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Heavy metals concentration levels in selected arable agricultural soils in South Western Nigeria

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The application of micronutrient supplements such as fertilizer, animal manure and sewage sludge in bid to enhance soil productivity and crop yield, poses the risk of heavy metals elevation and nutrients depletion in arable lands. Arable soils were collected from farmlands in use for the cultivation of food produce in selected farming communities in South Western Nigeria. The soils were air-dried, sieved to give <2 mm grain size and digested according to standard methods. The concentrations of Lead (Pb), Cadmium (Cd), Zinc (Zn) and Copper (Cu) were measured using flame atomic absorption spectrophotometer (FAAS). The concentration of Zn ranged from 12.98 to 38.94 µg/g, and was the highest amongst the measured heavy metals. This was followed by Cu, 6.17 to 20.87 µg/g and then Pb, 0.79 to 8.35 µg/g, while the concentration of Cd, 0.26 to 5.75 µg/g was the least. Geo-statistical analysis on the concentrations of the measured heavy metals revealed a significant ($p < 0.05$) spatial correlation (γ) with the soil pH and organic carbon (OC) (Pb, $\gamma = 0.74$; Cd, $\gamma = 0.67$; Zn $\gamma = 0.57$; Cu, $\gamma = 0.52$) and (Cd, $\gamma = 0.79$; Zn $\gamma = 0.59$; Cu $\gamma = 0.51$), respectively. The OC levels predispose soils to the retention of soil heavy metals and micro/macro-nutrients depending on the nature of OC-metal interaction. The concentrations of the heavy metals were below the European Economic Community (EEC) maximum allowable concentrations (MACs) in agricultural soils, except for Cd. About 56% of the farmland soils contained more than 3 mg/kg of Cd, while about 44% were within the 1 to 3 µg/g EEC MAC for Cd in agricultural soils. Although, the concentration levels of the measured heavy metals in the soils do not appear to be of serious concern, the study results provides evidence of gradual accumulation of Cd in farmlands

Key words: Heavy metals, arable agriculture, farmland, micronutrient supplements, concentration.

INTRODUCTION

Supplementing soil with essential minerals, nutrients and organics fluxes in arable agricultural land is on the increase in a bid to enhance soil productivity and crop yield (Drechsel and Gyiele, 1999; Akinrinde, 2006). This is because nutrient regeneration processes such as weathering of soil minerals, nitrogen fixation, and atmospheric deposition in rain and dust are unable to meet up with the rate of nutrient depletion. Although trace elements and heavy metals occur naturally in all agricultural soils (Alloway, 1990; IPNI, 2008), elevated

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levels of Lead (Pb), Arsenic (As), Copper (Cu), Cadmium (Cd) and Zinc (Zn) have been reported (Chang and Page, 2000; Alloway, 2004).

Their sources are suspected to be anthropogenic, such as the application of micronutrient fertilizer, animal manure, sewage sludge, pesticides and atmospheric deposition (IPNI, 2008; Tracy and Baker, 2010; Wuana and Okieimen, 2011).

The use of fertilizers, organic manure and other soil nutrients replenishing additives, in order to improve crop yield especially in nutrient depleted soils is on the increase. Too much of fertilizers, manure or sewage sludge can be problematic, while too little means nutrients are not replenished (Akinrinde, 2006). Studies revealed that heavy elements are slowly accumulating in arable soils, especially in soils with depleting trace minerals receiving soil treatments of fertilizer, manure, etc. (Chang and Page, 2000). An estimated over 75% of garden allotment soils in the United Kingdom were reported to be contaminated with potentially toxic metals (Alloway, 2004). Culbard et al. (1988) reported higher mean concentrations of Pb and Zn as a result of pollution, although garden soils tend to contain higher levels than agricultural soils. There is a delicate margin between safe and harmful levels in view of the potential bioavailability, ecosystem redistribution and bio-magnification in higher heterotroughs (Islam et al., 2007).

The build-up of heavy metals in soils occurs at a slow rate, but on large areas (Keller et al., 2001). There may be spatial variability and geographical heterogeneity in heavy metals levels in arable soils, and this may be small and localized in same soil type within an ecosystem community, or regional involving large scale differences (Du Feng et al., 2008). This, however, depends on the physicochemical properties of the farmland soil ecosystems, and their impact on physical and biological factors including soil origin and structure, topography, vegetation cover and soil exposure, soil microclimate, various land use systems and land management (Lipiec et al., 2004; Ithier-Guzman, 2010).

The accumulation and spatial changes in natural soil concentration characteristics of heavy metals is of environmental and health concern. Soils heavy metal accumulation trends may not be detected on time, because metal contamination may not lead to immediate concern in terms of toxicity, except in the case of hot spot pollution (Keller et al., 2001). High concentrations of heavy metals such as Cu and Zn in soils can result in phyto-toxicity, for example, distortion in photosynthetic electron transport, and impairment of carbohydrate metabolism (Tsonev and Lidon, 2005; Mishra and Dubey, 2005). The ubiquitous character and the increase of heavy-metal which flows through the soil system may also cause serious problems for soil fertility, ground water quality, and food chains (Keller et al., 2001). Excess concentration levels of heavy metals have caused the disruption of natural terrestrial ecosystems (Wei et al., 2007; Yadav et al., 2009).

Qualitative and quantitative information about the concentration of heavy metals and trends of heavy metals fluxes, soil withholding capacity/release potential and the stability of heavy metals within soil mineral aggregates in many farmlands in Africa and especially Nigeria is lacking. Adequate and comprehensive information such as these is essential in order to achieve sustainable use, management of heavy metal regimes and preservation of the soil resources against heavy metal build-up, in the long-term. There is need to generate field and laboratory information on the concentration levels, and soil fluxes of heavy metals in arable agricultural soils. This constitutes an important means of access to precise and quantitative information, essential for environmental evaluation of soil quality, risk of soil pollution and retro-gradation of soil characteristics. This study investigated heavy metal concentration levels and fluxes in selected arable agricultural soils in some farming communities of South Western Nigeria, as a basis for the development of flux balancing tool required for the rational management of heavy metal contamination in agricultural soils.

MATERIALS AND METHODS

Study area

The study sites included selected farmlands at Obbo Ile (KW_1), Eleyin (KW_2), Apata Balla (KW_3), Lafiaji (KW_4) and Karati (KW_5) in Kwara State; Ilora-Iseyin Road (OY_1), Ahoro Dada (OY_2), Idere (OY_3), Eruwa (OY_4) and Alagutan Igbeti-Igboho Road (OY_5) in Oyo State; Kajola (OS_1), Odo Iju (OS_2), Majaroko (OS_3), Ikire (OS_4), Ikirun-Iragbiji Road (OS_5) in Osun State and Odeda (OG_1), Ayetoro (OG_2), Idi Iroko (OG_3), Papalanto (OG_4) and Sagamu (OG_5) in Ogun State (Figure 1). The farmlands are all located within the savannah and the rain forest vegetation of the South Western Nigeria.

Field sampling design and sampling

Field investigations and sampling were carried out between November, 2010 and March, 2011. Farmlands in use for the cultivation of food produce were selected in some farming communities in South Western Nigeria covering Ogun, Osun, Oyo and Kwara States (Figure 1). The sampling points (Table 1) were spatially located across each of the selected farmlands in order to capture variability in spatial environmental setting, in the distribution of heavy metals in soils. The soils were visually inspected and top soil and subsurface soils were collected from each sampling points from five arable farmlands in each of the investigated States. Control soil samples were also collected from bush fallows at locations remotely afar off from the farmland.

Soil sample preparation and laboratory analysis

Soil samples were air-dried at room temperature and the dried samples gently crushed with ceramic mortar and pestle after which they were sieved through 2 mm mesh sieves. The less than 2 mm size fraction was stored and sub sampled for the determination of soil parameters.

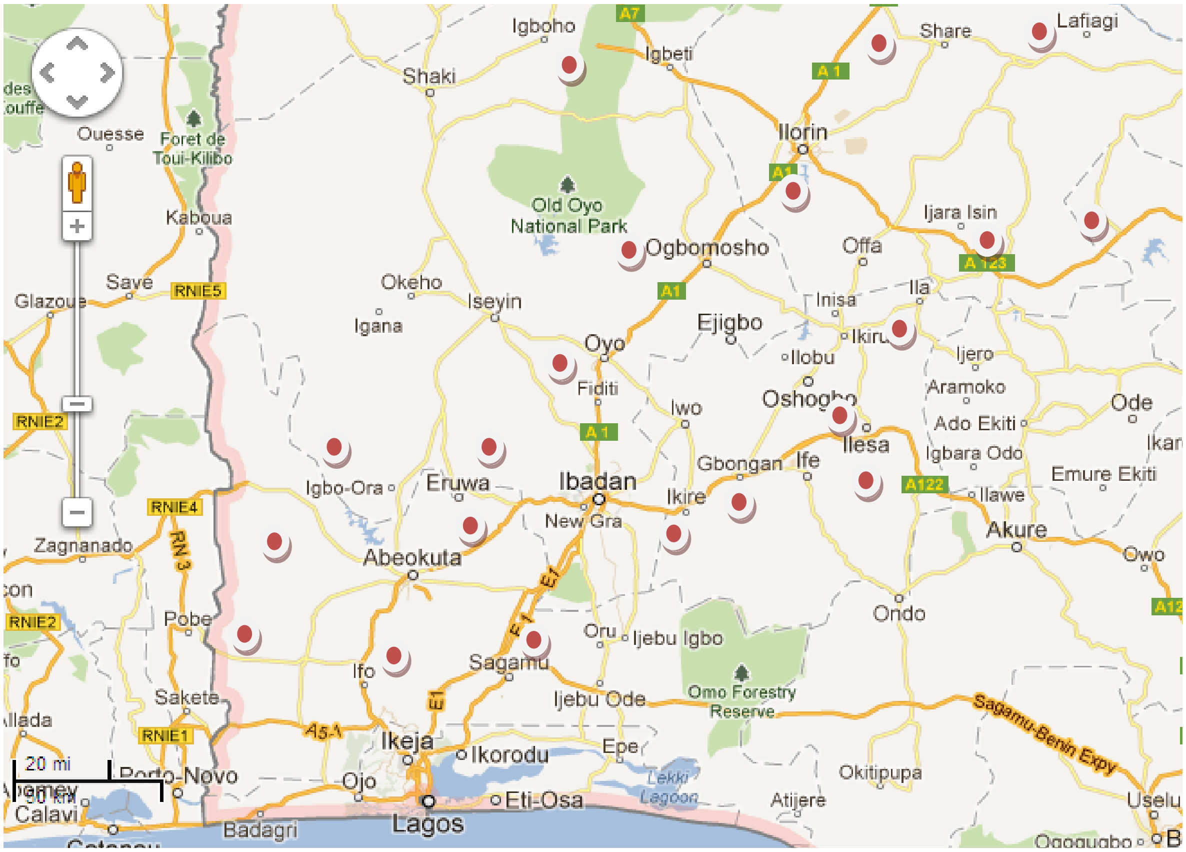

Figure 1. Map of South Western Nigeria showing the farmland study areas in Kwara, Ogun, Osun and Oyo States (Google Maps).

Table 1. Location of selected agricultural farmlands sampling station in some farming communities in Osun, Oyo, Ogun and Kwara States.

Sampling location	Coordinates		Sampling location	Coordinates	
	Northing	Easting		Northing	Easting
OS$_1$ Kajola	07°.721067	004°.636283	OG$_1$ Odeda	07°.344733	003°.647417
OS$_2$ Odo Iju	07°.580951	004°.704250	OG$_2$ Ayetoro	07°.244450	003°.043833
OS$_3$ Majaroko	07°.469752	004°.894567	OG$_3$ Idiroko	06^0.692133	002°.832317
OS$_4$ Ikire	07°.406233	004°.241533	OG$_4$ Papalanto	06°.594317	002°.949733
OS$_5$ Ikirun	07°.874167	004°.659701	OG$_5$ Sagamu	06°. 848321	003°. 604733
OY$_1$ Ilora-Iseyin Rd	07°.803917	003°.905133	KW$_1$ Obbo Ile	08°.071252	005°.302767
OY$_2$ Ahoro Dada	08°.154133	004°.020933	KW$_2$ Eleyin	08°.174167	005°.046583
OY$_3$ Idere	07°.495383	003°.252617	KW$_3$Apata Balla	08°.401067	004°.418133
OY$_4$ Eruwa	07°.552583	003°.445967	KW$_4$ Lafiaji	08°.868330	005°.323401
OY$_5$ Alagutan,	08°.595517	003°.402567	KW$_5$ Karati	08°.878833	004°.900333

Codes: OS, Osun; OY, Oyo; OG, Ogun; KW, Kwara.

Determination of pH and conductivity

The pH of the farmland soils were determined according to the method described by Mclean (1982). A 1:1 mixture of soil and distilled water was prepared and allowed to stand for about 30 min. The pH and conductivity of the suspensions were then measured

Table 2. Results of the determination of pH, OC and concentration levels (µg/g) of some heavy metals in selected agricultural soils in some farming communities in Osun, Oyo, Ogun and Kwara States.

Sampling location	pH	Organic carbon (%)	Pb (µg/g)	Cd (µg/g)	Zn (µg/g)	Cu (µg/g)
Osun (N = 20)						
Minimum value	4.1	1.24	0.19	2.15	21.28	7.91
Maximum value	6.8	2.51	8.35	5.75	38.94	20.87
Mean value	6.05	1.80	3.32	3.92	30.00	15.02
Standard deviation	0.68	0.36	1.99	1.15	6.62	3.88
Oyo (N = 20)						
Minimum value	4.5	1.03	1.04	1.17	15.19	6.34
Maximum value	6.5	1.77	5.23	3.94	27.80	16.74
Mean value	5.65	1.34	3.22	2.29	21.85	12.48
Standard deviation	0.54	0.22	1.34	0.74	4.75	3.25
Ogun (N = 20)						
Minimum value	4.6	0.67	1.24	1.90	17.02	6.48
Maximum value	6.4	1.26	4.79	5.09	30.78	17.11
Mean value	5.68	1.01	3.27	3.47	24.09	13.38
Standard deviation	0.49	0.18	1.03	1.02	5.19	3.46
Kwara (N = 20)						
Minimum value	4.3	0.67	1.01	1.39	12.98	6.17
Maximum value	6.5	1.24	4.70	3.74	23.74	16.28
Mean value	5.42	0.95	2.96	2.55	18.75	12.14
Standard deviation	0.63	0.16	0.82	0.75	3.97	3.10
EEC guideline values (1993)			50 - 300	1 - 3	150 - 300	140 - 300

with pre-calibrated pH meter and conductivity meter electrodes, respectively.

Heavy metals (Cd, Cu, Pb, Zn)

About 2 g each of the <2 mm sieved soil samples were acid digested by the method of Onianwa (2001), and the digests dissolved in dilute HNO_3. The heavy metals (Pb, Cd, Zn, and Cu) in the digests were determined by atomic absorption spectrophotometer (AAS)

Organic carbon (OC)

OC of the farmland soil samples were determined by the rapid dichromate oxidation method described by Walkley and Black (1934) and reviewed by Schumacher (2002).

RESULTS

The digestion and analysis of replicate spiked soil samples (n = 4) showed good recovery between 87.54 and 95.81% and relative standard deviation (RSD) of 4.09 to 15.54%. The recoveries and RSD for the metals were ranged: Pb, 90.58 to 94.75%, RSD, 5.97 to 10.38%; Cd, 91.32 to 93.80%, RSD, 4.01 to 6.54%; Zn, 92.75 to 95.81%, RSD 6.94 to 15.54% and Cu: 87.54 to 90.49%, RSD, 8.46 to 10.72%. The percentage recovery of each metal falls within the generally acceptable recovery 100 ± 20%.

Physical and chemical characteristics

The results of the determination of pH, OC and the concentrations of the heavy metals Cd, Cu, Pb and Zn in soil samples collected from selected agricultural farmlands in Osun, Oyo, Ogun and Kwara States are presented in Table 2.

Soil pH and organic carbon (OC)

The farmland soils were slightly on the acidic to near neutral range (4.1 to 6.8) in surface to deeper 20 cm subsurface soils (Table 2). The pH of the sampled farmland soils in Osun, Oyo, Ogun and Kwara States ranged from 4.1 to 6.8 (6.05 ± 0.68), 4.5 to 6.5 (5.64 ± 0.54), 4.6 to 6.4 (5.68 ± 0.49), and 4.3 to 6.5 (5.42 ± 0.63) µg/g, respectively. OC content of the farmland soil samples are generally low (0.67 to 2.51%). The OC composition content in the soils sampled from the various farmlands in Osun, Oyo, Ogun and Kwara States ranged from 1.24 to 2.51 (1.80 ± 0.36)%, 1.032 to 1.77 (1.34 ± 0.22)%, 0.67 to 1.26(1.01 ± 0.18)%, and 0.67 to 1.24 (0.95 ± 0.16)%, respectively.

The metal content of the soils

Heavy metals occur at measurable concentration in all the agricultural farmlands. The concentrations of Pb, Cd, Zn and Cu in the soils were variable. The distributions of the metals were not of any definite pattern hence, no specific trend was observed for the metal levels in the farmland soils.

The concentrations of Pb in soils of the farmlands in Osun State measured the highest Pb levels which ranged from 0.19 to 8.35 (3.32 ± 1.99) µg/g (Table 2) than in the soils collected from the other States. The least Pb concentrations were measured in farmland soils collected in Kwara State [1.01 to 4.70 (2.96 ± 0.82) µg/g)]. Soil concentrations of Pb in the farmland soils collected in Oyo and Ogun States ranged from 1.04 to 5.23 (3.22 ± 1.34) and 1.24 to 4.79 (3.27 ± 1.03) µg/g, respectively. The concentration of Cd (1.17 to 5.75 µg/g) was the least among the measured metals. Cd concentrations in Osun State farmland soils ranged 2.15 to 5.75 (3.92 ± 1.15) µg/g. This was followed by farmland soils in Ogun State which ranged from 1.90 to 5.09 (3.47 ± 1.02) µg/g, and then Kwara State 1.39 to 3.74 (2.55 ± 0.75) µg/g. The least Cd concentration (0.26 to 5.75 (2.29 ± 0.74) µg/g) were detected in the soils from Oyo State.

Zn levels in agricultural farmlands soils of Osun, Oyo, Ogun and Kwara States were ranged from 21.28 to 38.94 (30.33 ± 6.62) µg/g, 15.19 to 27.80 (21.85 ± 4.75) µg/g; 17.02 to 30.78 (24.09±5.19) *µ*g/g and 12.98 to 23.74 (18.75±3.97) *µ*g/g, respectively (Table 2). Farmland soils of Osun State had the highest Zn concentration, while farmland soils of Kwara State had the least Zn concentration. Cu levels in all the agricultural farmland soils were ranged from 7.91 to 20.87 (15.02 ± 3.88) µg/g, 6.48 to 17.11 (13.38 ± 3.46) µg/g, 6.34 to 16.74 (12.48 ± 3.25) µg/g, and 6.17 to 16.28 (12.14 ± 3.10) µg/g in Osun, Ogun, Oyo and Kwara States, respectively.

DISCUSSION

Agricultural soils are complex environmental systems influenced by natural and anthropogenic activities (Prieler and Anderberg, 1996). Visual inspection of the soils in the study areas showed that the farmland soils are porous, aerated, well drained, moderately weathered and ferruginized. Their texture transits typically between sandy loam - clay loam on the surface, and clayey in the subsoil horizons except in farmland of Kwara State which are mostly loamy to sandy loam on the surface.

The concentration of heavy metal available in soils is largely controlled by adsorption and desorption processes occurring in soils and this depends on soil mineral assemblage, organic matter (OM) and chemistry. Lewis (2005) reported that the mechanism of adsorption and desorption is influenced by the net electrostatic charges on the heavy metals and soil particulates, concentration of the heavy metals, soil pH, redox potential and other complex set of interacting soil characteristics. The magnitude of OC in soils and the accumulation of OM within soil is a balance between the returns or addition of plant residues and their subsequent loss due to the decay of these residues by microorganisms. OC levels in most of the farmland soils were lower than the 2.5% considered adequate for arable land crop production in South Western Nigeria. Eludoyin and Wokocha (2011) reported a mean of 0.96% OC in plot under repeated maize cropping and 2.02% OC in forest soils around Ibadan. About 26% of the soils contain less than 1.00% OC, while about 45% contains between 1.10 and 1.50% OC. About 21 and 7.5% of the soils had between 1.51 to 2.00% OC and greater than 2.00% OC, respectively with the highest level of 2.51% measured in Osun State. In general, OC levels in the farmland soils are the order Osun > Oyo > Ogun > Kwara States. There were significant ($p < 0.05$) spatial variation in soil OC levels and land use types with strong positive correlations above the least correlation value (γ_{min}) 0.64, at a 0.01 significant level in the different land uses.

Soil accumulation and availability of heavy metals are affected by soil OM, soil pH, grown crop species and crop rotation (IPNI, 2008). The concentration of Zn was the highest among the measured heavy metals in the agricultural farmland soils investigated, and ranged between 12.98 and 38.94 µg/g. This was followed by those of Cu which ranged from 6.17 to 20.87 µg/g and then Pb, 0.79 to 8.35 µg/g. The concentration of Cd, 0.26 to 5.75 µg/g was the least in all the sampled farmland soils. Geo-statistical analysis on the concentration levels of the measured heavy metals revealed spatial correlation with the soils pH and OC levels and characteristics, and this defines soils' holding capacity for heavy metals and other mineral nutrients. There is a linear threshold between the concentration levels of some heavy metals and the OC in the farmland soils, with significant correlation ($p < 0.05$) between OC levels and the heavy metal content in the soils (Pb, $\gamma = 0.74$; Cd, $\gamma = 0.67$; Zn $\gamma = 0.57$; Cu, $\gamma = 0.52$). The OC levels predispose soils to the retention of soil heavy metals and micro/macro-nutrients, although this depends on the nature of interaction between them.

Soil pH regulates almost all biological and chemical reactions in soil (Brady and Weil, 2002; Kabata-Pendias, 2001), thus the distribution of soil pH may provide a useful index for the potential soil holding capacity for heavy metals, nutrients and fertility of soil types. The observed mean pH of the farmland soils were in the acidic: 6.05 ± 0.68, 5.64 ± 0.54, 5.68 ± 0.49 and 5.42 ± 0.63 µg/g (Table 2) in Osun, Oyo, Ogun and Kwara States, respectively. Solomon (2008) reported that pH value of less than 5.5 is considered as a problematic for most microbial activities, and this affects the availability soil heavy metals and nutrients, consequently, there may be less heavy metals in the farmland soils collected in Kwara. The soil pH threshold variance showed significant correlation ($p < 0.05$) with the heavy metal levels in soil (Cd, $\gamma = 0.79$; Zn, $\gamma = 0.59$; Cu, $\gamma = 0.51$) except for Pb (Pb, $\gamma = 0.39$). This suggests that, the pH of soils may determine the solubility's of metals in soil solution and their erosion pattern in the farmland soils.

Spatial information about the prevalence of heavy metals according to the soil parent material in most arable agricultural farmland soils in Nigeria is scarce. The detected concentration levels were geochemically indexed in comparison to the European Economic Community (EEC, 1993) recommended maximum allowable concentration (MAC) threshold in agricultural soils, in order to ascertain whether the investigated soils contain metal levels that may be of concern. The measured concentration levels of the heavy metals were below the EEC MACs, except for Cd. Over 56% of the farmland soils contained more than 3 mg/kg of Cd, while about 44% were within the range of 1 to 3 mg/kg EEC MAC for Cd in agricultural soils. The concentration levels of the metals in the surface and subsurface farmland soils were within the normal range of values in unpolluted soils as reported for different countries of the world, except for Cd (Alloway, 1990; EEC, 1993; Brady and Weil, 2002). Furthermore, there was no significant difference ($p < 0.05$) between the values reported for the surface and subsurface soils, although values recorded in top soil were slightly higher than that recorded in subsurface soils. Thus, it can be suggested that the heavy metal concentrations of soil samples from the study areas do not indicate heavy metal contamination of the soils except for Cd, which were 1.2 to 1.9-fold higher than the EEC threshold, especially in Osun and Ogun States. Interpolating the metals concentration data and their spatial distribution on the farmlands, most soils in Osun State appeared to contain higher levels of the metals compared to other states, which may be associated with organic sequestration. According to Fennessy and Mitsch (2001), total nutrient of soil may decrease due to prolonged usage, hence the need to enhance the essential nutrients and minerals quality of arable farmlands. Although, the use of fertilizer on the farmlands was common, the observed levels were apparently a product of the natural background and inputs from diffused sources which are not readily ascertained. The prevention and/or rational management of heavy metal contamination through the application of fertilizer, sewage sludge, manures and other soil nutrient supplement in agricultural soils, requires the use of flux balancing technique.

Conclusion

The concentration levels of heavy metals in the evaluated farmland soils do not appear to be of serious concern for now, except for Cd. The study results provide evidence of gradual accumulation of Cd in arable farmlands, while the concentration levels of the heavy metals in the evaluated farmland soils do not appear to be of serious concern. The sources of the metals in farmlands are suspected to be either from the use of nutrient replenishing materials (such as fertilizer), traffic and aerial deposition.

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