn oxides controls Ni levels in soils and that substitution of Ni^{2+} for surface Mn in manganese oxides may be responsible for much of the adsorption (Jenne, 1968). The second most significant Ni-containing fraction was the organic matter, accounting for 25 to 55% of the total Ni. The high amount of Ni in the oxides and the organic matter phases suggests that it would be less available in those soils.

Lead (Pb)

Lead was found associated with the residual, oxides and organic matter fractions. Its abundance ranging from 10 to 75%, 20 to 45% and 10 to 55%, respectively in all sites (Figure 2.15). This result is similar to that of Li et al. (2001) who found percentages of Pb in soil fractions decreasing in the order of: residual > Fe-Mn oxide > organic matter > carbonate > exchangeable. Metals contained in the crystal lattices of the minerals or residual phase are strongly bound and consequently unavailable to the plants (Zhou et al., 1998; Wong et al., 2002; Chao et al., 2007).

Total metals

Total heavy metal contents in both soil and composted organic wastes are shown in table 2.4 and 2.5, whereas those in the vegetables are displayed in tables 2.6 and 2.7. The mean concentrations followed the sequence: Mn > Zn > Cr > Cu > Pb > Ni > Co > Cd. With the exception of Zn and Cu that exhibited their greatest levels in Pikine, all the other metals were more concentrated in Rufisque, followed by Pikine, Rao and Essyl. The highest metal contents found in Rufisque and Pikine sites may be related to the long term application (at least 20 years) of composted wastes. The lower metal concentrations observed in Rao and Essyl may be explained by the application of small amounts of raw animal manure for shorter periods (10 and 5 years respectively). The highest metal concentrations detected in the amended soils were: 155±48 for Mn, 46.4±19 for Zn, 47.1±9.9 for Cr, 14.9±5.3 for Cu, 10.4±5.8 for Pb, 14.2±7.3 for Ni, 4.22±2.1 for Co and 0.70±0.1 mg kg^{-1} for Cd (Table 2.4). All metal contents were lower in the control soils, suggesting that their increase in the cultivated soils was due to agricultural activities. Metal concentrations were very low (Table 2.8) compared to the maximum permissible levels of metal in soils recommended by World Health Organization (WHO) (Organization, 2014). Except for Zn that was more concentrated in the composted wastes from Pikine (PM), all the other metals were

higher in the composted waste from Rufisque (RM). This result suggests that composted waste from Rufisque was more contaminated. Metal concentrations were in the following order: Mn > Zn > Cu > Cr > Pb > Ni > Co > Cd. The maximum metal contents in the composts were: 160±6.5 for Mn, 101±6.2 for Zn, 22.8±0.9 for Cu, 19.3±1.6 for Cr, 9.7±0.6 for Pb, 7.0±0.3 for Ni, 1.8±0.1 for Co and 0.4±0.0 for Cd (Table 2.5). These values were well under the Pollutant Concentration Limits (PCL) which is the maximum concentration of each pollutant allowed in organic wastes and biosolids for land application proposed by the USEPA (Table 2.5) (USEPA, 1994). This result of low metal concentration in the compost of animal manure and slaughterhouse wastes may reflect the small quantity of metal concentration in the animal diet. For the vegetable analyses, results showed low concentrations of titanium, indicating that there was minimal contamination from soil particles. All metals were within the safe limits in both areas, except Cd and Pb in all vegetables and Zn in lettuce, which were above WHO referenced values. The highest concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb, Ti and Zn in the vegetables were: 4±0.2, 0.4±02, 1±0.8, 21±0.0, 76±4, 4±4.1, 13±0.0, 2.6±0.1 and 115±0.0, respectively (Table 2.6 and 2.7).

Cadmium (Cd)

In this study, the concentration of Cd in the amended soils ranged from 0.06±0.1 to 0.7±0.1 mg kg^{-1} (Table 2.4), which is below the permissible limit recommended by WHO, 3 mg kg^{-1} (Table 2.8) (Organization, 2014). Some African researchers have detected greater Cd concentrations in soil samples from urban agricultural areas (Table 2.9). For instance, Mutune et al. (2014) found a Cd concentration of 2.64±0.09 mg kg^{-1} when analyzing urban and peri-urban industrial soils along the Nairobi River, Kenya. Additionally, in Lagos, Nigeria, a maximum Cd concentration of 1.33 mg kg^{-1} was detected in vegetable gardens soils alongside major highways (Atayese et al., 2008). Cadmium content in the organic wastes ranged between 0.23 to 0.4 mg kg^{-1}, respectively in the

compost applied in Pikine (PM) and Rufisque (RM) (Table 2.5). Both values were very low compared to the Pollutant Concentration Limits of 39 mg kg^{-1} (Table 2.5) (USEPA, 1994). For vegetables, the highest concentration of Cd was detected in onion leaves, 4±0.2 mg kg^{-1} at Pikine and in lettuce, 0.5±0.0 mg kg^{-1} at Rufisque (Table 2.6 and 2.7). The average Cd concentration was 0.3±0.0 mg kg^{-1} in both carrot (Rufisque) and tomato (Pikine). The results also showed that the vegetables from Pikine were more contaminated than those from Rufisque, which may be due to the application of wastewater for irrigation in Pikine. Cadmium concentration in all vegetables were above the normal range proposed by WHO, 0.1 mg kg^{-1} (Table 2.8). Similar levels were reported for Cd (0.5 - 4.9 mg kg^{-1}) in a study conducted in Lagos, Nigeria on amaranthus cultivated along highways (Atayese et al., 2009). However, in a study conducted in Accra, Ghana, Lente et al. (2014) reported lower Cd levels ranging between "not detected" to 0.5 mg kg^{-1} in local vegetables irrigated with wastewater.

Cobalt (Co)

The maximum permissible concentration of Co in soils recommended by WHO is 50 mg kg^{-1} (Table 2.8) (Organization, 2014). In this study, Co concentration varied between 0.81±0.2 to 4.22±2.1 mg kg^{-1} (Table 2.4), very far below the recommended limit. Opaluwa et al. (2012) have found very low soil Co contents (0.58, 0.63 and 0.33 mg kg^{-1}) in agricultural lands around dumping sites in Lafia Metropolis, Nigeria. The concentration of Co in both composted materials ranged between 1.3 mg kg^{-1} in PM and 1.9 mg kg^{-1} in RM (Table 2.5), which is very low. Cobalt concentration in all vegetables ranged between "not detected" to 0.4±0.2 mg kg^{-1}, which is well below the WHO permissible limit of 50 mg kg^{-1} (Table 2.8). In onion leaves, Co concentration ranged from 0.1±0.2 in Rufisque to 0.4±0.0 in Pikine. It was not detected in lettuce grown at the Pikine site, but was found in lettuce from Rufisque at a concentration of 0.2±0.0 mg kg^{-1} (Table

2.6 and 2.7). Cobalt content was under the limit of detection in carrot and very low in tomato (0.1±0.1 mg kg^{-1}). Similar levels of Co concentrations were detected by Sobukola et al. (2010) in leafy vegetables (0.10±0.0; 0.02±0.0 to 0.4±0.0 mg kg-^{1}) from selected markets in Lagos, Nigeria. In contrast, Bambara et al. (2015) found a wider range of Co concentration in wastewater irrigated vegetable farms at Loumbila and Paspanga, Burkina Fasso. The reported values ranged from 0.50±0.06 - 2.10±0.02 mg kg^{-1} in cabbage, 1.26±0.1 mg kg^{-1} in spinach and 1.28±0.08 mg kg^{-1} in lettuce.

Chromium (Cr)

The maximum permissible level of Cr in soils recommended by WHO is 100 mg kg^{-1} (Table 2.8) (Organization, 2014). In this study, the mean of Cr value ranged between 4.37±1.0 to 47.11±9.9 mg kg^{-1} (Table 2.4), which is under the recommended value. The highest Cr concentration obtained (47.11±9.9 mg kg^{-1}) was very low compared to that (271 mg kg^{-1}) found in gardens soils irrigated with wastewater in Skhirat region, Morocco (Zouahri et al., 2015). Similarly, Abdu et al. (2011) observed an elevated Cr content of 72 mg kg^{-1} in wastewater irrigated vegetable garden soils of Kano, Nigeria (Table 2.9). Chromium concentration in the studied organic wastes PM and RM ranged between 3.02 to 20.9 mg kg^{-1} (Table 2.5), which is low. In almost all vegetables, Cr was below the detectable limits. In Pikine, only onion leaves accumulated Co with a concentration of 1±0.8 mg kg^{-1}. In Rufisque, Co was found in carrot and onion leaves at concentrations of 1±1.1 and 0.7±0.7 8 mg kg^{-1}, respectively (Table 2.6 and 2.7). These mean concentrations are just under the permissible limit, 2.3 mg kg^{-1} (Table 2.8). Muamar et al. (2014) have reported very high Cr concentrations in vegetables irrigated with wastewater from industrial effluents in Rabat, Morocco. Their Cr level ranged between 5.83 in cabbage to 28.73 in mint,

which were approximately 2.5 to 12.5 times higher than 2.3 mg kg^{-1} value set by WHO (Organization, 2014).

Copper (Cu)

The maximum permissible level of Cu in soils recommended by WHO is 100 mg kg^{-1} (Table 2.8) (Organization, 2014). Copper concentration in these soils was under the WHO guideline and ranged from 2.04±0.2 to 14.9±5.3 mg kg^{-1} (Table 2.4). The highest Cu concentration found in this study was greater than that (7.66 mg kg^{-1}) found in vegetable garden soils from Eastern Cape, South Africa (Bvenura and Afolayan, 2012). However, in table 2.9, higher Cu contents of 75.4 and 185.7 mg kg^{-1} were reported in Kenya and Morocco (Mutune et al., 2014; Muamar et al., 2014). The Cu concentration was around 22 mg kg^{-1} (Table 2.5) in both organic materials which is very low compared to the Pollutant Concentration Limit of 1500 mg kg^{-1} set by the USEPA (Table 2.5) (USEPA, 1994). The highest Cu concentration in vegetables from both sites were detected in lettuce, 9±0.0 8 mg kg^{-1} in Pikine and 21±0.0 mg kg^{-1} in Rufisque, while the lowest levels were found in onion bulbs (4.4±0.4 - 5±0.1 mg kg^{-1}) (Table 2.6 and 2.7). However, Cu content in all vegetables was under the permissible limit set by WHO, 73 mg kg^{-1}. Greater Cu concentrations of 23, 56, 69 and 23 mg kg^{-1} were found in leaves of okra, lettuce, roselle and onion in vegetable gardens irrigated with gray wastewater in Yola and Kano, Nigeria (Chiroma et al., 2014).

Manganese (Mn)

The maximum permissible concentration of Mn in soils recommended by WHO is 2000 mg kg^{-1} (Table 2.8) (Organization, 2014). The mean Mn value observed ranged from 24.5±7.1 to 155±48 mg kg^{-1} in the study areas (Table 2.4), which is very low compared to the maximum permissible limit. Bvenura and Afolayan, 2012 reported higher mean values of Mn ranging from 377.61 to 499.68 mg kg^{-1} in South African vegetable soils that were amended with compost or animal manure (Bvenura and Afolayan, 2012). In contrast, Lente et al. (2014) detected lower Mn concentration of 61 mg kg^{-1} in wastewater irrigated soils in Ghana. In general, all these published Mn levels were well below the maximum recommended concentration in soils. Manganese contents in PM and RM ranged between 138 to 166.5 mg kg^{-1} (Table 2.5), which is within the safe range for land organic wastes applications. Data from the vegetable analyses showed that Mn concentrations ranged from 12±0.0 to 76±4 mg kg^{-1} in lettuce and onion leaves from Pikine and between 8±0.0 and 49±2.5 mg kg^{-1} in carrot roots and onion leaves from Rufisque (Table 2.6 and 2.7). However, the average Mn concentration in all vegetables were well below the permissible recommendation limit of 500 mg kg^{-1} (Table 2.8).

Nickel (Ni)

The maximum permissible level of Ni in soils recommended by WHO is 50 mg kg^{-1} (Table 2.8) (Organization, 2014). Nickel concentration in the soils varied from 0.7±0.2 to 14.2±7.3 mg kg^{-1} (Table 2.4), which is under the recommended value. Lower levels of Ni (0.31 and 0.42 mg kg^{-1}) were found in vegetable garden soils around dump sites in Lafia Metropolis, Nigeria (Opaluwa et al., 2012) while a greater concentration (46.8 mg kg^{-1}) was found by Muamar et al. (2014) in wastewater irrigated garden soils in Morocco. Nickel content in the organic wastes was 6.1 and 7.3 mg kg^{-1} in PM and in RM, respectively (Table 2.5). Both values are low compared to the Pollutant Concentration Limits of 420 mg kg^{-1} set by USEPA (Table 2.5) (USEPA, 1994). Nickel in all vegetable samples were under than the recommended value of 67 mg kg^{-1} (Table 2.8). In Pikine Ni ranged from "not detected" to 4±4.1 mg kg^{-1} in onion roots and tomato, respectively. While in Rufisque, it concentration varied between 0.6±0.2 and 2±0.0 mg kg^{-1} in carrot roots and lettuce (Table 2.6 and 2.7). Similar Ni concentration ranges were found by Nabulo et al. (2010) in leafy vegetables grown in urban areas at Kampala, Uganda. The reported values were 0.460 - 4.66, 0.38 - 4.42 and 0.24 - 3.43 mg kg^{-1} in amaranthus, cabbage and eggplant, respectively. Opaluwa et al. (2012) also reported very low Ni contents of 0.01, 0.02 and 0.04 mg kg^{-1} in leaves of roselle and spinach and okra fruits grown around dump sites in Lafia, Nigeria.

Lead (Pb)

The maximum permissible concentration of Pb in soils recommended by WHO is 100 mg kg^{-1} (Table 2.8) (Organization, 2014). Lead concentration in the studied soils ranged from 2.6±0.3 to 10.4±5.8 mg kg^{-1} (Table 2.4) and was under the guideline. A higher Pb content of 20.94 mg kg^{-1} was found in urban and peri-urban vegetable garden soils contaminated by fuel spills and other waste flowing from the industrial zone in Nairobi, Kenya (Mutune et al., 2014). However, the level of Pb in both studies is under the permitted maximum value (100 mg kg^{-1}). In the composts, Pb concentration varied between 9.4 to 0.3 mg kg^{-1} (Table 2.5) in PM and RM, which is very low when compared to the Pollutant Concentration Limits of 300 mg kg^{-1} (Table 2.5) (USEPA, 1994). Lead concentration in vegetables from all sites were well above the maximum permissible level, 0.3 mg kg^{-1} (Table 2.8). In Pikine, Pb concentration ranged from 3.7±0.0 - 12±0.0 mg kg^{-1} in onion roots and lettuce and between 9±0.7 and 13±0.0 mg kg^{-1} in onion and carrot roots from Rufisque (Table 2.6 and 2.7). Most of the Pb was found in the organic, oxide and residual fractions of the soil. However, small Pb amounts were found in the carbonate fraction, which is more soluble and may be responsible for the high Pb levels observed in the vegetables. Similarly, elevated concentrations of Pb (14.3 and 13.5 mg kg^{-1}) recorded in tomatoes and onions grown in waste dumpsite soils along the Challawa River bank in Nigeria were attributed to untreated effluents from tannery industries (Yabe et al., 2010).

Zinc (Zn)

The maximum permissible level of Zn in soils recommended by WHO is 300 mg kg^{-1} (Table 2.8) (Organization, 2014). After Mn, Zn was the second most abundant metal in the soils. However, mean Zn concentration was under the maximum recommended value and ranged between 12.3±3.8 to 46.4±19 mg kg^{-1} (Table 2.4). Mapanda et al. (2005) found a wider range of Zn concentration (14 and 228 mg kg^{-1}) in Zimbabwean vegetable garden soils irrigated with wastewater. Zinc concentrations were well below the Pollutant Concentration Limits of 2800 mg kg^{-1}, 64.4 and 107.2 mg kg^{-1}in RM and PM, respectively (Table 2.5). In vegetables, Zn concentration varied between 24±0.2 and 92±20 mg kg^{-1} in onion roots and leaves from Pikine and ranged from 15±0.8 to 115±0.0 mg kg^{-1} in onion leaves and lettuce collected in Rufisque (Table 2.6 and 2.7). The highest Zn concentrations in these vegetables were greater than those found in soils and also exceeded the WHO recommended value of 100 mg kg^{-1} (Table 2.8). Similar to Pb, the higher Zn concentration in the vegetables compared to the soils may be the result of Zn variability in soils due to sampling time (soils samples were collected in 2015 and vegetables in 2016). Yabe et al. (2010) reported Zn concentration of 130.1± 6.6 mg kg^{-1} in spinach cultivated in soils irrigated with from Akaki River, Ethiopia, which was polluted with untreated sewage and industrial effluent. Similarly, they reported a Zn concentration of 221 mg kg^{-1} in locally grown vegetables (cabbage and pepper) from Harare, Zimbabwe, due to the use of sewage sludge in agricultural soils.

Summary

In general, results of the total metal from the acid digestion showed that all metal concentrations increased in amended soils compared to their controls, however all of them were below the WHO maximum permissible limit in soils. Similarly, metal contents in the organic wastes were under the USEPA referenced values for land application. However, in vegetable samples, all studied metals were within the normal ranges except Cd, Pb and Zn that were above the WHO maximum permissible limit for metal content in vegetables. Sequential extraction procedure showed that most metals were primarily associated with the oxides, organic matter and residual fractions. This suggests they would not be easily released in the environment, unless there are changes in the redox conditions and intensive degradation of the organic matter. Small quantities of Mn, Zn and Pb were also found in the carbonate fraction that is very sensitive to acidic conditions, meaning that these heavy metals would be more easily released and potentially bioavailable if soil pH decreases. This may explain the high level of Zn observed in onion leaves. However, based on the SEP the high concentrations of Cd and Pb found in vegetables was unexpected. Plant samples were taken approximately one year after the soil samples. Changes in Cd and Pb in the soils due to different types of organic compost and changes in concentrations in wastewater used for irrigation may be responsible for these elevated levels.

CONCLUSION

Over the last few decades, the agricultural soils of the Niayes region have experienced a transition from traditional to intense urban agriculture that has been consistent with practices in many other urban areas in Africa. This agricultural intensification was promoted by climate variabilities encountered in arid and semi-arid regions and resulted in the increased use of organic wastes. Animal manures been applied to agricultural lands as organic amendments to improve soil fertility and productivity. However, in recent years, this practice was found to increase heavy metal accumulation in soils. Generally, metals found in animal manures are derived from additive feeds used to enhance livestock growth and reproduction. This study showed that the application of organic wastes such as raw and composted animal manure and slaughterhouse wastes, has increased all metals (Cd, Co, Cr, Cu, Mn, Ni Pb, and Zn) in the amended soils. The heavy metals were more abundant in Rufisque and Pikine, where the greatest quantities of composts are applied compare to Rao and Essyl that received lower amounts of raw manure. Additionally, metals were mostly associated with the oxides, organic matter and the residual fraction, making them less potentially bioavailable to biota, unless reducing or oxidizing conditions arise. Based on the maximum permissible levels of metals in soils proposed by WHO, the trace element concentrations in these Senegalese garden soils are not alarming. Also, in comparison to the USEPA guideline for the Pollutant Concentration Limits in organic waste and biosolids for land-application, heavy metal contents in the composted wastes were very low. Finally, concentration of heavy metals detected in vegetables from Pikine and Rufisque sites were below the maximum permissible limits of metal in vegetables proposed by the World Health Organization, except Cd, Pb and Zn in all vegetables. Based on this study, vegetable gardeners in the Niayes region and in Essyl should increase the soil pH or keep it circumneutral by adding agricultural lime in order to decrease metal

availability and uptake. As agriculture and urban growth continue to intensify, additional studies will need to be conducted to monitor increases in heavy metal concentrations in those local Senegalese soils.

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Table 2.1. Tessier's sequential extraction procedures of heavy metals in soil (Tessier et al., 1979)

Fraction	Solution (1g soil)	Equilibrium conditions
Exchangeable	8 ml 1M $MgCl_2$ (pH 7)	1h, room temperature
Carbonates	8 ml 1M NaOAc (pH 5)/acetic acid	5 h, room temperature
Fe and Mn oxides	20 ml 0.04 M NH_2OH/HCl in 25% HOAc	6 h, 96°C + 3 agitations
Organic matter	3 ml 0.02 M HNO_3 + 5 ml 30% H_2O_2 (pH 2)	2h, 85°C
Residual	HNO_3-HCl digestion (3:1) (+40 ml H2O)	20 min, room temperature

Table 2.2: Soil physiochemical parameters in all sites. Control 1: Uncultivated soil from Niayes region site and control 2: Uncultivated soil from Essyl site. Particle size and total carbon (TC) (mg kg^{-1}), estimated CEC (cmol (+) kg^{-1}), electrical conductivity (EC) (dS m^{-1}), nutrient contents (P, K, Ca Mg) (kg ha^{-1})

	Location					
Parameter	Control 1	Pikine	Rufisque	Rao	Control 2	Essyl
Clay	-	0.00	137800	9000	-	21100
Silt	-	19100	240300	78200	-	101700
Sand	-	980900	622000	912900	-	877200
pH	5.9	5	7.9	7.2	5.1	6.5
TC	1600	16000	36600	8300	2800	14100
Estimated CEC	1.5	10.83	26.4	9.13	1.6	7.06
EC	0.04	1.77	0.40	0.64	0.2	0.18
P	16.8	1117	196	619	55	224
K	39.2	276	114	500	34	145
Ca	541	3412	10653	3215	512	2560
Mg	65.0	289	693	382	49	121

Table 2.3: Organic matter physiochemical parameters. PM: Composted animal manure and slaughterhouse waste collected from Pikine. RM: Composted animal manure and slaughterhouse waste collected from Rufisque. Total carbon (mg kg^{-1}), estimated CEC (cmol (+) kg^{-1}), nutrient contents (P, K, Ca Mg) (kg ha^{-1})

Parameters	Concentrations in organic wastes	
	PM	RM
pH	7.6	7.1
TC	164000	179000
Estimated CEC	32.2	23.9
P	3181	1136
K	4366	2095
Ca	6477	7111
Mg	2531	848

Tables 2.4: Total heavy metal concentration (mg kg^{-1}) ± SD in controls and amended soils. Control 1: Uncultivated soil from the Niayes region. Pikine, Rufisque and Rao: amended soils from the Niayes region. Control 2: Uncultivated soil from Essyl site. Essyl: amended soil from Essyl site nd: not detected

	Metal Concentrations in soils					
Element	Control 1	Pikine	Rufisque	Rao	Control 2	Essyl
Cd	0.03±0.1	0.24±0.1	0.70±0.1	0.23±0.1	nd	0.06±0.1
Co	0.33±0.3	0.81±0.2	4.22±2.1	3.69±1.1	0.23±0.1	0.94±0.2
Cr	1.57±1.4	5.36±1.8	47.1±9.9	4.37±1.0	1.47±0.6	4.52±1.3
Cu	1.9±1.8	14.9±5.3	9.8±1.8	2.04±0.2	0.87±0.1	2.12±0.4
Mn	9.43±7.9	42.02±16	155±48	69.6±6.5	5.57±0.6	24.5±7.1
Ni	0.50±0.5	2.13±0.8	14.2±7.3	2.9±0.9	0.33±0.5	0.7±0.2
Pb	2.20±1.9	10.3±2.1	10.4±5.8	2.6±0.3	2.2±0.1	3.17±0.6
Zn	3.43±2.9	46.4±19	40.8±15	13.8±2.7	3.6±0.9	12.3±3.8

Tables 2.5: Total heavy metal concentration (mg kg^{-1}) ± SD in the organic amendments and the Pollutant Concentration Limits (PCL) for land-applied biosolids (USEPA, 1994). PM: Composted animal manure and slaughterhouse waste collected from Pikine. RM: Composted animal manure and slaughterhouse waste from Rufisque.

	PCL	Metal Concentrations in Organic Wates	
Element		PM	RM
Cd	39	0.23±0.0	0.4±0.0
Co	-	0.7±0.6	1.8±0.1
Cr	-	3.0±0.2	19.3±1.6
Cu	1500	22.4±1.8	22.8±0.9
Mn	-	124±14	160±6.5
Ni	420	4.3±1.8	7.0±0.3
Pb	300	8.8±0.6	9.7±0.6
Zn	2800	101±6.2	61.6±2.8

Table 2.6: Heavy metal concentration (mg kg^{-1}) ± SD in vegetables grown in Pikine site and the World Health Organization (WHO) Permissible level of metals (PLM) in vegetables (Organization, 2014). nd: not detected

	Metal Concentrations								
Part	Cd	Co	Cr	Cu	Mn	Ni	Pb	Ti	Zn
Onion roots	1.5±0.2	nd	nd	5±0.1	15±0.1	nd	3.7±0.0	nd	24±0.2
Onion leaves	4±0.2	0.4±0	1±0.8	7±0.2	76±4	1±0.5	6.9±0.0	1.3±0.0	92±20
Tomato fruits	0.3±0.0	0.1±0.1	nd	8±1.4	22±14	4±4.1	4.8±0.0	0.4±0.5	54±16
Lettuce	nd	nd	nd	9±0.0	12±0.0	2±0.0	12±0.0	nd	39±0.0
PLM	0.10	50	2.3	73	500	67	0.3	-	100

Table 2.7: Heavy metal concentration (mg kg^{-1}) ± SD in vegetables grown in Rufisque site and the World Health Organization (WHO) Maximum Permissible Level of metals (MPL) in vegetables (Organization, 2014). nd: not detected

	Metal Concentrations								
Parts	Cd	Co	Cr	Cu	Mn	Ni	Pb	Ti	Zn
Carrot roots	0.1±0.1	nd	nd	6.7±8	8±0	0.6±0.2	13±0.0	0.1±01	22±2.3
Carrot leaves	0.3±0.0	0.1±0.0	1±1.1	13±0.4	36±0.4	1±0.3	11±0.3	2.6±0.1	40±0.2
Onion roots	0.2±0.0	nd	nd	4.4±0.4	12±1.3	1±0.1	9±0.7	nd	28±1.7
Onion leaves	0.1±0.2	0.4±0.1	0.7±0.7	16±0.6	49±2.5	1±0.2	9.5±0.0	1.2±0.3	15±0.8
Lettuce	0.5±0.0	0.2±0.0	nd	21±0.0	35±0.0	2±0.0	11±0.0	0.9±0.0	115±0.0
MPL	0.1	50	2.3	73	500	67	0.3	-	100

Table 2.8. The Maximum Permissible Level Limits (MPL) of heavy metals (mg kg^{-1}) in irrigation water, soils and vegetables established by the World Health Organization (WHO) (Organization, 2014)

Chemical Element	Maximum permissible level in irrigation water	Maximum permissible level in soils	Maximum permissible level in vegetables
As	0.1	20	-
Cd	0.01	3	0.10
Co	0.05	50	50.00
Cr	0.55	100	2.3
Cu	0.017	100	73
Fe	0.50	50000	425.00
Mn	0.20	2000	500.00
Ni	1.40	50	67.00
Pb	0.065	100	0.30
Se	0.02	10	-
Zn	0.20	300	100

Tables 2.9: Highest heavy metal concentration (mg kg^{-1}) in vegetable garden soils from this study, other African studies and the World Health Organization (WHO) Maximum Permitted Level (MPL) of metals in soils (Organization, 2014)

	Citations					
Element	This study	(Abdu et al., 2011)	(Mutune et al., 2014)	(Muamar et al., 2014)	(Hodomihou et al., 2015)	MPL (Organization, 2014)
Cd	0.8	4.8	2.6	1	0.2	3
Co	6.3	-	-	-	-	50
Cr	57	72	1.4	271	93.5	100
Cu	20.2	18	75.4	185.7	7.2	100
Mn	203	-	-	85.7	48.3	2000
Ni	21.5	17	-	46.8	14	50
Pb	16.2	46	20	75	7.2	100
Zn	65.4	285	198	555	25	300

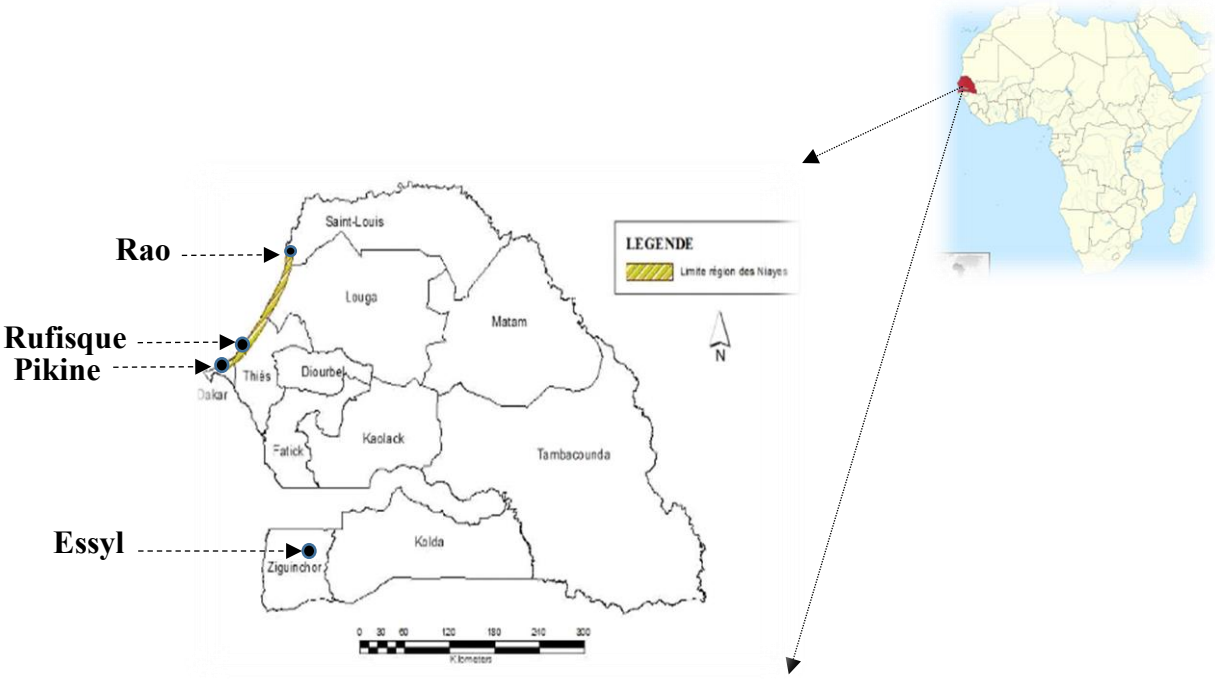

Figure 2.1: Map of Senegal, the Niayes region sites and Essyl site. http://www.memoireonline.com/08/10/3840/m_Limpact-du-maraichage-dans-la-degradation-des-ressources-naturelles-dans-les-niayes-de-la-bordur1.html

Figure 2.2: Vegetable gardens in Pikine site, Dakar, April 2015

Figure 2.3: Wastewater and animal manure used in Pikine gardens, Dakar, April 2015

Figure 2.4: Vegetable gardens in Rufisque site, Dakar, April 2015

Figure 2.5: Animal manure used in Rufisque gardens, Dakar, April 2015

Figure 2.6: Vegetable gardens in Rao site, St. Louis, April 2015

Figure 2.7: Vegetable gardens in Essyl, Ziguinchor, April 2015

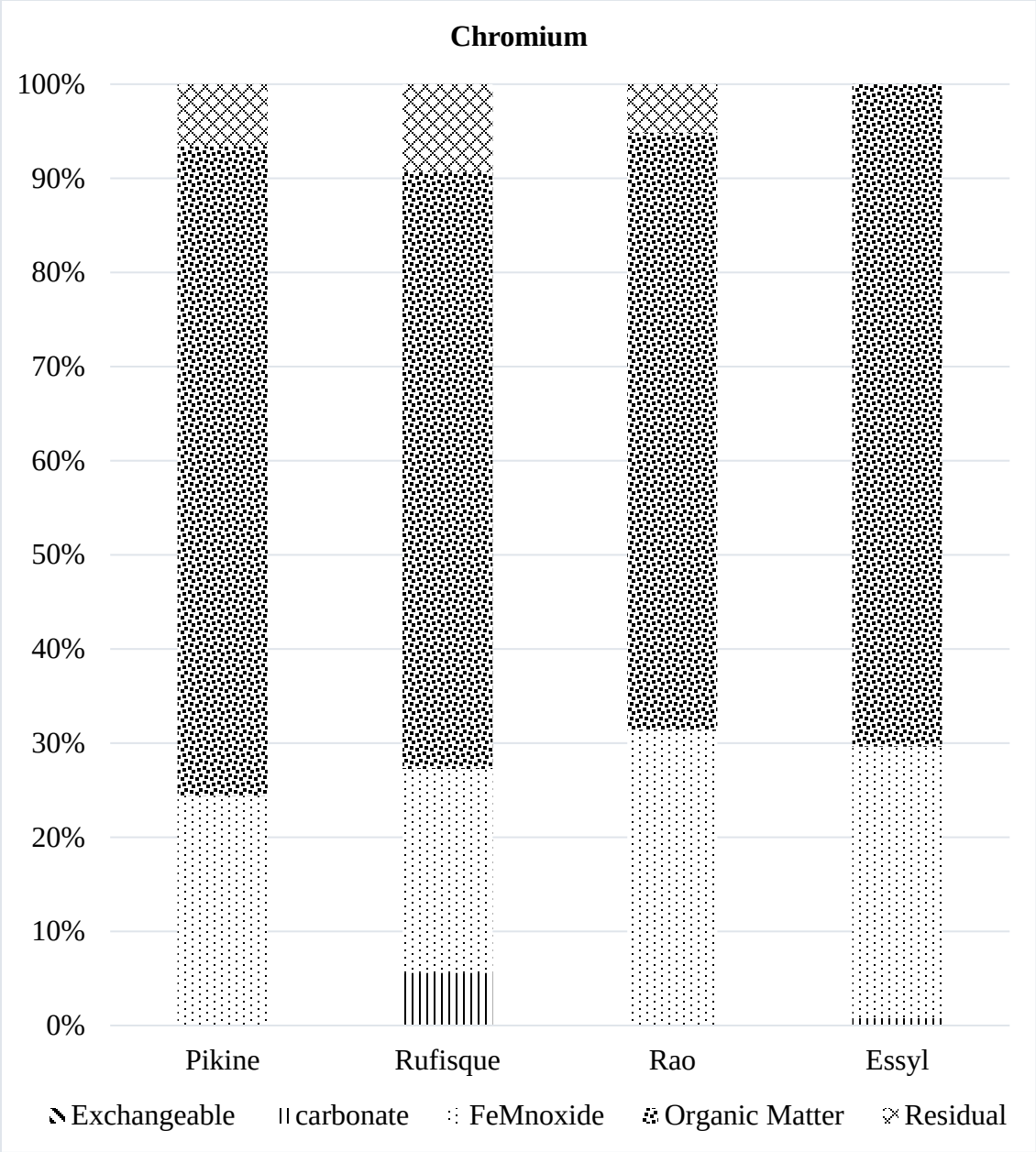

Figure 2.8: Chromium distribution in market garden soils of the Niayes region and Essyl

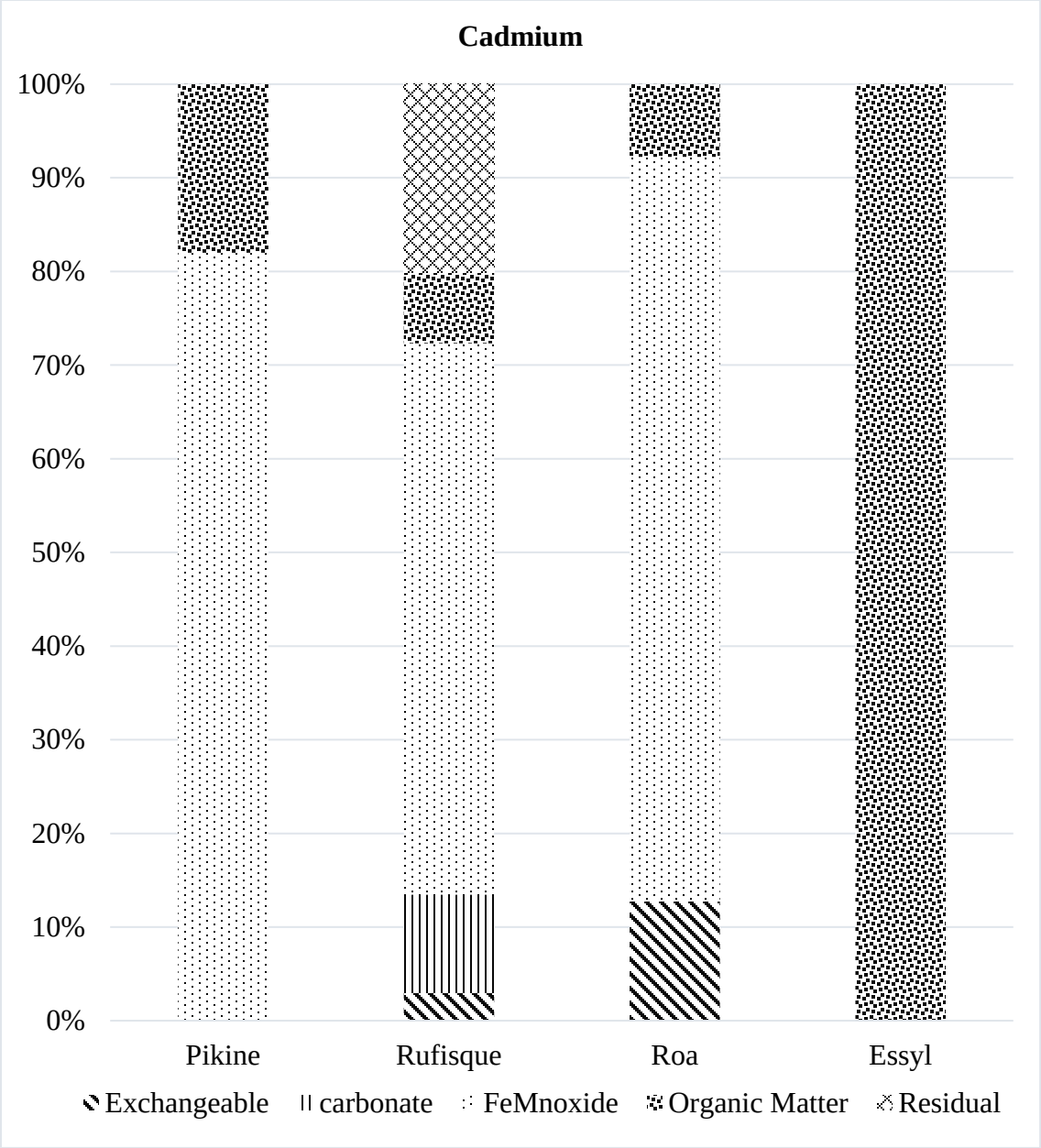

Figure 2.9: Cadmium distribution in market garden soils of the Niayes region and Essyl

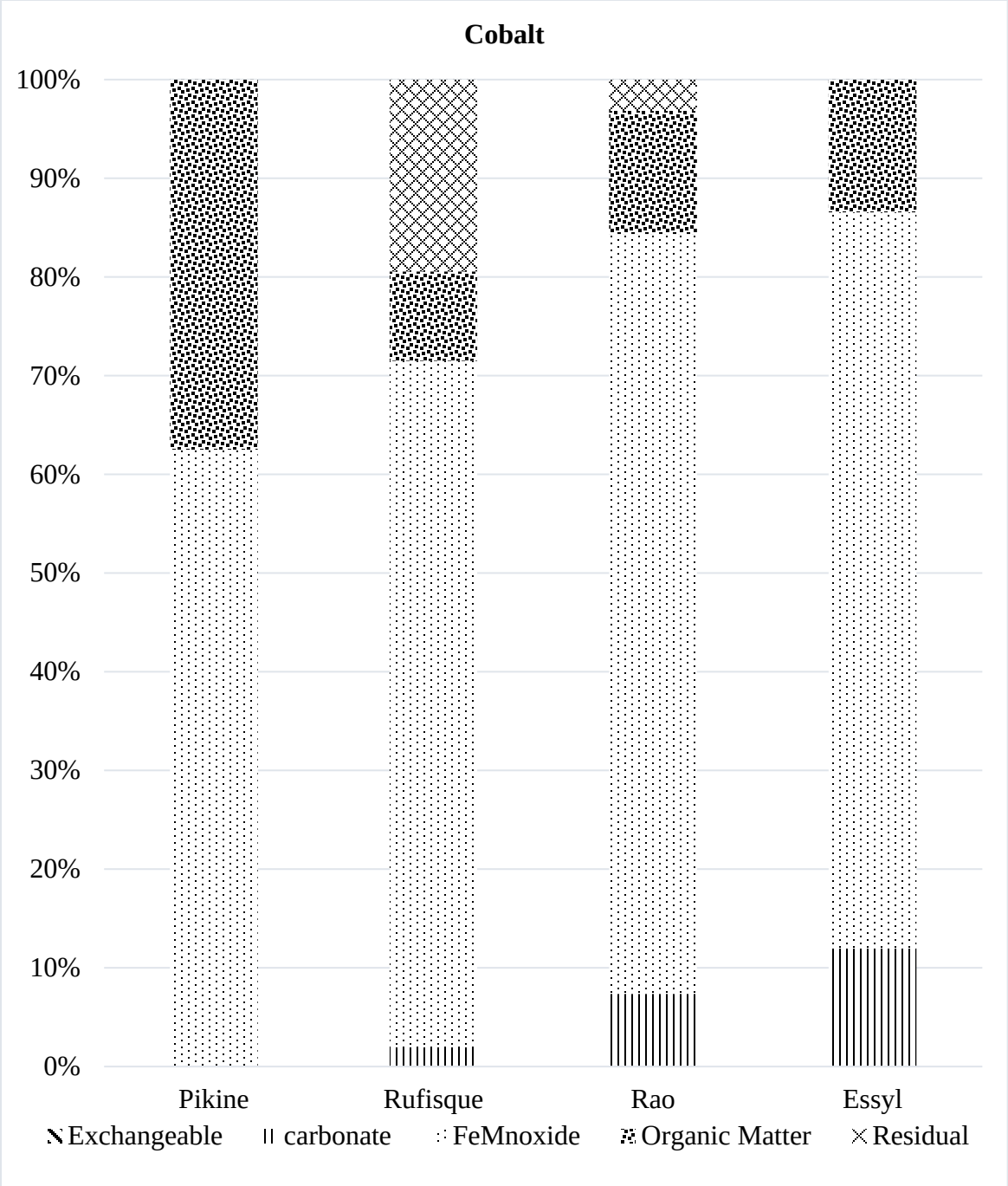

Figure 2.10: Cobalt distribution in market garden soils of the Niayes region and Essyl

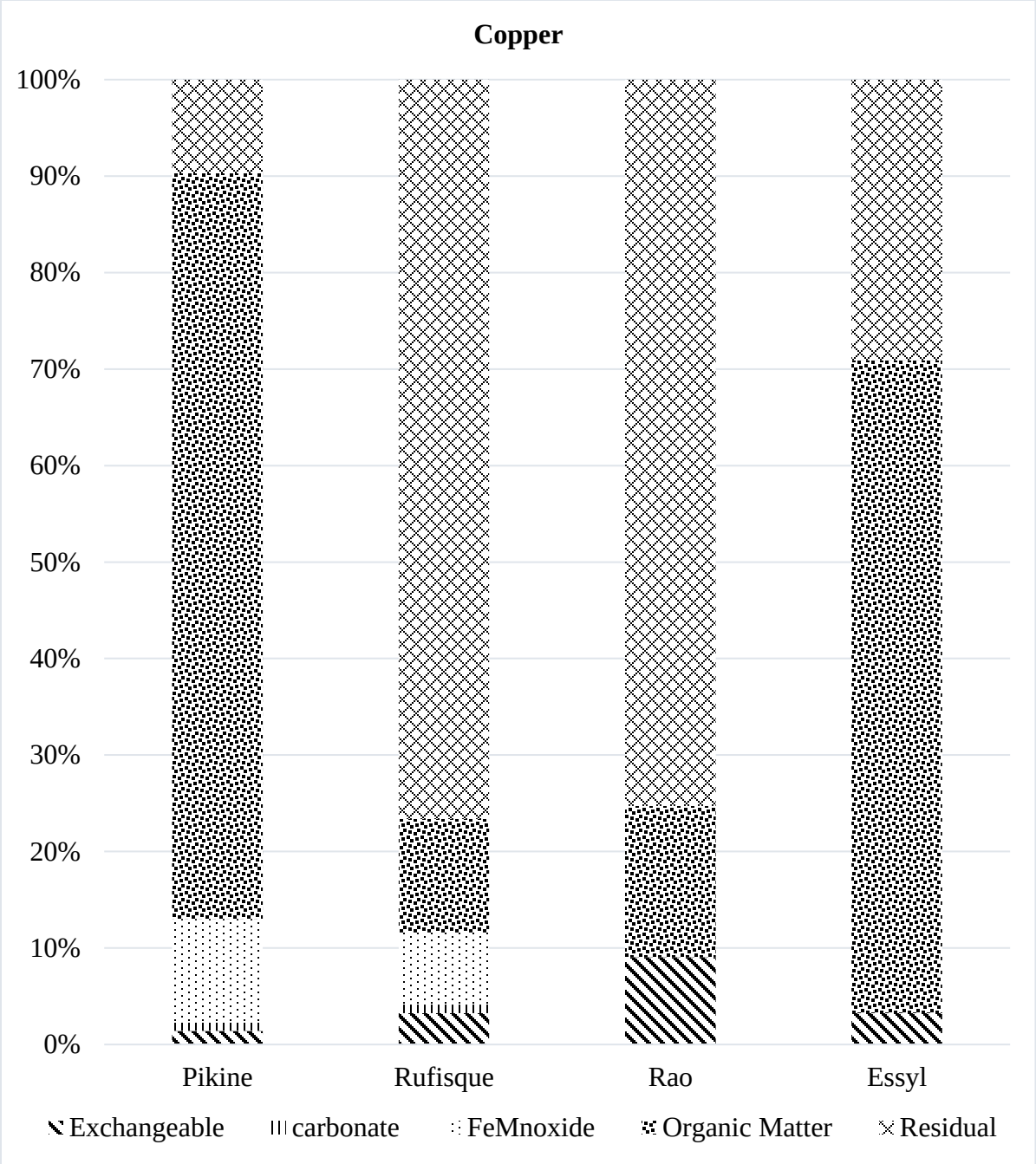

Figure 2.11: Copper distribution in market garden soils of the Niayes region and Essyl

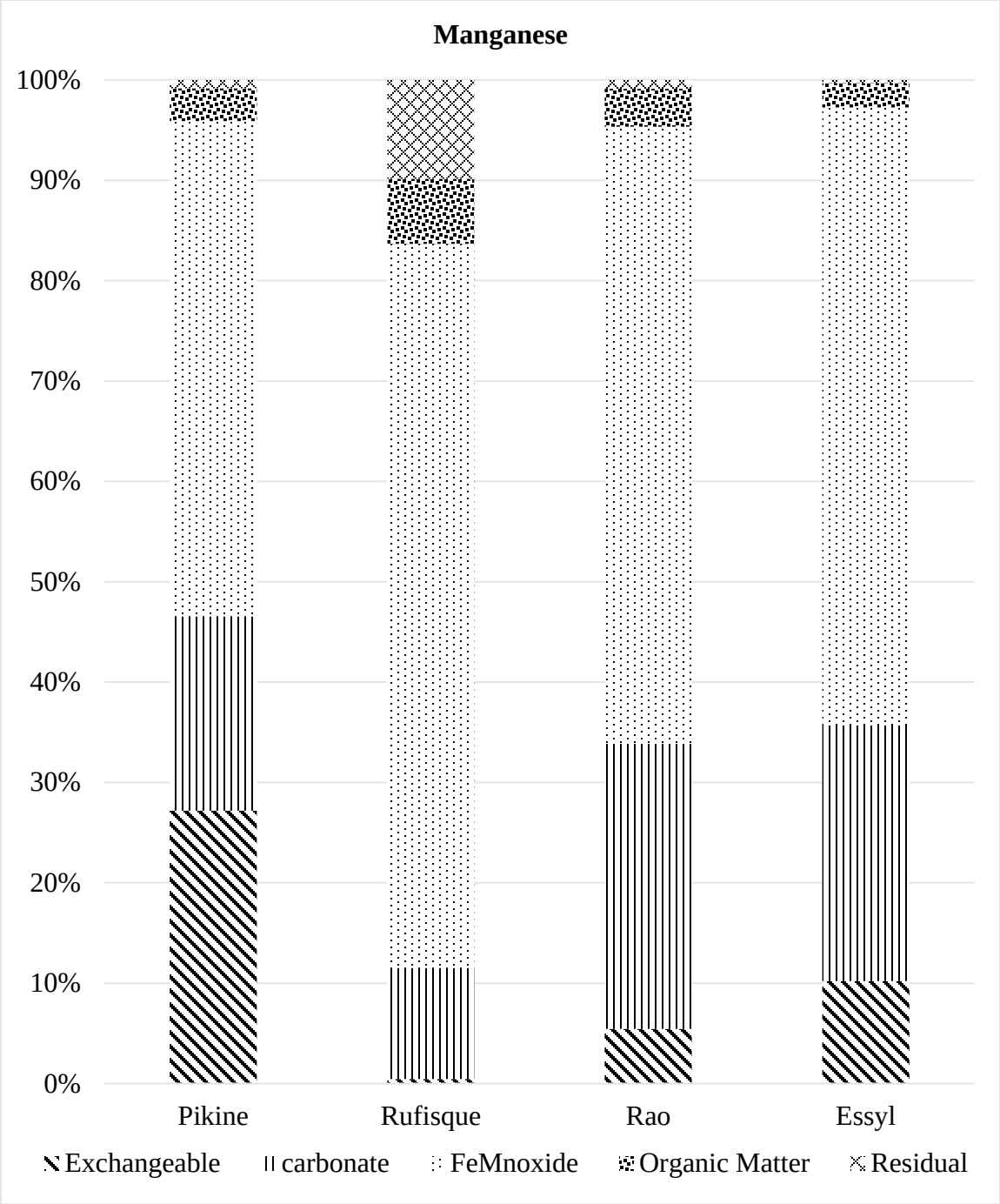

Figure 2.12: Manganese distribution in market garden soils of the Niayes region and Essyl

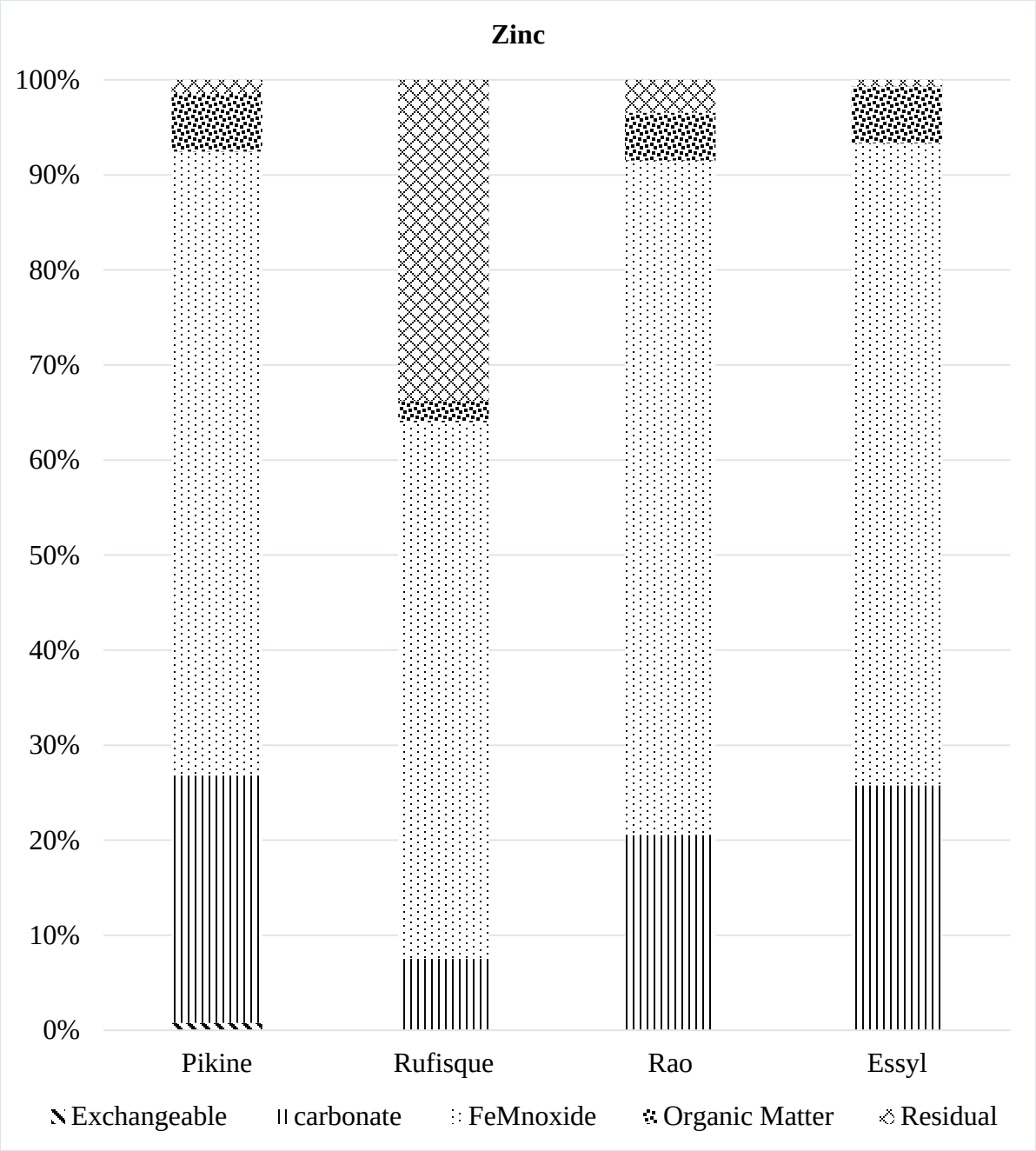

Figure 2.13: Zinc distribution in market garden soils of the Niayes region and Essyl

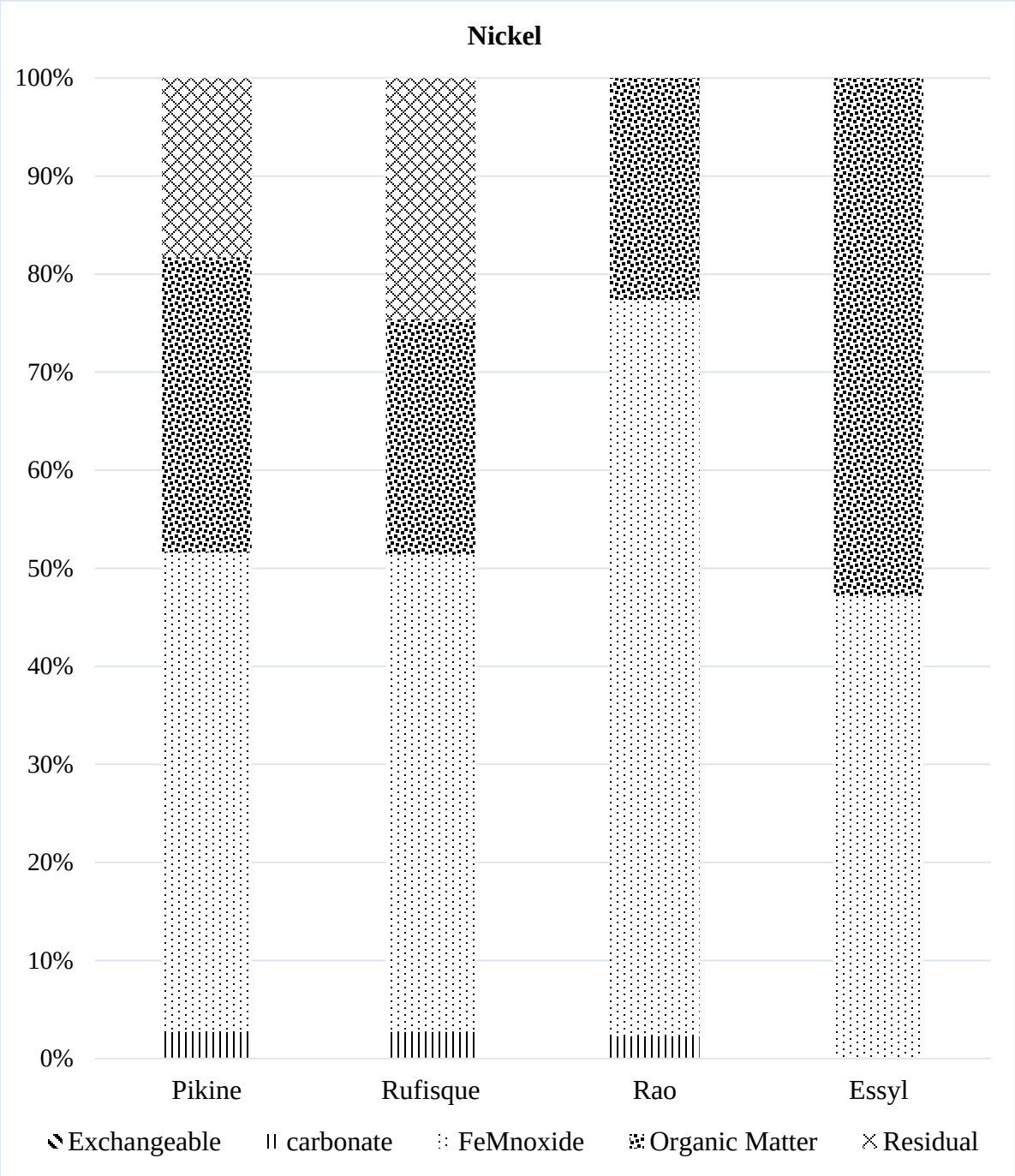

Figure 2.14: Nickel distribution in market garden soils of the Niayes region and Essyl

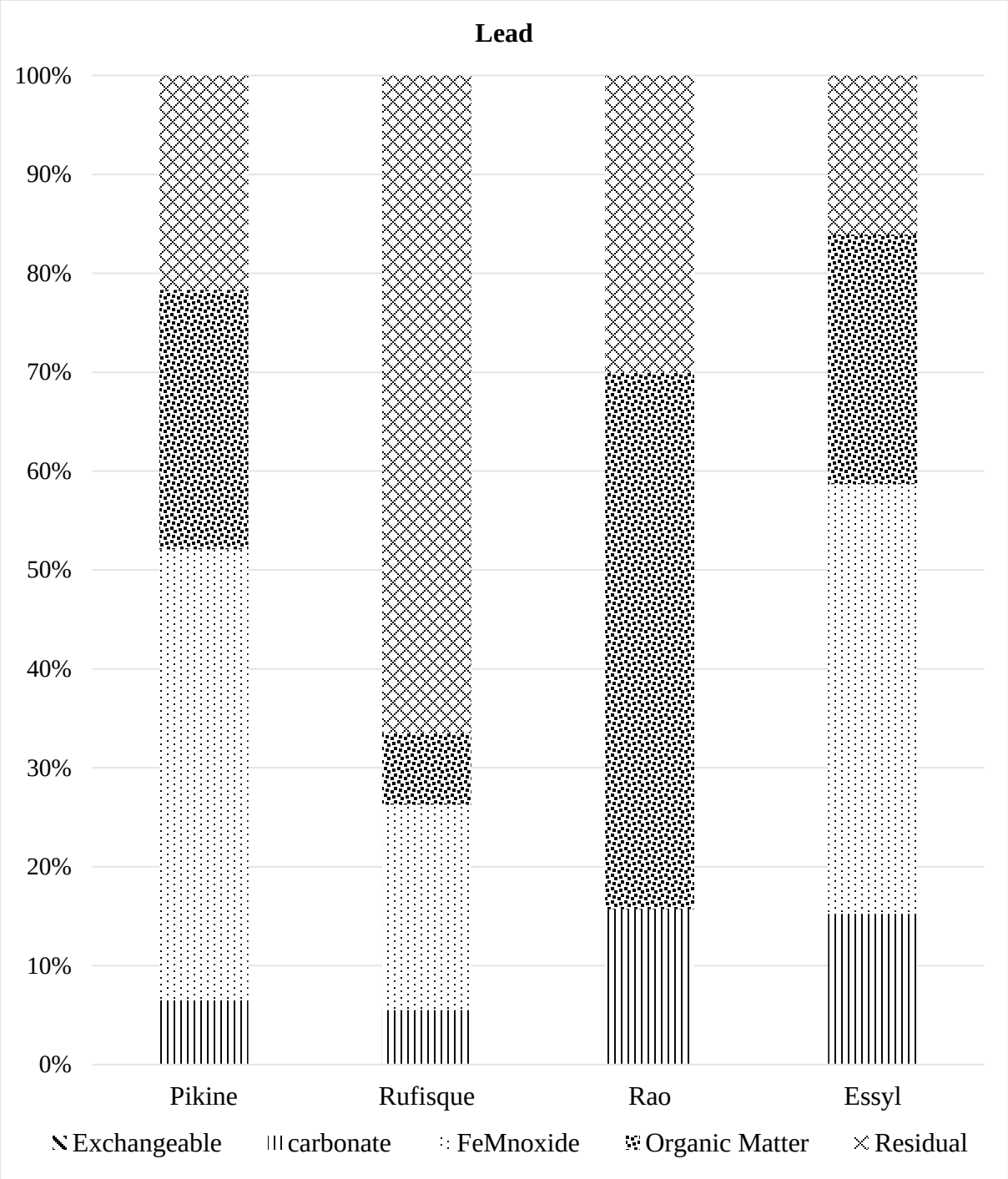

Figure 2.15: Lead distribution in market garden soils of the Niayes region and Essyl