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► To cite this version:

Mor Mbodji, Nadia Baskali-Bouregaa, Frédérique Barbier-Bessueille, Linda Ayouni-Derouiche, Cheikh Diop, et al.. Speciation of metals by sequential extractions of agricultural soils located near a dumpsite for prediction of element availability to vegetables. *Talanta*, 2022, 244, pp.123411. 10.1016/j.talanta.2022.123411 . hal-03675539

HAL Id: hal-03675539

<https://hal.science/hal-03675539v1>

Submitted on 22 Jul 2024

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Speciation of metals by sequential extractions of agricultural soils located near a dumpsite for prediction of element availability to vegetables

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Abstract

In this paper heavy metal pollution has been investigated by comparing total concentrations and speciation of heavy metals (Cr, Cu, Mn, Zn, Pb and Sr) in soils from four agricultural fields (S1, S2, S3, S4) located in the direct vicinity of the largest landfill in Senegal. The sequential test allowed discriminating between various fractions of heavy metals, namely the acid-extractable fraction, the fraction bound to Fe oxides, the fraction bound to organic matter and the residual fraction. It was proven that the most important fractions of metals (Cr, Cu, Pb, Mn, Sr and Zn) are bound to the residual fraction, more than 50% for most sites, and thus they may be relatively hardly liberated into the environment. The results also showed that the metal pollutions in S3 and S4 were more severe than in other sampling sites, especially for Mn and Zn. In addition, the exchangeable fraction, which is the most available, represents from 10 to 47% of the total concentration for Sr, Mn and Zn, indicating that a non-negligible part of these elements may be easily released. Matrix correlation between soil characteristics and the elemental concentrations was tested to study and to detect a possible trend of metal mobilization from organic matter or oxides to agricultural soils. Vegetable grown from the four sampling sites were analyzed, Cr, Zn and Pb concentrations were high in many studied foodstuffs, (up to 54 mg/kg; 45.8 mg/kg and 3.4 mg/kg for Mn, Zn and Pb respectively) and higher than the threshold values of FAO/WHO. Calculation of hazard indexes suggested no potential health risks associated with consuming the vegetables with the exception of cassava and cassava leaves.

1. Introduction

The contamination of agricultural soils by metallic elements has been a hot-button issue in the world for several years. Indeed, metals when accumulated in soils can be absorbed by plants and can have serious repercussions on human health after consumption [1]. Market gardening occupies an important place in the consumption and nutrition of the populations of the world, in urban and peri-urban areas. Market gardening is often threatened by metallic contamination of anthropogenic origin, which generally comes from various sources such as past industrial and mining activities [2], automobile, urban and industrial waste [3]. Recycling of waste electronic and electrical equipment (WEEE) is one of the main causes of soil contamination and especially when performed as informal activity [4,5]. Through several studies, it has been shown that the recycling of WEEE generate the pollutants such as metallic elements, with higher concentration in dusts rather than soils, the consequence is a potential transfer through wind and rain to the surrounding of the recycling site [6,7]. Pradhan reported that in India informal recycling of WEEE is the main cause of soil contamination [8]. The authors found that plant samples collected around a WEEE recycling site located near the Mandoli industrial area were contaminated with Cu (23.07 mg/kg), Zn (78.18 mg/kg), Fe (106.37 mg /kg), Zn (68.48 mg/kg), Pb (0.76 mg/kg), Cd (0.049 mg / kg) [8]. Metals accumulated in soils can therefore pose an environmental problem concerning a possible transfer of the latter to the aquatic environment, and thus include them in the food chain [9].

The contamination of foodstuffs, more specifically vegetables, by metallic elements has become a public problem and a major concern for human health. In order to avoid potential dangers associated with food consumption, it is important to monitor and control the presence of metals in the food chain from soil to food [1]. Most metals are essential for living organisms (animals, plants and microorganisms), these are usually reported as "trace elements". Trace elements are involved in enzymatic activities and immunological reactions [10]. Deficiency in some trace elements, such as Zn, Cr(III), Fe is still an important health problem, especially in developing countries. Other metals have no metabolic use, such as Hg, Pb, Cd and As, these can be toxic even at very low concentrations. Whether or not they are essential for life, once absorbed at higher concentrations, metals can put the development and growth of plants and organisms at risk [11]. The prediction of metal uptake by plants is extremely important to understand the effects of contaminated soil. Accessing to the levels of trace elements in agricultural soils leads to prevent the potential risk to human health. Indeed, plants cultivated in contaminated soils can accumulate toxic metals at high concentrations causing serious risks to human health when consuming crops.

The total concentration of metals in soils does not always supply the fraction available to organisms and / or plants [12] and does not give much information on their mobility and toxicity. However, the chemical state in which metals are bound to soils (easily exchangeable ions, metal carbonates, oxides, sulfides, organometallic compounds, metal in crystal lattices of minerals ...) should be known to better evaluate their mobility, bio-availability and toxicity [13]. Depending on the evolution of physicochemical conditions, they can change forms, move to other components of the soil and thus become more available to plants [14]. Speciation refers to the identification and determination of the different species of an element that occur in a material [14].

In order to determine the speciation and the level of mobile and bioavailable metallic elements in the soil, various chemical extraction have been developed. Selective extractants are employed to isolate the metallic elements associated with the various phases of the soil. Single extraction (use of a single reagent per test) and sequential extractions (use of multiple reagents submitted on the same sample) are chemical analysis methods that are more widely used to assess the bioavailability of metals. Sequential extractions are well described and often applied for assessing metal mobility in sediments origins, sewage sludge amended soils, different contaminated soils and waste materials [15]. Among the sequential extraction procedures proposed to study the distribution of heavy metals in soil and sediments, the five and six-step extraction schemes developed, respectively, by Tessier [14] and Kersten [16] have been the most commonly used [17,18]. Many authors have used these protocols by varying either the number of steps or the extraction reagents. Wang *et al* identified the fractions of Cd, Cu, Pb, Fe and Mn, in marine sediments in northeast China, by the sequential modified Tessier extraction method [19]. There are several other studies reporting the development of sequential extraction schemes to determine the fractionation of metals in soils [20]. Indeed, due to the diversity of sequential extraction procedures, the results often obtained are not easily comparable [21].

In this context, a group of experts, working under the auspices of the Commission of the European Communities; Community Bureau of Reference (now Standards, Measurement and Testing Program) has launched a program to harmonize various sequential extraction protocols, thus allowing the development of a three-step sequential extraction scheme [12]. This approach provides information regarding the heavy metals availability, especially that they are divided into acid-soluble fractions which corresponds to the exchangeable and carbonate-bound fraction, reducible fraction (bound to oxides), and oxidizable fraction (bound to organic matter) [22]. The exchangeable fraction represents the most labile part of the metallic elements in soils [11], and potentially more toxic to the environment [23]. The reducible fraction represents metal bond to iron and manganese oxides/hydroxides. These oxides/hydroxides are excellent to associate with some trace metals that may be weathered but also transformed from the initial source. The oxidizable fraction represents

metal bonded to various forms of organic complexes and sulfides. These organic matters can lead to release soluble metals after oxidization in water.

The BCR sequential extraction procedure is based on the use of a series of more or less selective reagents. These reagents are chosen to identify the main binding sites and phase associations of trace elements in soils and helps in understanding geochemical processes to predict potential remobilization of the elements and their fate in the environment and the risks induced [11]. This procedure has been modified and used by Bakircioglu *et al* [24] to study metallic trace elements in agricultural soils and their transfer to wheat plants, in Edirne, Turkey and to estimate the availability of heavy metals to vegetables. They studied the exchangeable, reducible and oxidizable fractions of Cd, Pb, Ni, Cu and Zn in the samples using, respectively, solutions of CH₃COOH, H₂NOH.HCl and CH₃COONH₄.

In Senegal, one of the most important agricultural areas is located in the direct vicinity of the Mbeubeuss landfill. In this landfill, the recycling of solid waste, in particular WEEE, is a common practice. WEEE, which is recycled by open incineration and dismantling in Mbeubeuss, generates pollutants which can be dispersed in the environment and contaminate the market garden soil near the landfill. This study aims to assess the level of metallic contamination of the soil in the market garden production area linked to the recycling of WEEE near the Mbeubeuss landfill, as well as the risk of these metals being transferred to the crops grown there. In this study, the potential health risk, through the consumption of vegetables grown in the market gardening zone of Mbeubeuss, was also undertaken. No such work has yet been done in this area. Thus, the basis of our work consisted of sequential BCR extraction in three steps and the determination of the content of metallic elements in vegetables grown alongside of Mbeubeuss.

2. Experimental

2.1. Soils and vegetables

The soil samples studied in this article come from four market gardening sites in the “Niayes” zone in Malika, in the Dakar region in Senegal Fig.1. These sites are located in the direct vicinity of the Mbeubeuss landfill, a wild dump that receives almost all domestic waste from the 3 million inhabitants from the area, but also e-wastes and several e-wastes recycling sites.

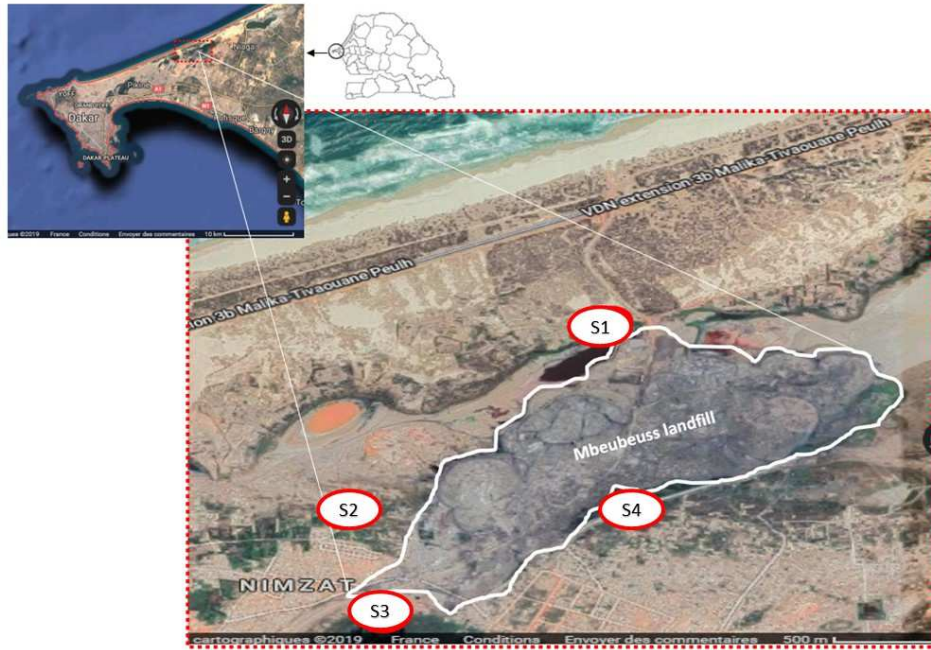


Fig. 1. Geographic location of the study area

Soil and vegetable samples were collected at four sites (S1, S2, S3 and S4) in the “Niayes” area of the municipality of Malika, in the immediate vicinity of the Mbeubeuss landfill. The soils from S1 and S2 are located between the ocean and the Mbeubeuss landfill, while soils from S3 and S4 are between the lake (Malika) and the Dakar city. Site 1 (S1: 14°48'N 17°18'W) and site 2 (S2 14°47'N 17°19'W) are on one side of the landfill, site 3 (S3 14°47'N 17°19'W) and site 4 (S4 14°47'N 17°18'W) on the other side Fig. 1. These four sites are part of the most important vegetable production area in the country. The soil samples were taken at the level of cultivated plots, collected in polystyrene flasks, at random on the H0 surface (< 5 cm). The samples were transported to the laboratory and stored at 4 °C before being analyzed. A total of twenty samples were collected (i.e. five for each location). Along with soil, vegetables were collected from producers working on the different sites. The different items were green onion from S1 beetroot and zucchini from S2, green pepper, salad, leek, cassava and cassava leaves from S3, green onion, tomato and cassava from S4. Vegetables were dried (105°C) and ground before applying the digestion procedure.

2.2. Physical characterization

According to the protocol described by Al Majou [25] and derived from the so called “pipette method”, grain-size analysis was performed from the samples collected from S1, S2, S3 and S4 areas to allow separation of the fractions: clay (< 2 μm) , loam (2-50 μm) and sand (50-200 μm). Results

expressed as percentage of the total mass are presented on table 1. The pH of the soil was measured using color-fixed test strips (MACHEREY-NAGEL), to do this, 2g of each sample was mixed with 5ml of de-ionized water.

Table 1: Physico-chemical characterization of soils. Uncertainty are expressed as and presented as min-max values for grain size. In the case of oxides and cations standard deviation σ is calculated from $n=5$ replicates of the determination.

	S1	S2	S3	S4
Al₂O₃ (%)	3.6 (0.3)	4.2 (0.4)	7.9 (0.6)	5,9 (0.6)
Fe₂O₃ (%)	2.8 (0.4)	1.8 (0.2)	3.6 (0.4)	2.4 (0.1)
Ca²⁺ (meq/kg)	481	360	410	360
K⁺ (meq/kg)	41	43	57	71
Mg²⁺ (meq/kg)	141	110	110	75
Na⁺ (meq/kg)	25	10	11	33
Loam (Average %)	1.5	1.8	2.7	2.8
Min-Max (%)	0-5	0-4	0-12	0 -13
Clay (Average %)	2.8	2.6	2.0	2.1
Min-Max (%)	0-15	0-14	0-18	0-17
Sand (Average %)	95	92	90	88
Min-Max (%)	81-100	80-100	65-98.5	62-95
OM (%)	0.8 (0.2)	1.1 (0.3)	1.0 (0.1)	1.7 (0.3)
pH	7.0	7.0	6.5	7.0

To obtain the organic matter content (OM %), an aliquot of each soil sample (3.5 g) was weighed in crucibles and first dried at 105 °C for 72 hours until a constant weigh was reached to remove moisture [26]. The loss on ignition method was employed to determine the organic-matter percentage; it is based on gravimetric weight change associated with high temperature oxidation of organic matter. The samples were ignited in a muffle furnace for 2 hours at 450 °C.

Iron and Aluminium were analysed by ICP-MS after sample digestion as described in 2.3, to obtain oxides level. To obtain the exchangeable bases Ca²⁺, Mg²⁺, K⁺ and Na⁺, the soil was leached using a 1 M ammonium ethanoate solution at pH7 and diluted samples were measured by ICP-MS.

All the reagents used were of analytical grade. Calibration solutions for metals were prepared by serial dilution of 1000 mg/L SPEX (SigmaAldrich France) standard solutions of the appropriate elements and diluted with ultrapure 18.2 M Ω cm resistivity water (Elga Labwater, UK). A Certified reference materials were used to verify the accuracy of the results for soil analysis (NIST 142 sandy Soil) and for plant analysis (CRM402 White clover). Suprapure nitric acid, hydrogen peroxide (Merck, Germany), and analytical grade acetic acid, hydroxylamine hydrochloride and ammonium acetate (Sigma Aldrich,

France) were used for extraction and wet digestion. Soil samples (70 mg) and vegetables (200 mg) were digested using nitric acid. For the certified materials, the average trueness of digestion procedure was 90% for CRM 402 and 95% for NIST 142.

2.3. Sequential extraction procedure

To discriminate the different fractions of the metallic elements (Cr, Cu, Mn, Pb, Sb, Sr and Zn), the soil samples were subjected to a three-step BCR sequential extraction, as described in Table 2. After each step of the extraction, the supernatant and the residue were separated by centrifugation (6000 rp/min) for 10 minutes. Supernatant was analyzed while the residue followed the next extraction step. For each soil, the BCR procedure was repeated in three replicates. For each sampling site the five soil samples were evaluated, which makes a total of twenty samples. For the measurements suitable blank for all the reagents were measured.

Table 2 Summary of experimental conditions of BCR sequential extraction

Step	Fractions	Extraction procedure
1	Exchangeable: water and acid soluble	10 ml of ethanoic acid (0.11 M CH ₃ COOH) added to 0.25 g of dry soil
2	Reducible: bound to Fe-Mn hydroxides	To the residue from step 1, 10 ml of hydroxylamine hydrochloride (NH ₂ OH-HCl; 0.1 M) and nitric acid (HNO ₃ ; 0.15 M)
3	Oxidizable: bound to organic matter and sulfides.	To the residue from step 2, 5 ml of hydrogen peroxide (H ₂ O ₂ ; 8.8 M) for 1 h at 25 °C; then 2 ml were added at 85 °C, 9 ml of solution (CH ₃ COONH ₄ ; 1 M).

2.4. Instrumentation

An ICP-MS instrument (7900, Agilent, United states) with a micro-mist nebulizer and Scott double pass spray chamber was used for the determination of elements in acid digest of soils. An ICP-HRMS (ElementXR, Thermo scientific, United states) was employed for the determination of the elements in each of the fractions obtained from the BCR sequential extraction procedure. Operating conditions for the 7900 ICP-MS instrument were: forward power 1.50 kW, plasma gas flow rate 12 L min⁻¹, nebulizer gas flow rate 1.04 L min⁻¹ and 400µL/min solution uptake. The dwell time per isotope was 3 ms and 100 sweeps were used. Operating conditions for the ElementXR ICP-MS instrument were: forward power 1.20 kW, plasma gas flow rate 12 L min⁻¹, nebulizer gas flow rate 1.20 L min⁻¹ and 200µL/min solution uptake. The dwell time per isotope was 20 ms and 100 sweeps were used. An Ultrawave (Milestone, Italy) microwave digestion system was used for wet acid digestion of the soils and vegetables samples. For isotopic ratio measurement, the standard bracketing method was employed

using NIST SRM 981 lead isotopic standard. Isotopic measurements are adapted from reference [27,28] and previously described on another element.

Most calculations and statistical data treatments (correlation tests, hierarchical cluster classification) were performed using Excel and Xlstat (Addinsoft (2022). XLSTAT statistical and data analysis solution. Paris, France). For quantitative element analysis, concentrations are provided by the ICP-MS instrument's software using an appropriate calibration.

3. Results & discussion

3.1 Physical characterization

The results of the analysis of the physico-chemical characteristics of market garden soils studied near Mbeubeuss are presented in Table 3. Organic matter content of the soils are different from one site to another, the sites are characterized by contents between 0.8% (S2) and 1.7% (S4). A value below 14% is considered as very low in organic matter, which is a main drawback for an agricultural soil. The results of the water pH of the soil show values which are rather neutral (at 7) in S1, S2 and S4. In addition, on the S3 soil samples, the indicated soil water pH is slightly acidic and is 6.5. This is in agreement with the high sand composition of the soils (table 1). As seen from table 1, the soil has a high concentration of iron oxides (1.8-3.6%) and exchangeable cations. The study of similar soils located in the area, with high sand and high exchangeable cations has already been reported [29]. Even if the soil is bearing low OM % and high sand levels, it should be mentioned that common agricultural practice in the region allows three to four campaigns during year, as a consequence, a regular fertilizer addition to the soils as poultry manure is made to improve soil quality. The composition and texture of agricultural soils is therefore modified both due to agricultural practices but also due to the potential contaminations brought by the dumpsite.

3.2 Speciation using BCR 3-steps sequential extraction

The objective is to evaluate the fraction of heavy metals potentially available, it is generally recognized that the first three fractions are more available than the residual fraction [17]. They are weakly bound to soils and can easily equilibrate in phase aqueous and become more bioavailable [30]. The element speciation in the three fractions of the soil samples at the different sites is displayed in Table 3. Five samples of each of the four sites are evaluated, the extraction procedure is repeated three times on each soil. The total concentration measured after digestion of soils is also presented in table 2, the residue is not presented. To discuss the element content of this residue, a verification was

made on a few samples. As the measurement was in good agreement with the calculated value (ratio measured/calculated between 1.2 and 0.85), the residue is not presented for the sake of clarity.

The agricultural soils sites are sampled in five locations distant of 10 to 50 meters. Even if ICP-MS measurement precision is less than one percent, an important dispersion of metal concentration was observed within a single site (fig. SP1). This uncertainty is depending on the element and the sampling site rather than the concentration. The total concentration of Zn, Mn and Pb are the most scattered, especially on sites S3 and S4. So for the fraction concentrations, the uncertainty is calculated from an average standard deviation, obtained from the three extraction replicates, for Cu, Cr, Sr, Mn, Zn and Pb. Antimony is only detected in a few samples and therefore, no uncertainty is presented.

An overview of the results shows that the major part of the elements is associated to the residual fraction, i.e. the less available fraction [31]. Figure 2 illustrates the distribution of elements in fractions. Metals are separated in groups according to partial similarity in their distribution between the four fractions.

Table 3 Concentrations and uncertainty (mg/kg) of metals between various fractions determined by the BCR extraction test. The residual fraction was determined from the difference between the total content of the metal and the sum of the metal contents in the steps 1–3 of the BCR test. (σ , $n=3$). Guidance values are taken from a [32],and b [33].

		Sb*	Pb	Sr	Cr	Cu	Mn	Zn
Guidance values		2 a	70 b	-	64 b	63 b	2000 a	250 b
S1	Exchangeable	<LOD	0.20 (0.05)	15 (1)	0.16 (0.03)	0.21 (0.02)	5.9 (0.3)	4.9 (0.5)
	Reducible	0.2	0.60 (0.06)	2.0 (0.3)	0.37 (0.03)	0.48 (0.04)	2.8 (0.3)	3.8 (0.5)
	Oxidisable	0.3	1.0 (0.2)	1.7 (0.4)	1.2 (1)	1.2 (0.1)	0.94 (0.08)	5.1 (0.6)
	Total (mg/kg)	0.5*	3.2	50.5	6.0	4.4	31.8	48.5
S2	Exchangeable	<LOD	0.13 (0.01)	5.3 (0.3)	0.2 (0.02)	0.29 (0.02)	23.9 (2)	8.8 (0.9)
	Reducible	0.2	0.8 (0.1)	1.3 (0.1)	0.33 (13)	0.95 (0.,6)	5.9 (0.6)	3.8 (0.9)
	Oxidisable	0.1	1.0 (0.1)	1.46 (0.3)	1.48 (0.2)	1.6 (0.2)	1.1 (0.2)	7.6 (0.8)
	Total (mg/kg)	0.2*	4.0	28.1	4.8	4.7	49.0	47.0
S3	Exchangeable	<LOD	0.22 (0.2)	10.7 (0.5)	0.15 (0.02)	0.35 (0.04)	47.3 (0.4)	21.0 (2)
	Reducible	0.3	2.8 (0.3)	4.0 (0.3)	0.51 (0.05)	1.3 (0.1)	65.7 (3)	16.1 (1)
	Oxidisable	<LOD	1.0 (0.05)	1.1 (0.2)	2.4 (0.3)	1.9 (0.2)	2.5 (0.4)	8.0 (0.9)
	Total (mg/kg)	0.3*	8.2	22.8	7.1	9.0	175.5	73.1
S4	Exchangeable	<LOD	0.5 (0.08)	12.0 (0.2)	0.6 (0.1)	0.32 (0.05)	42.0 (5)	33.5 (3)
	Reducible	<LOD	7.5 (0.1)	5.0 (0.3)	0.5 (0.1)	1.7 (0.2)	49.8 (6)	41.2 (3)
	Oxidisable	0.1	3.3 (0.2)	0.55 (0.05)	0.8 (0.2)	3.0 (0.2)	2.9 (0.2)	12.4 (1.5)
	Total (mg/kg)	0.3*	13.3	33.8	8.3	8.2	119.0	94.7

**samples containing Sb<LOD are excluded from average calculation*



Fig. 2. Percentage distribution of metals between various fractions determined by the BCR extraction test in the soils from the four sampling sites.

Copper, Lead and Chromium

The total concentration of Cu, Pb and Cr are within acceptable limits for guidance values reported from soils [32,33]. Copper is between 4.4 and 9 mg/kg with a maximum total value at 9.2 and 17.2 in two of the samples collected from the S2 and S1 areas, respectively. The maximum guidance value of 60 mg/kg for an agricultural land is not reached indicating a non-toxic soil for crops. The average total value is nevertheless increased by a factor of two between the area close to the ocean (lower total values) and the area close to the dumpsite. The lead concentrations and behavior is similar to that obtained for copper. The lead concentrations are lower in S1 and S2 (3.2 to 4.0 mg/kg) and twice higher for S4 and S3 areas (8.2 and 13.3 mg/kg respectively). The boxplot from figure SP1 also exhibits the highest dispersion of lead values reported from the measurements in S3 and S4 areas, two aliquots of S4 area reaching 21 and 22 mg (Pb) /kg. The wind transport of small particles containing lead could explain this lack of homogeneous composition, the value are lower than the CCM guidance value for agricultural soils i.e. 70 mg/kg. For chromium the values are between 4.8 and 8.3 mg/kg, it is below the total recommended value for chromium: 64 mg/kg. If the chromium was only occurring as the more toxic hexavalent Cr VI, the values could be considered close to some of the published guidance values (10 mg/kg-from [34]), but Cr in soils occurs mainly as the essential form CrIII. The total concentrations are dispersed and similar on all sites, suggesting a water leaching from the dumpsite or a different origin (fertilizers).

The distribution patterns of Cu, Pb and Cr at four sampling sites were alike with high residual and low exchangeable fractions. The residual fraction represents a part of the metal probably strongly bounded to the mineral silicate or alumino-silicate of the sandy soils. This strong retention of metals to the soil is reported for polluted soils [35]. For the three metals it represents from 39 to 61% of the element concentration for copper, 60 to 77% for chromium and 44 to 53% for lead in S1, S2 and S3 and 15% in S4. The residual fraction is poorly available and especially less available for plants. For Cu, Cr and Pb, the exchangeable fraction is less than 10%. This fraction is generally the most toxic one as it could be easily mobilized through water leaching. For these elements, the agricultural soils exhibit low concentrations in the exchangeable fraction ranging from 0.13 to 0.5 mg/kg for lead, 0.15 to 0.6 mg/kg for chromium and 0.21 to 0.35 mg/kg for copper. The fraction (%) linked to Fe-Mn oxides is lower for Cr and Cu in comparison with Pb, ranging from 0.33 to 0.51 mg/kg for chromium while it is from 0.48 to 1.3 mg/kg for copper to 0.6 to 7.5 mg/kg of the total element for lead. The percentage of Cr, Cu, Pb bounded to organic matter represents 20 to 36% of the total concentration of each element with the exception of Cr in S4 (9%) and Pb in S3 (12%). For Cu, Cr and Pb this percentage is significantly higher than for the three other elements. Formation of organic complexes or association with humic substances of the organic phase is often reported for copper [30].

Strontium, Manganese and Zinc

In the case of Zn, Sr and Mn, the total concentrations are ranging between 22.8 to 50.8 mg/kg for Sr, 31.8 to 175.5 mg/kg for Mn and 47 to 94.7 mg/kg for Zn. The values are low in comparison with the guidance values expressed in table 3, 2000 mg/kg for Mn and 250 mg/kg for zinc. No guidance value is reported for Sr as this element is very abundant in rocks and soils and significantly less toxic to humans (Rfd (Sr) = 0.6 mg/kg/day in comparison with Rfd (Zn) = 0.3 mg/kg/day and Rfd (Mn) = 0.14 mg/kg/day). In some soils collected from the S3 and S4 area the concentration of Mn and Zn could be over 200 mg/kg, with a high dispersion of the values as presented from fig SP1. As Zn and Mn were main pollutants found in the Mbeubeuss dumpsite soils (ref), the occurrence of these elements in the agricultural field is not surprising. Their uptake and soil speciation is therefore important to establish.

In the case of Zn, Sr and Mn, the residual part is still mainly present in the four sites (varying between 31% to over 60% for Sr, 34 % to 70% for Mn and 38 to 72 % for Zn) but the exchangeable part is more present with 10 % to 47% for the three elements. The exchangeable fraction is the most easily transferred fraction, weakly sorbed Mn and Zn retained on soil surface by relatively weak electrostatic interactions may be released by ion-exchange processes [14]. The result indicates that considerable amount of Sr, Mn and Zn may be released into environment if conditions become more acidic [9]. The concentration involved in this fraction are from 5.3 mg/kg to 15.0 mg/kg for Sr, 5.9 mg/kg to 47.3 mg/kg for Mn and 4.9 to 33.5 mg/kg for Zn. The high values observed for both Mn and Zn are consistent with the vicinity of the Mbeubeuss landfill which was found rich in these elements [36]. The landfill gathers all domestic wastes from the Dakar area with a dangerous mixture of e-waste, automobile lead-acid batteries, alkaline batteries and other conventional domestic wastes. Elements Mn and Zn are also found at significant concentrations in the reducible fractions from S3 and S4, it results from the fixation of the element Fe-Mn oxides. This conclusion is consistent with the more elevated concentration of manganese detected in soils from sites 3 and 4 (table 3). The iron level (not presented) is also two times higher in soils from sites S3 and S4 in comparison with soils from S1 and S2. The fraction bounded to organic matter is moderate for Sr and Mn (i.e. from 1 to 5% of the total), its increases to 6 to 16% for Zinc. With the elevated total concentration of zinc it may represent up to 12.4 mg/kg in the S4 soil. Due to the activity of micro-organisms linked to organic matter, the availability of this fraction to plant is not negligible.

Antimony

Antimony is only present in a few sample, it appears randomly distributed in the samples. According to our results it was only present in less than 50% of the soils aliquots (Table3; fig. SP2). The average concentration is only taking into account the samples containing the element. The detected

concentration are 0 to 0.5 mg/kg which is lower than the reported guidance value [33]. Found in plastics as a flame retardant, antimony can contaminate soils by dust deposit, this phenomenon may explain the dispersed values obtained. In our case the level remains below mg/kg, from 0.2 to 0.5 mg/kg. Its speciation depends on the site, it was mainly linked to the residual fraction in the soils samples in S4 and is predominant in the oxidizable fraction in S1 with a low 0.3 mg / kg level. The Sb is never found into the exchangeable fraction. The strong binding of Sb in the residual S4 fraction as well as the very low concentration found indicate that the metal is poorly available.

The agricultural soils are located in an environment very close to the Mbeubeuss landfill, exposed to weathering events and this area, together with fields located in the northern part of figure 1 are producing more than 80% of the vegetables consumed by the Dakar population. Therefore it is essential to estimate the fate and origin of metallic pollutants.

Origin and mobility of metals

From the physico-chemical properties of the soil presented in table 1, a correlation matrix is built to evaluate the possible association of metal content (Cr, Cu, Mn, Zn, Pb and Sr) with the pH, OM %, clay % and the sum of the cation concentration. The results are presented as a pearson correlation matrix on table 4. An r coefficient over 0.6 indicates a significant correlation between parameters.

Table 4 Correlation matrix (pearson), colored from -1(blue) to +1 (red).

	Pb	Sr	Cr	Cu	Mn	Zn
pH	0.03	0.01	-0.13	-0.12	-0.37	0.18
OM (%)	0.51	0.06	0.57	0.62	0.52	0.83
Clay (%)	-0.83	0.71	-0.76	-0.87	-0.86	-0.85
Pb		-0.07	0.60	0.79	0.43	0.78
Sr			0.52	0.22	0.09	0.12
Cr				0.90	0.74	0.68
Cu					0.77	0.75
Mn						0.55
Al ₂ O ₃ (%)	0.62	-0.72	0.62	0.85	0.81	0.66
Fe ₂ O ₃ (%)	0.17	-0.10	0.47	0.60	0.67	0.28
Ca ²⁺	-0.50	0.74	-0.11	-0.34	-0.30	-0.41
K ⁺	0.80	-0.39	0.79	0.78	0.73	0.80
Mg ²⁺	-0.81	0.55	-0.60	-0.62	-0.49	-0.81
Na ⁺	0.54	0.58	0.66	0.11	-0.10	0.56

The data, exhibits no correlation between acidity and the metal concentrations. In the limited pH range obtained, the pH of the soils from the different sites does not seem to influence the mobility and bioavailability of metallic elements in the soils. The organic matter content is positively correlated to Zn and Cu concentrations and with a lower coefficient to Cr, the common origin of organic matter and these elements could explain the correlation. The values of organic matter are extremely low ranging from 0.2 to 4.1 % with most important values obtained from soils in the S4 site. As mentioned above, copper is found linked to the organic matter fraction in the sequential extraction. High amount of metals coming from manures employed in the agricultural fields [37] could be responsible for this phenomenon. The role of organic matter is complex, according to our results, it is either the origin of some metals or it can also promote their incorporation to soil. Elements are not correlated with clay amount, with the exception of Sr. As seen previously from table 1, the soil is a sandy soil and the agricultural fields are all close to the Atlantic ocean so that the clay amount is very low and the cation level high. Cu and Mn strongly correlates with the aluminium and iron oxides, while Sr is not. Ca and Mg cations are negatively correlated with metals, opposite to Na⁺ and K⁺, the metals investigated are not easily leached from the soils, as we could see from results in the BCR extraction experiment. The positive correlation between Cu and Cr is high, with a coefficient of 0.9. The metals Cu and Zn also correlates with Pb, while Cr and Cu both correlates with Mn and Zn indicating a possible similar anthropic origin of these metals.

Analysis of vegetables

In order to study the transfer from soils to vegetables, the total concentration of the elements Cr, Mn, Cu, Zn, Sr, Sb and Pb in the vegetables studied (mg/kg dry weight) is presented in table 5.

Table 5 Content of metallic elements (mg/kg of dry weight) in vegetables grown in the Mbeubeuss market garden area. Uncertainties, n=5 with confidence level of 95% are in parentheses.

		Cr	Mn	Cu	Zn	Sr	Sb	Pb
Reference limits *		2.3		40	20			0.3
S1	Green onion	3.5 (0.05)	39 (1)	9.4 (0.1)	52 (5)	44.0 (4)	<LOD	0.9 (0.3)
S2	Beetroot	2.6 (0.4)	12 (3)	9.9 (0.8)	45.8 (0.8)	14.7 (4)	<LOD	0.9 (0.3)
S2	Zucchini	2.2 (0.1)	13.3 (0.6)	15.7 (0.1)	40 (2)	26.6 (0.6)	<LOD	0.5 (0.1)
S3	Green pepper	2.5 (0.1)	22.7 (1.3)	5.9 (0.9)	30 (2)	9.6 (0.7)	<LOD	0.9 (0.3)
S3	Leek	2.9 (0.6)	36 (7)	9.4 (0.9)	29 (4)	30 (5)	0.1	1.2 (0.2)
S3	Salad	2.9 (0.9)	48 (9)	8 (2)	36 (4)	27 (9)	0.2	1.8 (0.3)
S3	Casava leaf	4.5 (0.5)	54 (2)	11.3 (0.9)	30 (4)	65.7 (0.1)	0.4	3.4 (0.1)
S3	Casava	2.3 (0.4)	5.4 (0.9)	3.0 (0.4)	35.7 (0.8)	20.8 (2)	0.1	0.6 (0.1)
S4	Casava	2.8 (0.4)	23 (3)	3.8 (0.4)	32.5 (0.8)	24.7 (2)	0.2	1.7 (0.1)
S4	Tomato	3.3 (0.9)	10 (4)	11 (2)	42 (4)	8 (4)	0.1	0.6 (0.1)
S4	Green onion	3.1 (0.05)	39 (1)	7.7 (0.1)	45.7 (4)	53.3 (4)	<LD	1.1 (0.2)

* limits reported from FAO WHO [38] and ref [2]

The content of the elements studied in plant species cultivated in S1, S2, S3 and S4 was variable from one vegetable to another. The levels of Cr, Zn and Pb found in vegetables were above the maximum limits recommended by FAO / WHO [38], 2011 and the Chinese national food safety standard [2], with the exception of Cr in zucchini at S2 and in cassava at S3. The highest concentrations were found in cassava leaves in S3 for Cr (4.4 mg/kg) and Pb (3.4 mg/kg) and in green onion in S1 for Zn (52.0 mg/kg). Regarding Cu, the concentrations found in plant species are below the maximum limit (40 mg/kg) with the highest concentration found in zucchini from S2 (15.3 mg/kg). For Elements with no guidance values, the concentrations of Mn, Sr and Sb found in vegetables were varying from 5.2 to 53.2 mg/kg; 11.8 to 50.6 mg/kg and up to 0.4 mg/kg, respectively. As observed for soils, Sb occurs randomly in some vegetables. Contamination due to specific particles originating from the landfill or other particle source, scarce burning of specific materials and especially plastics could explain this sporadic occurrence of the Sb element in plants and soils. The origin of its occasional emission and occurrence remains unclear. These results obtained on the analysis of Cr, Mn, Cu, Zn, Sr, Sb and Pb in vegetables indicate contamination of the latter by Cr, Zn and Pb. This could be attributed to contamination of agricultural soils linked to practices of burning wastes and recycling WEEE in the nearby Mbeubeuss landfill. A recent study [36] in the Mbeubeuss area showed high levels of metallic elements such as zinc, iron and manganese in soil. Like Zn, Mn and Cu are essential elements for human life which occurs naturally in plant species. However, when it exceeds the tolerable limit in living organisms it becomes

toxic. In addition, the results also show the concentrations of metals are greater in leafy plants (cassava leaves, green onion and salad) than in fruit plants (tomato, zucchini and green pepper) and roots (cassava and beetroot). This agrees with the comments of [39] who clarified that the levels of metal accumulation in plant species, leaf, fruit or root are different. A hierarchical clustering analysis performed on the vegetables according to either their cultivation site or their type (i.e. root, fruit or leaf type) showed that the similarity is very well associated to the type of the vegetable rather than with the site of production. The dendrogram (fig.3) shows two clusters each divided into two sub-clusters. The two main leaves on the left represents a cluster made from leafy vegetables while the root type and fruit type vegetables are both located in the right hand side sub-clusters.

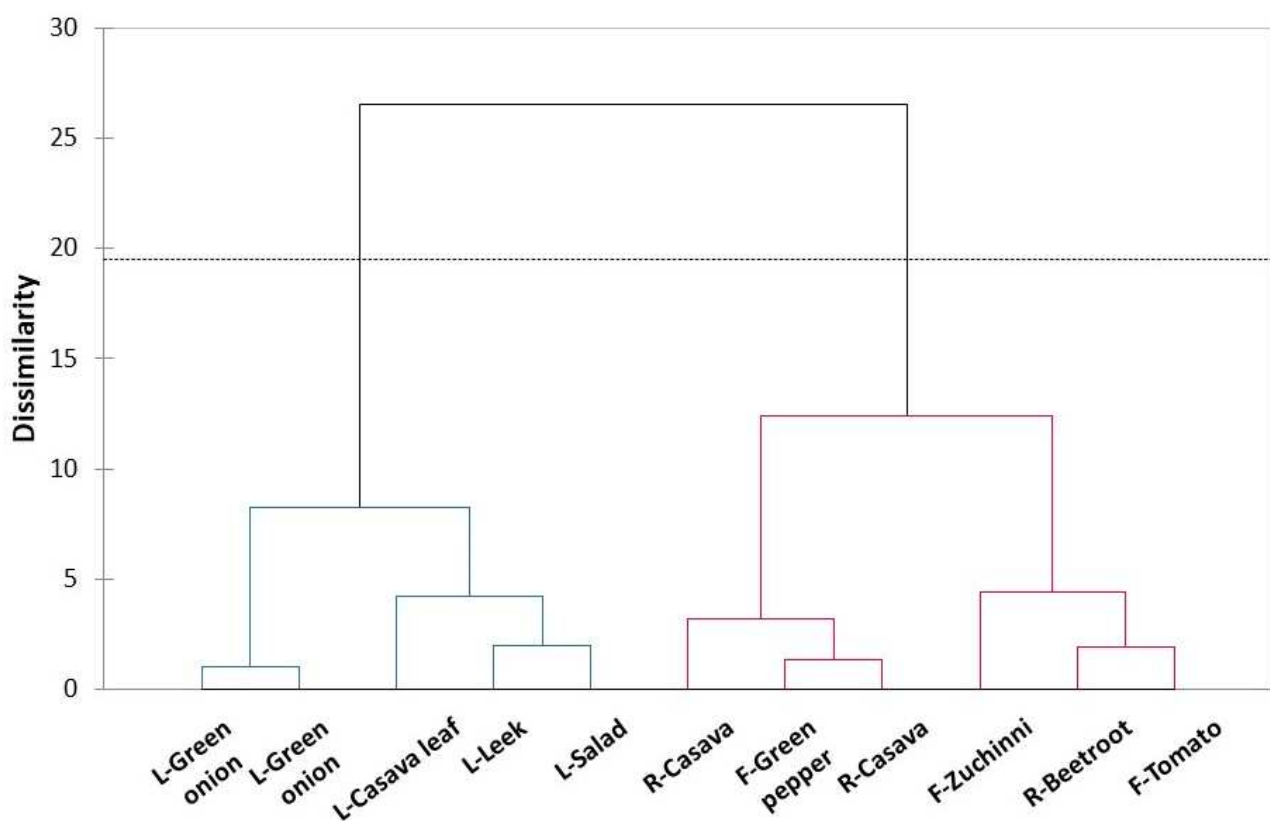


Fig.3. Hierarchical clustering analysis of vegetable according to their level in metals. (L: leaf, F fruit, R: root type vegetable)

Metal transfer from soils to vegetables

The level of lead in the dried vegetables and soils allowed tracing the isotopic fingerprint of the element. The introduction of lead in soils occurs mainly by atmospheric deposition, as the atmosphere is the major initial recipient for this element, it is transported through wind from the lead containing polluted areas, or is released by deposition of urban aerosols containing both particles from various combustion processes including vehicle exhaust particles [40,41]. This contamination could also,

enters surface and groundwater along with the rain, leaching lead present in atmosphere or in landfill soil. Lead isotopic analysis has been introduced as a “finger-printing” technique for lead contamination [42]. As each source of lead may have a specific isotopic composition and the differences in this composition may be used to discriminate between possible sources. From figure 4, the $^{208/206}\text{Pb}$ and $^{206/207}\text{Pb}$ isotopic ratios exhibits three distinct signatures for vegetables and only one group for soils. The first vegetable group is isotopically different from other vegetables and soils. The two green onion samples appeared contaminated with a less radiogenic lead source ($^{206}\text{Pb}/^{207}\text{Pb} = 0.98$). The difference observed with the isotopic ratios measured in soils indicates a different lead source, probably linked to a very local lead source; the cultivation process of onion a specific container ... The second vegetable group: including salad, zucchini, beetroot and green pepper has a lead isotopic signature different from third group (leek, manioc and tomato). The S1, S2, S3 and S4 soils have similar isotopic fingerprint with $^{206/207}\text{Pb}$ values ranging from 1.029 to 1.079. Soils measurements are significantly more dispersed than the measurement uncertainty estimated from the variation of the CRM 981 isotopic standard ratios employed for bracketing (i.e variation range $^{206/207}\text{Pb}$: 1.094 to 1.096). This could mean that the Pb found in the soils has several origins: lead from e-waste recycling activities, lead from gasoline combustion and other combustions. Vegetables of group 2 and 3 are more probably directly contaminated by lead originating from the soils S1, 2, 3 and 4. Due to the higher radiogenic value for group 3 additional contribution of another lead source is also possible.

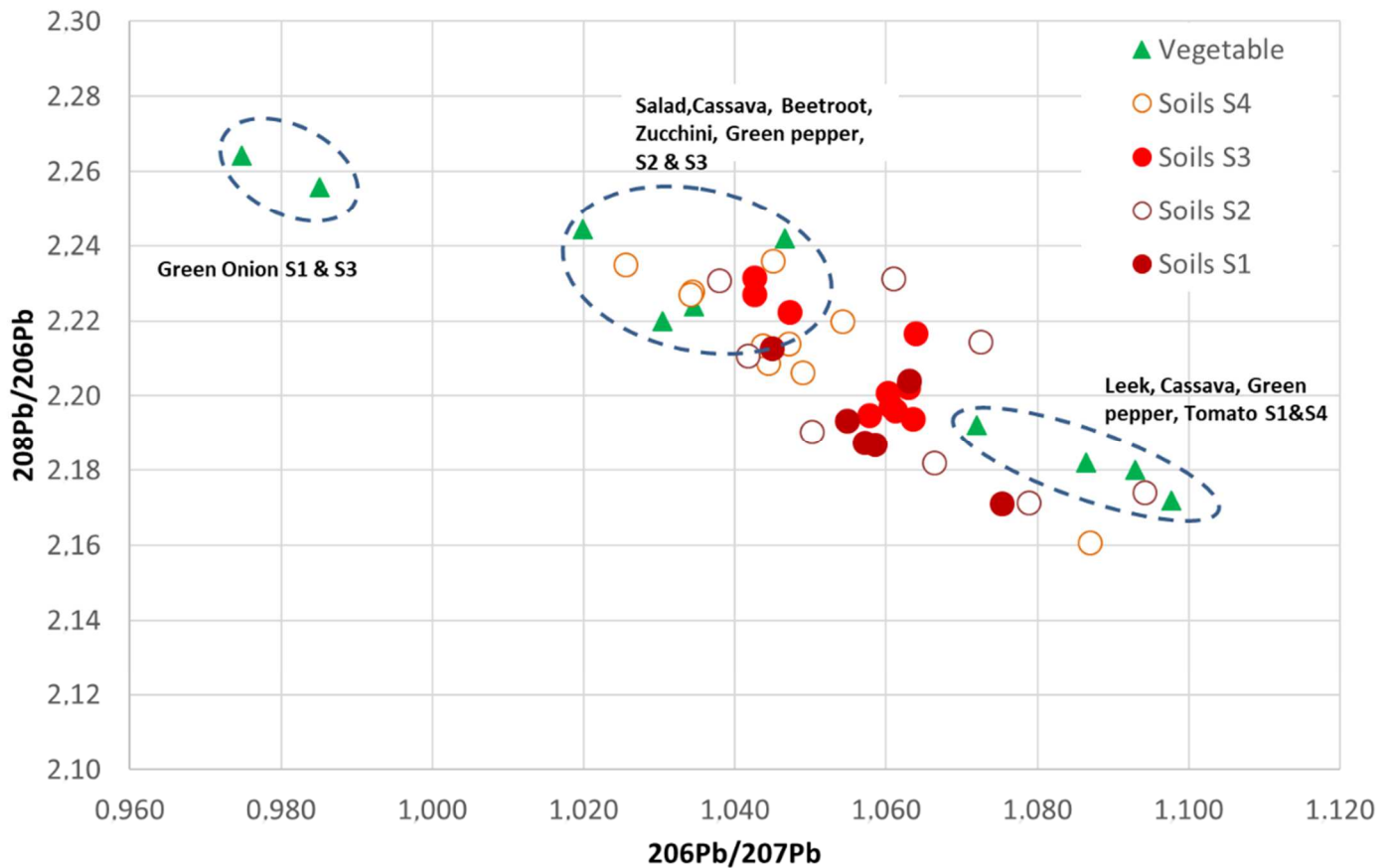


Fig. 4. Lead isotopic ratio measured in soils and vegetables cultivated from the same soils.

The element concentration in agricultural soils and vegetables from the close area of the Mbeubeuss landfill is presented on figure SP1. The boxplots of total element concentration highlights a similar evolution for Cu, Mn, Pb and Zn with higher values from soils in the S3 and S4 sites. These two sites are located on the eastern part of the landfill in the onshore wind direction. According to the situation of the agricultural fields, wind blowing from the Atlantic Ocean, from west to east could transport pollutants from the landfill to S3 and S4, while S1 and S2 would be protected. In addition, we have to take the probable origin of contamination by rain leaching landfill soil into consideration. This is serious hypothesis.

On the contrary Sr is higher in S1 than in the other sites and Cr remains quite constant (i.e. within uncertainty) from S1 to S4. Average concentration of vegetables grown from the different soils is added on figure SP1, no trend is observed according to the site. The accumulation of metal depends more on the vegetable specie rather than on the site where the vegetable is grown. As an example, green onion concentrates similar amount of manganese 38 mg/kg and 39 mg/kg whereas the soils S1 and S4 have very different Mn concentrations; 31 mg/kg and 119 mg/kg, respectively.

Health Risk Assessment (TQH; HI)

In order to estimate the risk to human health, the US-EPA (United States Environmental Protection Agency) has suggested a calculation of the target hazard quotient (THQ) [43]. The THQ is the assessment of the non-carcinogenic risk of individual metals from the consumption of the affected foods (i.e. the sum of the individual THQ_i for vegetables). THQ_i was calculated using the following equation:

$$THQ_i = \frac{DI_i \times C_i \times Ed \times Efr \times Cf}{RfDI \times Bw \times AT} \times 0.001$$

In this equation, DI_i is the average daily intake of the vegetable in g per day; C_i is the concentration of the element (mg/kg dry weight basis), Ed is the duration of exposure (70 years), Efr is the frequency of exposure to the element, Cf is the ratio of conversion of the weight of fresh vegetable to dry weight (which is 0.085). RfDI is the reference oral dose (in mg/kg/day) [44], in the case of chromium, the CrVI value is selected, Rfd = 0.003 mg/kg_{BW}/d. Bw is the body weight of an adult (70 kg) and AT the average exposure time (65 years x 365 days). The Hazard Index (HI) is the sum of the individual target hazard quotients of the items assessed for each vegetable. The value of ΣTHQ takes into account a total weight of 340 g of vegetable distributed according to ref [44] between cassava, cassava leaf, green pepper, tomato green onion, beet zucchini and salad.

Table 6: Values of target risk quotient and hazard Index for metal elements in vegetables

		Cr	Mn	Cu	Zn	Sr	Pb	HI
S1	Green onion	0.34	0.08	0.07	0.05	0.02	0.08	0.64
S2	Beet	0.25	0.02	0.07	0.04	0.01	0.08	0.47
	zucchini	0.21	0.03	0.11	0.04	0.01	0.04	0.44
S3	Leek	0.31	0.08	0.08	0.03	0.02	0.11	0.63
	Cassava	0.22	0.13	0.25	0.40	0.10	0.55	1.65
	Cassava leaf	0.43	0.11	0.08	0.03	0.02	0.28	0.95
	Green pepper	0.24	0.05	0.04	0.03	0.01	0.07	0.44
	Salad	0.28	0.10	0.06	0.03	0.01	0.15	0.63
S4	Cassava	0.27	0.05	0.03	0.03	0.01	0.14	0.53
	Tomato	0.32	0.02	0.08	0.04	0.01	0.05	0.52
	Green onion	0.30	0.08	0.06	0.04	0.02	0.09	0.59
ΣTHQ		2.7	0.62	0.84	0.69	0.21	1.01	

The data in table 6 shows the ΣTHQ of Mn, Cu, Zn and Sr associated with the consumption of plant species (THQ_i) which is <1 (cutoff value). However, the ΣTHQ of the metallic elements Cr and Pb associated with the consumption of all vegetables together gives values of 2.7 and 1.01 in the case of

S3 cassava and 1.45 in the case of cassava from the S4 site, which exceed the limit value 1. The high contributions of these elements are mainly due to their higher toxicity together with the accumulation detected in cassava. Among the vegetables tested in the different sites, the HI of cassava and cassava leaves in S3 is 1.65. The HI value obtained for cassava leaf is also elevated, 0.95, so that consumption of both cassava and its leaves would represent a risk due to significant metal absorption. In the case of Chromium, using the CrVI value, the THQ values are all between 0.21 to 0.34. If the the Cr III Rfd value is considered (0.15 mg/kg/d) the THQ values all drops between 0.004 and 0.008, leading to a global value below 1.

Vegetables are consumed often with fish or rice, which can increase the potential risk associated with metals in food. The fate of metals in foods and especially in vegetables should be more considered as an indicator of population exposure to metal contamination. The surveillance of metals and their speciation in food products should be taken into account.

3 Conclusion

Samples from four agricultural soils located near the largest dumpsite of Senegal were analyzed for their heavy metals (Cu, Cr, Pb, Sr, Mn, Zn, Sb) total concentration and their speciation. Sequential extraction from BCR protocol enabled to realize metals speciation between exchangeable, reducible, oxidizable and residual fractions. Results shown that for Cu, Cr and Pb, exchangeable fraction, the most available and so toxic one, is less than 10%. For Sr, Mn and Zn, however, the exchangeable fraction represented 10 to 47% according to the sites with maximum values reached of 14.9 mg/kg for Sr, 47.5 mg/kg for Mn and 33 mg/kg for Zn. These high values are explained by the direct vicinity of the landfill where high concentrations of Mn and Zn have been found in precedent works. In the reducible fraction, Mn and Zn concentrations were significant, from 16.1 to 65.7 mg/kg, in S3 and S4. In the oxidizable fraction Zn rate in S4 reached 12.9 mg/kg. For Sr, Mn and Zn, the availability was proven. The case of Sb is different as only few samples have given concentration above LOD without exceeding 0.5 mg/kg and it has been found almost exclusively in residual fraction. Antimony availability was so excluded.

To study origin and mobility of metals, a correlation pearson matrix has been done with pH, moisture and organic matter data. Organic matter was positively correlated with Zn and Cu which can be explained probably by their common manure origin. Positive correlations between Cu with Mn, Zn, Pb and Cr with Cu and Zn with Pb seemed to show the possibility of an anthropic origin of these metals.

Concentration of metals in vegetables grown from the studied agricultural soils exhibited contaminations in Zn, Cr and Pb. The contamination was clearly more important for the leafy vegetables no mater of the cultivation site. For most vegetable the lead isotopic ratio was very similar

from the soil's one indicating a common pollution origin probably linked to the practices of burning of domestic wastes and recycling WEEE in the nearby Mbeubeuss landfill. Total hazard indexes calculated from the vegetables pointed out the potential risk linked to the metal accumulation in cassava and cassava leaves grown in the studied agricultural soils. These vegetables should be frequently inspected for their metal content to protect population health.

Acknowledgement: This research was partially funded by "Campus France" Cooperation France/Senegal Fund N° 948481. Mr Mbodji Ph.D thesis was funded by BDI.

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