

Level of Selected Precedence Pollutants in Soils of the Industrial Regions of Welmera District (Oromiya Special Zone around Finfinne), Ethiopia**Melkamu Biyana***Wollega University, College of Natural & Computational Sciences, Department of Chemistry, P.O.Box 395, email: malkako2011@gmail.com***Abstract**

Melkamu Biyana, Level of selected precedence pollutants in soils of the industrial regions of Welmera district (Oromiya Special Zone around Finfinne), Ethiopia, Journal of Science & Development 2(2) 2014, 123-135

Farm soils of Oromiya special zones around Finfinne in general, Welmera district in particular are recently become polluted through the continuous and intensive applications of pesticides apart from contamination by heavy metals from various sources. In the present study, soil samples collected from different sites of industrial regions in the Welmera district were tested for organochlorine pesticides (OCP) and heavy metals concentration and distribution using GC-MS and AAS respectively. The result shows that the value of heptachlor ranges from (ND-0.88±0.014), methoxychlor (ND-2.14±0.06), chlordane (0.07±0.002-0.98±0.023), DDT(o,p'-DDT+p,p'-DDT)(ND- 0.88±0.02), endosulfan(α) (0.53±0.01-3.05±0.07)mg/kg and As (0.436±0.022-7.29±0.008), Co(ND-15.13±0.022), Cr(ND-107.44±0.17), Ag(ND-1.06±0.008), Cd(ND-52.08±0.046), Ni(0.99±0.005-121.23±0.021)mg/kg in dry soil. The present result reveals that the farm soils contain a significant amount of these chemicals. The polluted soils can act as a secondary source of pollutants which makes the problem more complex. The current work provides new information regarding the levels of both selected persistent organochlorine pesticides and heavy metals in soils of Welmera district and therefore, it is very important to work on reducing the impact of these chemicals upon the environment. Based on the study result, specific regulations and restrictions upon pesticide use, making agricultural policies reform in order to encourage patterns of land use, farming practices, monitoring anthropogenic sources of heavy metals and uses of inputs which are in better concord with the environment are strongly recommended.

Key words: Floricultural industry, Oromiya special zone, pollutants, pesticides, heavy metals.

INTRODUCTION

Worldwide industrialization and agricultural activities have an effect on environmental pollution and the global ecosystem. The pollution of soil by highly persistent pollutants from various sources like anthropogenic sources is a serious environmental issue nowadays in many parts of the world. Soil is a complex medium

which both responds to and influences, environmental processes and conditions. Consequently, it is subjected to a number of pollutants due to different anthropogenic activities (industrial, agricultural, transport etc.) (Facchinelli *et al.*, 2001 and Jonathan *et al.*, 2004). The chemical composition of soil, particularly its metal content is

environmentally important, because toxic metal concentration can reduce soil fertility, further along with organochlorine pesticides, it increases the input into food chains, leading to accumulation of these pollutants in food stuffs, and finally endangers human health. Because of its environmental significance, studies to evaluate the risk caused by metals and pesticides in soil on human health and forest ecosystem have attracted attention in recent years (Denti *et al.*, 1998; Sandaa *et al.*, 1999; Arantzazu *et al.*, 2000 and Krzyztof Losk *et al.*, 2004).

Persistent organic pollutants (POPs) such as organochlorine pesticides (OCPs) and heavy metals are ubiquitous contaminants in different compartments of the environments including soil (Hong *et al.*, 1999; Doong *et al.*, 2002a; Martin *et al.*, 2003; Fu and Wu, 2005, 2006). These compounds are generally generated by anthropogenic processes and can be introduced into the environment through various routes. Due to their toxic, mutagenic, and carcinogenic characteristics, these persistent compounds are considered to be hazardous to the biota and environment. As soil pollution by pesticides can affect many biological systems, the widespread use of potentially harmful pesticides has recently become under scrutiny in Africa (Kaminska *et al.*, 2004 and Thrupp, 1996). Once contaminated by non-degradable chemicals like pesticides and heavy metals, the soil may take a long time to clear (Prenazzi and Ziglio, 1995) and there is always the danger of bioaccumulation (U.S.EPA, 1985; Fergusson, 1990; Younas *et al.*, 1998; Krishna and Govil, 2006).

Heavy metal and organochlorine pesticides contamination of the environment caused by parent materials in soils or anthropogenic activities, including fertilization, application of pesticides and traffic have been a worldwide concern to both the governmental and regulatory bodies that are anxious to prevent further environmental deterioration (Srivastava, 2001; Vidhya, 2001; Feng, 2003; Li *et al.*, 2004; Vidal *et al.*, 2004; Wong, 2004; Luo, 2006; Song, 2006; Hao, 2008; and Fang, 2010) and many studies revealed that industrial areas are highly polluted with these chemicals. Therefore, due attention must be given to proper environmental monitoring because they do not degrade naturally and can retain in soil even after thousands of years. Furthermore, the ultimate fate of these chemicals is that either they leach into ground water or surface water thereby contaminating them or can enter the food crops (Guo-li *et al.*, 2008; Suci *et al.*, 2008; Madjouma *et al.*, 2012). In addition to this, there is no scientific work carried out previously on soil quality in Welmera district. Hence, the objective of this study is to determine the levels and distribution of pesticides (Heptachlor, Methoxychlor, Chlordane, DDT (o,p'-DDT + p,p'-DDT) and Endosulfan (α)) and trace metals (As, Cd, Ag, Ni, Cr and Co) in soils from selected industrial regions in Welmera district, Ormiya special zones around Finfinne (Addis Ababa) in order to evaluate the pollution prospective of these pollutants.

Experimental

Study site

Welmera district (Fig.1) was selected as the study area due to the rapid increase of

various industries in the Oromiya special zones around Finfinne.

Reagents and solvents

High purity grade solvents, Acetone (Abron chemicals), n-hexane (Nice chemicals Pvt. Ltd cochin-682024) and HPLC grade acetonitrile (Fisher Scientific, UK) were used in this work. Analytical reagent grade of HNO_3 , H_2SO_4 and H_2O_2 from UNICHEM were used. All pesticide standards such as DDT (mixture p,p' DDT 92.2% and o,p' DDT 6.2%), endisulfan(α), Heptachlor, Methoxychlor and Chlordane were purchased from Dr. Ehrenstofer GmbH, Germany and metal standards were obtained from UNICHEM.

Analytical Methods

The soil sampling, preservation, transportation, preparation and analysis were performed following the standard methods. Soil samples were collected from

adjacent soils of floricultural industries in Welmera district. Four cut-flower plantations were selected from the mentioned district. Totally six composite soil samples labeled S1, S2, S3, S4, S5 and S6 were collected from different selected sites as shown in Fig 1. For each composite soil sample, about ten core samples were obtained from up to 30 cm depth. Random sampling technique was employed using soil auger for soil sample collection in the selected sites of cut-flower industry farm regions and adjacent soils found between the industries and the Holeta River. The 10 core soil samples mixed, homogenized, and its subsamples were placed in a clean polyethene plastic bag, labeled, transported to laboratory, air dried and sieved to pass through 2 mm sieve.

Sample preparation for pesticides analysis: extraction, cleanup and pre-concentration

Pesticides in sub-soil samples were extracted using the shake flask method in acetonitrile-water (70:30, v/v) mixture (Wolfgang, 2001 and Tadeo, 2008). 25g of soil sample, 70 mL of acetonitrile-water mixture were added in 250mL volumetric flask, capped and then shaken for one hour using mechanical shaker. The two phases formed were kept in contact for 6 hours and the supernatant was filtered using filter paper (Astme 832-81, 12.5cm, China). The extraction was repeated three times for a single sample with fresh solvent (20mL acetonitrile). The soil extracts were combined and then loaded on C18 sorbent which was conditioned using consecutive addition of acetone-hexane (20:80, v/v)., at a flow rate of 10 mL /minute under vacuum and the sorbent was rinsed using 10mL distilled water and then dried by aspirating air for 30 minutes. The analyte was eluted by addition of acetone-hexane mixture. The

final extract was concentrated to about 0.5mL using rotary evaporator and then diluted to 2mL by the addition of hexane, prior to GC-MS analysis.

Sample preparation for heavy metals analysis

All materials used during these experiments were soaked in 10% HNO_3 (v/v) for 24 hour and rinsed three times with deionized water and all reagents used in this study were analytical grade and prepared stock solutions with deionized water. Acid digestion of soil sample was carried out by taking about 0.2g of each soil samples into 25mL conical flasks and digested overnight with 5mL of conc. H_2SO_4 and then heated at 128°C until the evolutions of brown fumes ceased. 2mL H_2O_2 was added in the sample and heated at 125°C for one hour with the evolution of intense white fumes. Again

2mL H₂O₂ was added, made up to the mark with 2% HNO₃ and kept for AAS analysis. The determination of target metals was made by AAS equipped with graphite

furnace, hydride and cold vapour generator and Hollow cathode lamp (Zhang and Wang, 2010).

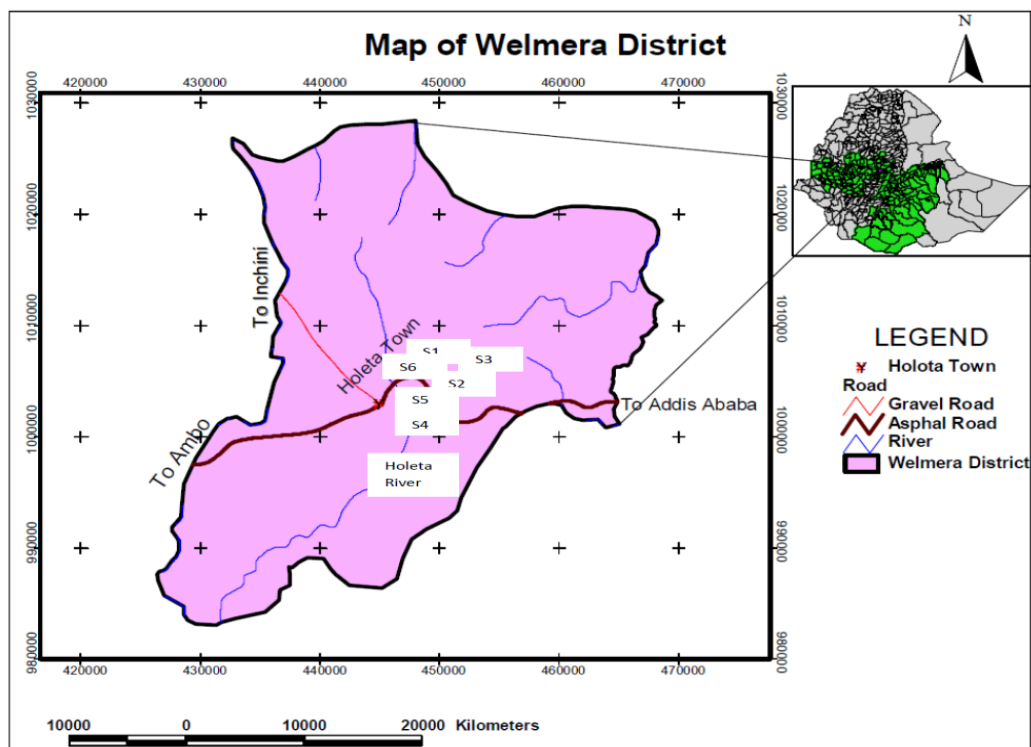


Figure 1: Map of Welmera district

Analytical curves

During the determinations of the pesticides and metals, external standard method (using analytical curves with five concentration levels in five replicates) was used.

Recovery studies

The efficiency of the extraction method used in this work was evaluated by analyzing the spiked soil samples using the developed method and obtained the percent recovery of 81-102 in both cases.

Method validation

The method used in this study was validated by carrying out criteria such as minimum detection limit (MDL), linearity, linear range, sensitivity, limit of quantification (LOQ), accuracy, inter and intra-assay precision using the standard concentrations of 0.001, 1, 3, 5, and 7 ppm for all target pollutants.

Gas Chromatography-Mass Spectrometry (GC-MS) Conditions

The determination of selected OCPs was carried out by gas chromatograph (GC-MS, PerkinElmer 600, USA) equipped with mass-selective detector (MS, PerkinElmer Clarus 600T, USA). The features and operating conditions of GC/MS system were as follows: GC, equipped with programmed temperature vaporizing (PTV) injector, DB-5MS 5% phenylmethylsiloxane fused silica capillary column (30m length, 0.25m i.d. and 0.25 μm film thickness), and helium (purity 99.999%) as carrier gas at constant flow-rate of 1.9mL/min. The injection volume was 2 μL and PTV was operated in splitless mode. PTV program was as follows: 80°C, 12°C/s to 350°C and hold at 350°C for 2min. The temperature of the ion source and MS transfer line were maintained at 170°C and 280°C, respectively. The oven program for OCPs was 60-280°C

temperature, 5-6 min holding time and rate of 15°C/min-end. MS detector was operated in selected ion monitoring (SIM) mode.

Atomic Absorption Spectrophotometer (AAS) conditions

The determination of target metals was made by AAS equipped with graphite furnace, hydride and cold vapour generator and Hollow cathode lamp. Standard solutions of all the metals were prepared by diluting AAS standard solutions (1000 ppm) of As, Ni, Cd, Cr, Co and Ag. From each stock solution, 0.1mL was taken into 100mL flask, filled upto the mark with 2% HNO₃ and after the measurement of absorbances linearity was achieved in each calibration curve. After checking the working conditions of the AAS, soil samples were subjected for metal determinations.

RESULTS AND DISCUSSIONS

In many parts of the world, contamination of soil with pesticides and heavy metals from agriculture is still a problem of primary disquiet. In the region of Indian sub-continent, particularly in the vicinity of Sundarban mangrove environment of Hugli estuary, common organochlorine pesticides DDT, DDD, DDE, HCH and aldrin were found in soil with following level: γ -HCH is detected in term of 0.0474ppm while the concentrations of α -HCH, β -HCH, ρ , ρ -DDE, ρ , ρ -DDT are 0.0388, 0.0179, 0.0710 and 0.01330 ppm, respectively present in the soil (Nawab et al., 2003). Soil acts as filter, buffer and degradation potentials with respect to storage of pollutant with the help of soil organic carbon (Burauel and Bassmann, 2005) but it is recognized that the soil is a potential pathway of pesticide transport to contaminate other segment of the environment including food-chains.

Pesticides residues in soil

The level of organochlorine pesticides identified in soil samples and selected physico-chemical properties of the soils were summarized in Table 1. Half of the soil samples were slightly acidic while the rest are nearly neutral and they fulfill the pH requirements for most plants growth. Generally, the soils texture is clay (Table 1).

Heptachlor

The soil contents of heptachlor were S5 (0.88) > S1 (0.51) > S3 (0.33) > S6 (0.13) > S2 (0.09) mg/kg and ND for S4. The highest level was detected at sites S5 and S1 while the lowest value was measured for S2. All soil samples have contained above the maximum permissible limits for individual pesticides (0.01 mg/kg) and total pesticides (0.05mg/kg) in soil set by European Union.

Table 1: Levels of pesticides in soil (mg/kg) as a mean of five replicate measurements (\pm SD)

(P = 0.05)

Target pesticides	S1	S2	S3	S4	S5	S6
Heptachlor	0.51 \pm 0.012	0.09 \pm 0.021	0.33 \pm 0.002	ND	0.88 \pm 0.014	0.13 \pm 0.022
Methoxychlor	0.29 \pm 0.16	ND	0.63 \pm 0.03	0.02 \pm 0.001	2.14 \pm 0.06	0.73 \pm 0.023
Chlordane	0.35 \pm 0.01	0.07 \pm 0.002	0.17 \pm 0.012	0.98 \pm 0.023	0.46 \pm 0.02	0.36 \pm 0.014
DDT(o,p'-DDT+p,p'-DDT)	0.88 \pm 0.02	0.91 \pm 0.04	ND	0.03 \pm 0.001	0.66 \pm 0.03	0.18 \pm 0.011
Endosulfan(α)	0.53 \pm 0.01	0.78 \pm 0.015	3.05 \pm 0.07	1.58 \pm 0.12	0.87 \pm 0.05	1.99 \pm 0.022
pH	6.3	6.8	5.1	7.2	6.5	7.1
Texture (%)	67.12	59.76(clay)	62.03(clay)	56.98(clay)	60.19(clay)	64.38(clay)

Methoxychlor

All soils detected for methoxychlor concentrations gave significant level except site S2 (ND). Highest level was recorded at site S5 (2.14 mg/kg) followed by S6 (0.73mg/kg), S3 (0.63mg/kg) and S1 (0.29mg/kg) while lowest level at S4 (0.02 mg/kg) and S2(ND). Except for S2, all samples contain far above the permissible limits for both individual and total pesticides in soil. Therefore, looking for better alternatives and reducing the use of this pesticide is very important.

Chlordane

Chlordane was found in all soil samples tested with high concentration at S4 (0.98mg/kg) and low concentration at S2 (0.07mg/kg). This pesticide is persistent and can undergo bioaccumulation in food chains. Apart from this, in all soil samples, it was found to be far above the recommended value in soil. This result indicates that great attention must be given to the reduction of further use of this chemical in the future.

DDT (o,p'-DDT + p,p'-DDT)

Except for S3, DDT was found in all soil samples with considerable concentrations ranging from ND-0.91mg/kg. S2 (0.91 mg/kg), S1 (0.88mg/kg), and S5 (0.66mg/kg) have recorded relatively high level while S4 (0.03mg/kg), S6 (0.18mg/kg) and S3 (ND) have recorded relatively low levels. The cumulative level of o,p'-DDT and p,p'-DDT in all soil samples was found to be above the standard values for individual and total pesticides in soil. Thus, preventive action is required so that it is possible to minimize its further effects on water systems and food-chains for human consumptions.

Endosulfan(α)

Endosulfan-alpha was found in all soil samples from different selected sites of industrial regions of Welmera district with range of 0.53-3.05mg/kg. Three sites, namely, S3, S4, and S6 contain above 1mg/kg, 3.05, 1.99 and 1.58mg/kg respectively. The other sites: S1 (0.53mg/kg), S2 (0.78mg/kg) and S5 (0.87mg/kg) contain less than 1.0mg/kg. The

present result is less than the concentration of endosulfan(α) (25mg/kg) reported in soil sample from Awash basin, Ethiopia (Ahmed, 2007) while it is greater than the values reported from other countries (0.003-0.067mg/kg and 1.8mg/kg) (Jean M.Cobb et al., 2007). Endosulfan-alpha was evaluated to be above the maximum permissible limits in farm soil and counteractions are essential.

Heavy metals in soil

The fate of metals in the soil environment is dependent on both soil properties and environmental factors. The concentrations of metals in soil solution is influenced by the nature of both organic and inorganic ligand ions through their influence on metal sorption processes (Naidu *et al.*, 2001). The concentration of available trace metals in the soil was presented as mg/ kg of dry soil in Table 1.

Table 2: Levels of trace metals in soil (mg/kg) as an average of five replicate measurements (\pm SD) ($p = 0.05$)

Soil sample	Soil trace metals content (mg/kg)					
	As	Co	Cr	Ag	Cd	Ni
S1	0.841 \pm 0.09	15.13 \pm 0.022	98.01 \pm 0.006	0.931 \pm 0.014	18.33 \pm 0.015	121.23 \pm 0.021
S2	0.436 \pm 0.022	0.89 \pm 0.011	107.44 \pm 0.17	0.793 \pm 0.004	3.46 \pm 0.025	71.97 \pm 0.092
S3	0.921 \pm 0.012	ND	104.02 \pm 0.056	ND	41.11 \pm 0.008	128.45 \pm 0.033
S4	0.611 \pm 0.034	3.01 \pm 0.005	76.25 \pm 0.054	0.492 \pm 0.007	ND	0.990 \pm 0.005
S5	7.29 \pm 0.008	6.53 \pm 0.031	ND	1.06 \pm 0.008	52.08 \pm 0.046	89.77 \pm 0.006
S6	4.18 \pm 0.018	2.09 \pm 0.024	17.91 \pm 0.066	ND	30.85 \pm 0.029	12.38 \pm 0.009

Arsenic (As)

The level of As in soil sample was found to be in the range between 0.436-7.29 mg/kg. The highest level was detected in S5 and S6 while the minimum concentration was found in S2. Arsenic is notorious as a toxic element; however, its toxicity depends on its form of existence.

Cobalt (Co)

The concentration of Co in soil ranged from 0.89-6.53 mg/kg. Co metal concentration in the soil samples is as follows: S1>S5>S4>S6>S2>S3. The concentration of Co at site S1 is higher than those of other sites followed by S5. The present result indicates that the amount of Co found in the soil samples was within the normal range for agricultural soils.

Chromium (Cr)

The level of Cr in the soil samples obtained from different sites in decreasing order is S2 (107.44) >S3 (104.02) >S1 (98.01) > S4 (76.25) > S6 (17.91) mg while it was not detected in S5. The highest Cr content recorded in the soil samples S2 and S3, which was above the permissible level (100 mg/kg) in agricultural soil, may be attributable to constant discharge of effluent from the floriculture enterprise and other anthropogenic sources. The Cr mean value reported in this study was higher than those reported by Mico *et al.* (2006), and Kabata-Pendias and Pendias (2001). All soils have high clay contents, which seems to suggest high Cr adsorption by this soil component. The presence of high clay content and human activities from the industrial enterprise can increase the normal content of Cr in the soils.

Silver (Ag)

Ag levels found in different soil samples were ranged from 0.492-1.06 mg/kg. Soil sample from site S5 contains high amount of this metal than others and it was not detected in S3 and S6.

Cadmium (Cd)

Cd concentrations accumulated in the soils from different sites were S5 (52.08) >S3 (41.11) >S6 (30.85) >S1 (18.33) >S2 (3.46 mg/kg) while it was detected in site S4. High level is recorded for site S5 and low level for S2. The soil concentration of Cd in the present study is greater than the permissible limit (0.8mg/kg) of Dutch standards. The application of agricultural inputs such as fertilizers, pesticides, and biosolids (sewage sludge), the disposal of industrial wastes or the deposition of atmospheric contaminants increases the total concentration of Cd in soils, and its bioavailability. Cadmium is very biopersistent but has few toxicological properties and, once absorbed by an organism, remains resident for many years.

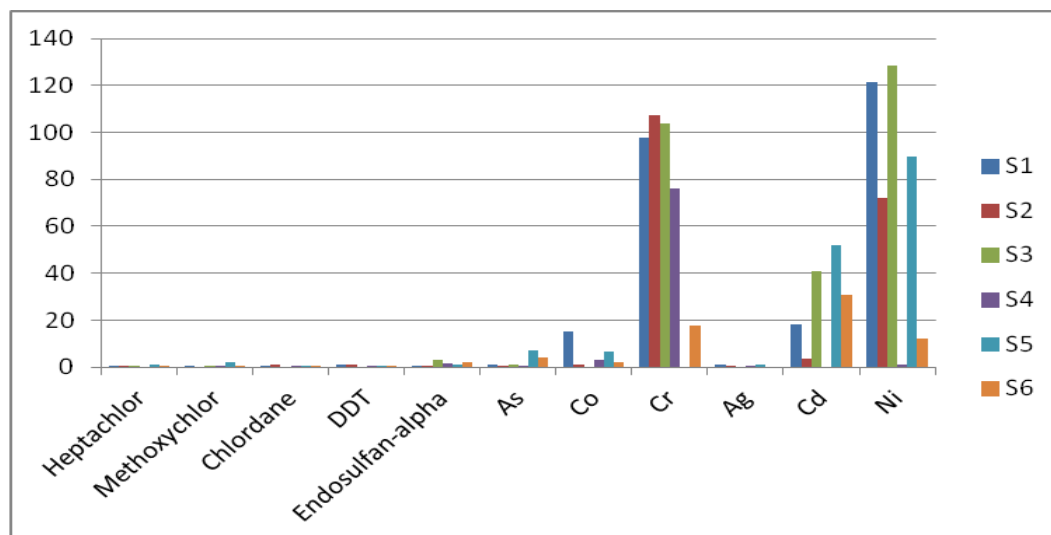
Nickel (Ni)

The Ni contents of the soils of selected sites in floricultural industry regions of Welmera district ranged between 0.99-128.45 mg/kg. High and low contents of Ni, 128.45 and 0.99 mg/kg were determined in S3 and S4 respectively. The Ni content reported for S1 and S3 in this study was higher than those reported by Mico et al (2006) and Campos (1997) in agricultural soils and also exceeded the reference value (100mg/kg) of Kabata-Pendias and Pendias (2001). The permissible limit for Ni in soil is 35mg/kg according to Dutch standards. Hence all soil samples subjected to trace metal determination contained above the recommended level except sites S4 and S6. The larger part of all Ni compounds that are released to the environment will adsorb to sediment or soil particles and become immobile as a result. In acidic soils, however, Ni becomes more mobile and often leaches down to the adjacent groundwater. Also, the mobility of the metal depends on soil pH and also depends on the organic matter and granulometric.

Comparison of OCP and Heavy Metals in Soil Samples

According to the report by Jyothish and Sujatha(2013), heavy metals (Fe, Ni, Mn, Mg, Co, Zn, Cu, Cd) as well as Organo chlorine pesticides in soil were analysed concurrently in Kerala, India. The observation resulted from the study signifies that, most of the area is contaminated by Ni

and Co in addition to, the concentration of endosulfan α (0.977 mg/kg). Similar pesticide and heavy metal residues were found in soil samples from flower industry region in Holeta town, Ethiopia. A comparison of residual pesticides and heavy metals level is shown in Figure 2.

Figure 2: Comparison of level of pesticides and heavy metals in soil samples

The level of heptachlor, methoxychlor, As, Co, Cr and Ni in soil sample S1 is relatively high. Soil samples S1, S2, S3, S4 contained high concentration of Cr while S1, S2, S3 and S5 contained maximum level of Ni. From the present study result, the level of

heavy metals is by far higher than that of organochlorine pesticides. This may be due to the organic matter content of the soil which can trap and degrade pesticides and reduce the time of their persistence in it than heavy metals.

CONCLUSIONS

The present study result reveals that the levels of both organochlorine pesticides and heavy metals in soil were on the average above the maximum permissible limits set for farm soils by different countries. The level of organochlorine pesticides: heptachlor ($ND-0.88 \pm 0.014$), methoxychlor ($ND-2.14 \pm 0.06$), chlordane ($0.07 \pm 0.002-0.98 \pm 0.023$), DDT(o,p' -DDT+ p,p' -DDT) ($ND-0.88 \pm 0.02$), endosulfan (α)($0.53 \pm 0.01-3.05 \pm 0.07$)mg/kg and heavy metals: As($0.436 \pm 0.022-7.29 \pm 0.008$), Co($ND-15.13 \pm 0.022$), Cr($ND-107.44 \pm 0.17$), Ag($ND-1.06 \pm 0.008$), Cd($ND-52.08 \pm 0.046$), Ni($0.99 \pm 0.005-121.23 \pm 0.021$)mg/kg dry soil were detected. This may attribute to the continuous discharge of effluents containing various agrochemicals from the agricultural

industries resided in the study region. The above detected chemicals are persistent and bioaccumulate in the environment. On the other hand, the polluted soils can act as a secondary source of pollutants which makes the problem more complex. Therefore, it is an important role for policy makers in reducing the impact of pesticides and heavy metals upon the environment. In addition to specific regulations and restrictions upon pesticide use, it is also necessary to reform agricultural policies in order to encourage patterns of land use, farming practices, monitoring the anthropogenic sources of heavy metals and uses of inputs which are in greater harmony with the environment are strappingly recommended.

ACKNOWLEDGEMENTS

The author is thankful to Wollega University for financial support for this research and the Chemistry laboratory of Ambo University for their materials support.

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