Accumulation of Heavy Metals in Agricultural Soils and its Impacts – A Review

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Received Jan. 03, 2018 Accepted Feb. 05, 2018

ABSTRACT *Today agricultural land is highly contaminated with pesticides, domestic waste, commercial waste and industrial waste and causes serious threat to environment. It was noticed that heavy metals are added to the soil by the addition of Cattle dung, Pesticides, Excess fertilizers and industries and these heavy metals accumulate in the soil then to leaves fruits and causes harm to them. Some of the heavy metals like Copper, Cadmium, Chromium and Arsenic Mercury in high concentrations are toxic to flora and fauna. This paper reviews on sources of heavy metals and its impacts. It also explains accumulation of heavy metals and reviews Atomic Absorption Spectrophotometer its types, analysis of metals by using Atomic Absorption Spectrophotometer*

***Key words**: Introduction to heavy metals: Impacts of heavy metals: Accumulation of heavy metals: Atomic absorption spectrophotometer.*

Introduction to heavy metals

Heavy metals are also known as trace metals and have relatively high densities atomic weights or atomic numbers. Iron, Copper and Tin are the earliest known metals. Silver, Gold are the precious metals. From 1809 onwards, light metals, such as Magnesium, Aluminum and Titanium are less well-known heavy metals including Gallium, Thallium and Hafnium. Some heavy metals are harmless like Iron, Cobalt and Zinc and used as nutrients. Cadmium, Mercury and Lead are highly toxic (https://en.wikipedia.org/wiki/Heavy_metals). Heavy metals are added in to the soils from various applications of pesticides in the soils to kill the pests. Application of sewage sludge, fertilizers and they preserve in the soil in the form of chemicals (Marina Efremova and Alexandra Izosimova2012). Heavy metals are present in almost of all the ecosystems on earth. The total concentration of heavy metals in soil and water however varies from local to regional and further to continental level. (Renu tyagi 2014) In the Faculty of Science (Chemistry) Soil is contaminated with the heavy metals due to excess utilization of pesticides. It is one of the serous ecological problems all over the world (Side Hafizes Raman 2012).

Generally the Pesticides are applied to the crops to eradicate the pests. Application of these pesticides and fertilizers contains some quantities of Cd, Pb and Hg which degrades the soil and effects the food chain. It percolates deep in to the underground and degrades or contaminates its quality. Pesticides are not degradable and they persist in the nature for a long time. Some of the phosphate fertilizers add cadmium and other dangerous elements like lead and mercury. (Raven et al., 1998)The supply of various bio solids for example, composts, cattle's manure and municipal sewage sludge (MSS) to land unconsciously points towards the build-up of heavy metals like Arsenic, Cadmium, Chromium, Copper, Lead as well as Hg, Se, Ni, Mo, Zn, Sb, in the soil (Basta et al., 2005).

Sources of heavy metals in agricultural soils

Heavy metals occurs in the soil by Pedogenesis process.or weathering which are called trace metals and these in excess concentration becomes toxic.(A.Kabata-Pendias and H.Pendias,2001) (G. M. Pierzynski,2000) Lead, Chromium, Arsenic, Zinc, Copper, Cadmium, Mercury and Nickel are common in contaminated soils. Soil is contaminated with heavy metals due to mine tailings, domestic waste, application of fertilizers and Pesticides, coal combustion etc. Some metals do not undergo micro and chemical degradation and they persist in the nature for a long time. Animal waste, Poultry waste, Cattle dung, Pig manures produced in agriculture are applied to pastures in the form of solids or pastures. Certain animal wastes such as poultry, cattle, and pig manures produced in agriculture are commonly applied to crops and pastures either as solids or slurries.(M. E. Sumner 2000) Agriculture is the first major influence on the soil. (A.Scragg 2006) Plants require macronutrients like N, K, S, Ca, and Mg and also micronutrients to grow and complete its life cycle. Heavy metals are added to the soils because of their deficiency. Co, Cu, Fe, Mn, Mo, Ni, Zn are added to compensate the deficiency. Large quantities of fertilizers are added to the soil contains the impurities of Lead and Cadmium.(L. H. P. Jones and S. C. Jarvis, "The fate of heavy metals," in The Chemistry of Soil Processes, D. J. Green and M. H. B. Hayes, Eds., p. 593, John Wiley & Sons, New York, NY, USA,

1981. View at Google Scholar). These metals are supplied in the form of foliar spray. (M.M. Lasat,200). M.M Lasat in 2000 said that animals absorb lead by eating of contaminated soils. Lead is released from food industry, sewage sludge large house hold waste, transport, Municipal solid waste and degraded sediment. Use of lead chemicals accounted for more than 40% of total input to municipal solid waste or even these uses only accounted for 8% of total consumption. (European Commission DG ENV. E3 Project ENV.E.3/ETU/2000/0058 Heavy Metals in Waste Final Report February 2002) Lead is also from the combustion of petrol, Zinc and Cadmium is added to soils through tyres and lubricant (USEPA, Report: recent Developments for In Situ Treatment of Metals contaminated Soils, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, 1996.)

Mercury is present as impurity in Zinc ore .It is also released from large house hold waster, lamps sewage etc. Cadmium is present batteries, Photovoltaic cells, Municipal solid wastes and release from these wastes .Chromium can be released from house hold waste, Remains of leather and steel. Cadmium, Copper, Lead, Cadmium, Zinc Iron and Manganese are present in different fertilizers and Pesticides. Fertilizers like Urea, Calcium super phosphate, Iron sulphate and Copper sulphate added these metals in to the soil and degrades the quality.(European Commission DG ENV. E3 Project ENV.E.3/ETU/2000/0058 Heavy Metals in Waste Final Report February 2002) Municipal and industrial waste waters are added to the land long back and it is the regular practice now this waste water contains metals and its concentration accumulates in the soil due to frequent usage. (S. C. Reed, et al 1995). Worldwide, it is also estimated that 20 million hectares of arable land are irrigated with waste water.

Impacts of heavy metals

Heavy metals in high concentration are toxic to soil, plants, aquatic life and human health. Heavy metals exhibit toxic effects towards soil biota by affecting key microbial processes and decrease the number and activity of soil microorganisms. (Singh et al.2011). Heavy metals n excessive concentration produce non specific compounds causing Cytotoxic effects (NIES 1999)Excessive amount of cadmium , copper and zinc interferes with control mechanisms of level of genes thus inhabiting the activity of microbial enzymatic proteins. It also can disrupt the homeostasis of soil. Apostasis of cells, inhibits nitrification and ammonification. The adverse influence of cadmium, copper zinc on microorganisms can be alleviated by the applications of organic and natural fertilizers.(Jadwiga Wyszkowska 2013). Metals are the natural components in the soil. (MM.L.Lasat,2000). Some metals like Cadmium Lead Cobalt, Mercury accumulate in the body of organisms and causes diseases.(E. Pehlivan,2009) Plants also require some heavy metals like Cu, Co, Zn, Fe, Mn, Ni, Mo to keep them healthy.(M.M. Lasat,2000) Contamination of food with heavy metals causes serious hazard to kidney, Renal and Liver damage.(Sathawa. ra, 2004). Excess accumulation of Manganese can cause Madness, Criminal behavior like attitude in human beings (http://www.livelongercleanse.com/heavy-metal-sources.html).Mercury drops the sugar levels, hunger, depression. Arsenic is present in the ashes of the coal. Arsenic compounds adsorb strongly to the soil and accumulates in ground and surface waters and effects skin cancer and damages the circulatory system (A. Scragg, 2006) Plants do not take up lead and lead don't accumulate in vegetables or fruit crops especially in corns, beans, squash, tomatoes, straw berries and apples. Lead concentration is more in leafy vegetables and can be seen on the surface of root crops. Risk of the lead occur only if its concentration is more than 300 ppm.

Accumulation of heavy metals

Many studies reveal that the fruits were contaminated with heavy metals. For example (S. E.Mahdavian et.al in 2009) have analyzed the heavy metal content in Mango, Grapes, Lemon Banana Sapota, Pear, Apple Guava and Pomegranate from the Bangalore city market .Heavy metals like lead, zinc, cadmium, copper, cobalt, chromium, iron, manganese and nickel were analyzed using Atomic absorption spectrophotometer(E.Mahdavian et.al in 2009).Trace elements in fruits and vegetables are caused due to their absorption from soil and sources such as vegetables agricultural waste and contaminated drifts. (Banu et al, 1985). Plants absorb heavy metals through air borne deposits on their parts and contaminated soils. Fruits and vegetables absorb metals through irrigation of contaminated soils. (M.s.Al Jassir et.al 2005) (M.A.Elbagermi er.al 2012) found that highest concentration of heavy metals Pb, Cu, Zn, Co, Ni and Cd were found in Mango, Melon, Spinach, Banana in Misurata city market Libya. Heavy metals are analyzed by using Atomic Absorption Spectrophotometer. Heavy metals like Cadmium, Chromium Copper and Zinc in the leaves of Plum were determined in Tuzla area by using Atomic absorption Spectrophotometry in order to get information about their impact on environment (Sanida Osmanovic et.al, 2014).The determined values of copper and cadmium content in the Plum leaves are higher than he natural content for plants in non polluted environment in many localities. Zinc in fruits of Plum is within the limit but Cadmium

concentration of fruit in most cities increased natural values of 0.8mg/kg. The concentration of Chromium was highest in Plum ie 2.25mg/kg.

Permissible limit for metals in soil

Table1

Name of the metal	Common range in soils Mg/kg
Aluminium	10,000-300,000
Arsenic	1-50; 1-40
Antimony	
Barium	100- 3,00010
Beryllium	
Cadmium	0.01-0.7
Chromium	10- 1,000; 5-3,00010
Copper	2-100
Iron	7,000- 550,000
Lead	2-2000
Manganese	20-3,000
Mercury	0.01-0.3
Nickle	5-500
Selenium	0.1-2.0
Silver	0.01-5.0
Thallium	
Zinc	10-300

Compiled by: Brent L. Balentine 7/95 (Direction of Everett Wilson) (http://www.occeweb.com/og/metals-limits.pdf)

Atomic Absorption Spectrophotometer AA- 6200
AA-6300

Atomic absorption spectrometer helps to analyze the concentration of elements in liquid samples based on the energy absorbed from wave length 190-900nm. It consists of hollow cathode lamp to atomize the sample, Monochromator and Photon detector. A graphite furnace is used for trace analysis in the place of flame burner to increase the sensitivity by several orders of magnitude in the parts per billion range.AAS is used in industries for environmental testing, analysis of metals, Semiconductor manufacturing, Pharmaceutical industries, Petroleum and chemical production. (https://www.labcompare.com/Spectroscopy/Atomic-Absorption- Spectrophotometer/). AAS is use log back and even continuing today. For example the AAS is described and its performance is illustrated by results long back (Barbara et al 1957).Atomic absorption Spectra also used in chemical analysis with vital advantages. It is also said that Atomic absorption spectra provides a method of chemical analysis with vital advantages over emission methods particularly from the view point of absolute analysis. (A.Walsh 1955-

1956).AAS is described and its performance is illustrated for analysis of solutions. Given sample is sprayed in to a flame and the absorption by the latter of atomic resonance line of the element to be estimated is measured and the absorption measurement is independent of any radiation emitted by the flame (A. Walsh 1955-1956).The first Atomic Absorption Spectrometers developed for element determinations and proposed in 1970S using flame and flame atomizers. This spectrometer is modified and used advanced technology and can determine up to sixteen elements in the year 2000.Even today the spectrometers are used with flame and furnace atomizers (SergioL.C. Ferreira. et,al 2018)

Working of AAS

AAS is an instrument that is used to analyze the concentration of element. It analyze samples to see whether it contains the particular element by using that light (http://www.liskeard. cornwall.sch.uk/images/Liskeard-Sixth-Form/Atomic-Absorption-Spectrometry.pdf) It is based on the phenomenon in which the atoms in the ground state absorb the characteristic wave length passing through the atomic vapor layer of element.AAS consists of light source, sample analyzer, spectroscope, photometer and a recording system. In light source hollow cathode lamp and discharge lamp are used.

Sample atomizer

It is of three types Flame type electro thermal type and cold water type. Flame type consists of burner and gas-flow regulator Where as in electric furnace and power source in electro thermal and cold vapor type consists of mercury generator and an absorption cell. A grating for light diffraction is used for spectroscope. Photometer consists of detector and the signal treatment system recording system has recording device and display system.

Procedure can be done by using any one of the method. Generally there are three methods i) Flame type 2) Electro thermal type and Cold type. For example in flame type light source lamp is connected to the lamp house and switch on the instrument wave length id adjusted ,ignite the mixture of these gases by using the combustible and supporting gas, then adjust gas flow rate and pressure make the zero adjustment after nebulizing the solvent in to the flame. Nebulize the test solution or standard solution or control solution prepared by the method prescribed elsewhere, and measure the absorbance. Determination can be done by using Calibration curve , Standard Addition method and Internal standard method (www.ffcr.or.jp/zaidan/ FFCRHOME.nsf/.../%24FILE/B03.pdf method)

The Modern Atomic Absorption Spectroscopy was discovered in the year 1950s and this was led by Sir Alan Walsh at CSIRO (Common wealth scientific and industrial research organization, Division of chemical physics, in Melbourne, Australia.(*McCarthy,2012)*

There are many models of AAS its type wave length, Vaporization mentioned in the table 2

Table 2

SNO	TYPE	LAMP TYPE	LAMPS	WAVE LENGTH	VAPORIZATION
1	AA Duo AAS Simultaneous Flame/Graphite Furnace Agilent Technologies	Hollow- Cathode and Deuterium	2-8 lamps	180-900nm range	Flame/Hybrid and Graphite furnace
2	AA140/AA240 Atomic Absorption Spectrometer Agilent Technologies	Hollow- Cathode Deuterium	4 lamps	180-900nm range	Flame Graphite furnace (upgrade)
3	AA240FS-Fast sequential AAS Agilent Technologies	Hollow- Cathode and Deuterium	4 lamps	185 - 900nm	Flame
4	AA240ZandAA280Z Zeeman AAS Agilent Technologies	Hollow- Cathode	4 lamps for AA240Z 8 lamps for AA280Z	185-900nm	Graphite furnace
5	AA280FS Atomic Absorption Spectrometer Agilent Technologies	Hollow- Cathode and Deuterium	8 lamps	185-900nm	Flame
6	SpectrAA50/55 Atomic Absorption Spectrometer Agilent Technologies	Hollow- Cathode and Deuterium	2 lamps	185-900nm	Flame Graphite furnace (upgrade)
7	TRACE Atomic Absorption Spectrometer Aurora Biomed	Hollow Cathode tube	Auto switch 8 lamp turret	185-900nm	Flame and/or Graphite furnace with optional hybrid generator add on
8	TRACE A11200 Atomic	Hollow Cathode	Auto aligned	185-	Flame and/or Graphite

	Absorption Spectrometer Aurora Biomed	tube	coded 6 lamp turret	900nm	furnace with optional hybrid generator add on
9	BA -15 Benzene Analyzer Lumex instruments	Inquire	Inquire	Inquire	Inquire
10	MGA 1000 Atomic Lumex instruments Absorption Spectrometer	High intensity electrodeless discharge lamps	Inquire	185-900nm	Graphite furnace
11	AA-6200 Atomic Absorption Spectrometer Schimadzu	Hollow- Cathode and Deuterium	2 lamps	190-900nm	Flame /Air/C2H2 and N20/C2H2 burners
12	AA-7000 Atomic Absorption Spectrometer Schimadzu	Hollow- Cathode and Deuterium	6lamp turret	185-900nm	Flame and/or Graphite furnace
13	240Z AA Atomic Absorption Spectrometer Agilent Technologies	Ultra AA lamp	Single light source up to 8 fixed lamp positions	Inquire	Zeeman Graph tube atomizer
14	280Z AA Atomic Absorption Spectrometer Agilent Technologies	Ultra AA lamp	Single light source up to 8 fixed lamp positions	Inquire	Zeeman Graph tube atomizer

Conclusion

The highest concentration of heavy metal accumulation was noticed in many articles. Lot of heavy metal impacts in different kinds of soil is noticed by dumping of waste, Mining and application of agriculture sols. These create lot of impacts to plants, animals and man. So there should be continuous monitoring of heavy metals to maintain healthy environment and improve the quality of human life.

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The pessimist sees difficulty in every opportunity. The optimist sees the opportunity in every difficulty.

~ Winston Churchill