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INVESTIGATING THE HEAVY METALS AND PESTICIDES CONCENTRATION IN AGRICULTURAL SOIL AND GROUNDWATER OF MANSA DISTRICT OF PUNJAB, INDIA: INSIGHTS INTO ITS IMPACT ON HUMAN HEALTH

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ABSTRACT

In the present study, we report presence of heavy metals and pesticides from the agricultural soil and groundwater samples of Mansa District of Punjab India. The investigation of the soil and water samples revealed presence of heavy metals Ni (47.7 mgkg^{-1}), Hg (23.8 mgkg^{-1}), Se (21.1 mgkg^{-1}) and Cd (3.1 mgkg^{-1}) above the permissible limit, as set by Ministry of Environment (MOE). Conversely, the level of Ba (0.066 mgL^{-1}) and Se (0.006 mgL^{-1}) detected in the water sample was below the permissible limit as set by MOE. Further analysis of the soil for the presence of cypermethrin a potent insecticide used by the farmers worldwide demonstrated varied presence of different isomer (I and III-0.019ppb, II-0.018ppb, IV-0.017ppb) in the soil. All other pesticides analyzed demonstrated their presence below the detection limit (BDL). In water, all pesticides observed were found below the detection limit. Significantly high level of soil contamination detected in this region indicates a potential risk to its soil as well as groundwater quality.

***Keywords*: Soil, Groundwater, Heavy Metal, Pesticide, Mansa, India**

I INTRODUCTION

India evidenced agricultural revolution i.e., green revolution leading to a major rise in crop and food productivity within a decade. Green revolution comprises of everything that could improve the crop yield such as use of pesticides, insecticides, chemical fertilizers, new crop varieties etc. The Punjab state of India, also known as India's bread basket, has laid the groundwork for green revolution in India, because of its tremendous agricultural background. Punjab ranks first in pesticide and chemical fertilizer usage in comparison to other states. Nearly, 10% of the total fertilizer consumption in the country is contributed by Punjab in just 2.98% of the cultivated area and 4.2% of cropped area of India. Its per hectare (192.5 kg/ha) usage of fertilizers is highest followed by Haryana (166.2) as compared to average use of 88.2 kg/ha in India [1]. Pesticide usage is also highest in Punjab (923 g/ha) followed by other states where pesticide usage is comparatively low [2]. Though, green revolution has made India self-reliant by increasing its agricultural output, however hold back certain risks with its uses to the farmers, who are injudiciously using pesticides and chemical fertilizers to prevent crop loss without even knowing their negative impact on the environment and human health. Even banned and restricted pesticides are being used without using preventive measures. This unjudicious use of these chemicals causes pollution [1]. The non-biodegradable nature of heavy metalsfound in fertilizersallows them to accumulate in soil for prolonged periods and finally they enter the food cycle via soil [3] .This has drastically changed the agricultural scenario in Punjab. Malwa region of Punjab, now referred to be a "cancer bowl" of country is currently suffering from the serious consequences of this practice [4]. As per the report issued by Department of Health and Family Welfare, 2013 (DHFW) [5], the occurrence of cancer (per million per year) in the Malwa region is found to be 1089 which is extremely higher than other two regions of Punjab, Majha (647/million/year) and Doaba (881/million/year). It also exceeds the national average of cancer occurrence in India (800/million/year). Studies have also related this high prevalence to unrestricted misuse of pesticides and chemical fertilizers in this region [6,4,7]. The excessive accumulation of heavy metals in human body promote oxidative stress further contributing to cancer genesis; as the oxidative stress is one of the major factor in cancer causation [8,9]. Not only cancer, incidence ofother health ailments such as mental retardation, premature hair greying, neurological and behavioural disorders, reproductive abnormalities and miscarriages are also increasing at a fast rate in this region [4]. Present investigation was aimed at analyzing the level of pesticide and heavy metal content from the soil and groundwater samples collected from the Mansa district of Punjab. Mansa comes under the high cancer stricken regions of Malwa with 1212 cancer deaths in the last 5 years (DHFW, 2013) [5]. The intention of the current study was to evaluate the soil and groundwater contamination in relation to heavy metal and pesticide pollution and its influence on human health. Currently, there is no published studies that could reveal the true extent of heavy metal and pesticide profile in Mansa. Also, the study will shed light into the potential threats, these contaminants can have on soil and water quality of this area as well other nearby areas.

II MATERIALS AND METHODS

2.1 Study area

Mansa district is located in the southern part of Punjab state and covers an area of about 2,171 sq.km. It lies between 29^0 32`: $30^0$ 12`North latitudes and 75^0 10`: $75^0$ 46` East longitudes. Map of Mansa district is shown in Fig 1. The district has total population of 768,808 as per census reports 2011 with 242 villages. Major soil types in this area are clayey loam and sandy loam. Climate of Mansa region is classified as subtropical steppe, semi arid and hot with mean maximum and minimum temperature 42^0C (May &June) and 3.9^0C (January) respectively. Main crops grown in this region are wheat, rice and sugarcane.

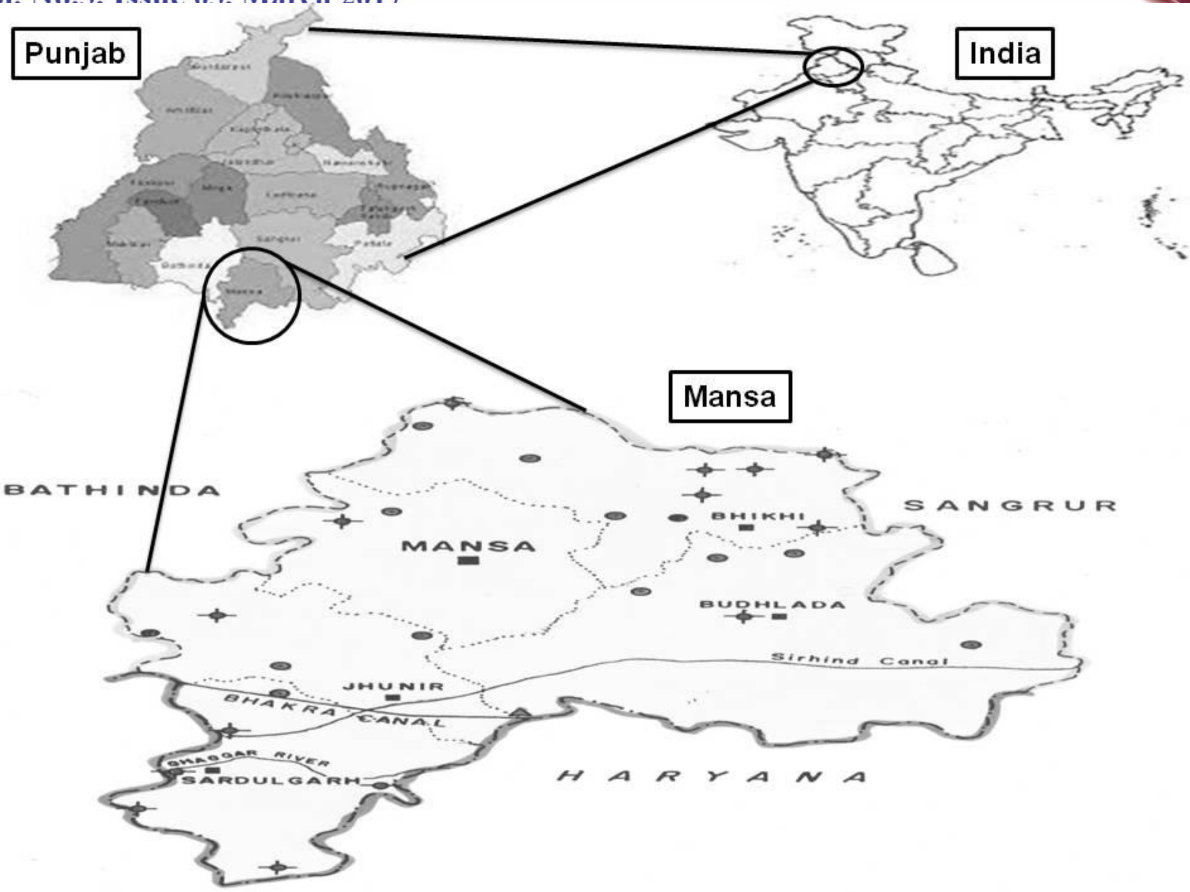

Figure 1 Geographical location of district Mansa in India

2.2 Soil sampling

The sampling was done in the month of January 2014. Temperature at the time of sampling was 12ºC. For sample collection, soil was dug upto the depth of 0-10 cm. Sample collection was done in clean plastic bags and was transported to PBTI (Punjab Biotechnology Incubator, Mohali, Punjab) laboratory for further analysis.

2.3 Water sampling

Ground water sample used for drinking and irrigation practices was collected in prewashed (with detergent, diluted HNO_3 and doubly de-ionized distilled water, respectively) bottles. 1% of HNO_3 was added to the bottle [10]. Sampling was done at the same time as that for soil. After collection, samplewas brought to PBTI laboratory for analysis.

2.4 Estimation of Metals in Soil and Water by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS)

2.4.1 Digestion of soil sample

0.25 gm sample of soil was digested with 6 ml of 70% HNO_3 and 1 ml of 30 % Hydrogen peroxide by Microwave Digestion system (MDS) (CEM Corporation, USA) using the following program: Power (watts) 800,

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Ramp time (min) 25, Temp. (^{0}C) 180, Hold time (min) 20, Cool down (min) 20. After mineralization, the sample was transferred to 50 ml volumetric flasks and brought up to the mark with the milli-Q water. Then, sample was analysed by ICP-MS (Test Method - AOAC 999.08).

2.4.2 ICP-MS analysis for soil and water

The ICP–MS analysis was carried out using Inductively Coupled Plasma-Mass Spectrometer (Agilent 7700 Series) for the analysis of heavy metals with the following conditions: Sample Introduction & Plasma: RF power (watts) 1390-1550, Plasma gas flow (L/min) 15, Auxillary gas flow (L/min) 1, Nebulizer gas flow (L/min) 1.04-1.22, Sampling depth (mm) 8, Sampling Cone Nickel, Skimmer cone Nickel, Sample uptake rate (ml) 0.40. Data Acquisition: Integration time 0.30, Peak pattern 6 points/peak, Repetition 3. Collision/reaction cell Parameter: Cell gas flow 4.0 ml /min He, Octapole bias -14 V.Digestion of sample is not required in case of heavy metal analysis from water sample. Water sample is acidified with conc. HNO_3 (about 1.5ml in 1 Litre of sample). After acidification, samples were analysed by ICP-MS (Test Method - APHA 3125 B). Instrument conditions were same as that for soil sample analysis.

2.4.3 Estimation of Pesticides in Soil and Water by Gas Chromatography-Mass Spectrometry (GC-MS)

Soil sample extraction was done using Quecher's method. Final volume of extracted sample was analyzed by injecting the samples into the instrument (GC-MS, Agilent technologies). The GC–MS analysis was carried out with gas chromatograph connected with mass spectrometer for the analysis of pesticides in soil sample with following conditions: Oven program: 70 °C for 2min , then 25 °C/min to 150 °C for 0 min , then 3 °C/min to 200 °C for 0 min , then 8 °C/min to 280 °C for 1 min, carrier gas He(Total flow:36.272 mL/min) with splitless injection, column 1 (Agilent 19091S-433HP-5MS 5% Phenyl Methyl Silox): 325 °C: 30 m x 250 μm x 0.25 μm, Column 2 (AgilentRet. Gap) 400 °C: 0.6 m x 150 μm x 0 μm. MS parameters: Ion source: EI, Source temp. (^{0}C): 300.Water sample was extracted using solid phase extraction. Final volume of extracted sample was analyzed using GC-MS. The instrument conditions were similar as that was used for soil sample analysis.

III RESULTS AND DISCUSSION

The results of heavy metal concentration in soil and groundwater of Mansa Table 1. The permissible levels for the concentration of Hg, Pb, Se, As, Ni, Cd, Cr and Ba in agricultural soil as proposed by MOE are 0.16 $mgkg^{-1}$, 45 $mgkg^{-1}$, 1.2 $mgkg^{-1}$, 11 $mgkg^{-1}$, 37 $mgkg^{-1}$, 1 $mgkg^{-1}$, 67 $mgkg^{-1}$ and 210 $mgkg^{-1}$ respectively. These permissible limits signify a level of metals at which there is no threat to humans, if exposed for prolonged period of time. The level of Ni (47.7 $mgkg^{-1}$), Hg (23.8 $mgkg^{-1}$), Se (21.1 $mgkg^{-1}$) and Cd (3.1 $mgkg^{-1}$) in soil was observed to be above the permissible limits, as set by MOE. All other metals detected in soil were below the permissible limits. The level of Ba (0.066 mg L^{-1}) and Se (0.006 mg L^{-1}) detected in water is below the permissible limit (Ba-0.61 mg L^{-1}; Se-0.005 mg L^{-1}). Rest of the metals were BDL. The results presented above gave a clear indication of metal contamination in soil and groundwater of Mansa region.

The high level of Hg contamination detected in soil is a great concern. Both natural and anthropogenic sources are contributors of Hg in soil, and ~15% of which is contributed by fertilizers, fungicides, and municipal solid waste. Nervous system and kidneys are the main targets for Hg (ATSDR, 1999) [11]. Additionally, it has damaging influence on gastrointestinal tract, leading to nausea, diarrhoea, or severe ulcers. Rapid heart rate and increased blood pressure are some of the other symptoms associated with increased Hg level (ATSDR, 1999). The genotoxic potential of agricultural soil from Amritsar was correlated with the content of Hg in soil [12]. Hg has the potential to increase the risk of breast cancer by mimicking the effects of estradiol [13].

Current study also revealed higher concentration of Cd in soil. The Cd (3.1 $mgkg^{-1}$) concentration in soil observed in present study was higher than that of the Cd (1.39$mgkg^{-1}$) levels observed in the agricultural soil of Amritsar. In the same study, heavy metal content in soil was related to genotoxicity indicating that Cd can have its toxic effects even at smaller concentration [14].Phosphate fertilizers are the major contributors of Cd in soil in addition to other soil inputs [15]. Cd in the soil is taken up by the agricultural crops that leads to its accretion in food chain followed by its lethal effects on kidney, skeletal system and respiratory system in case of prolonged consumption [16]. International Agency for Research on Cancer (IARC) [17] has classified Cd as carcinogenic to humans (Group 1). Cadmium can modify the gene expression and signal transduction pathways and reduces activities of proteins involved in antioxidant defence, interfering with DNA repair and modifying cancer development and brain function [18].

The study showed elevated Ni levels in soil. Chemical fertilizers can cause considerable contamination of Ni in soil [19], and the increase concentration of Ni can adversely affect lungs and has the potential to cause lung cancer at increased levels. Further, it can cause cancer of nasal sinus (ATSDR, 2005) [20]. IARC consider some nickel compounds as carcinogenic to humans. Esophageal cancer prevalence is reported to be high in the regions where Ni levels in soil were excessively high [21].

Selenium (21.1 $mgkg^{-1}$) levels in soil in the present study were very much higher than the Se (4.08 $mgkg^{-1}$) reported in the agricultural soils of China. They also linked the high Se contamination of agricultural soil to its high presence in food further indicating its potential health risks [22]. Excessive Se can lead to selenosis. Decreased sperm counts, increased abnormal sperm, changes in the female reproductive cycle are the defects linked to increased Se levels (ATSDR, 2003) [23]. The epigenetic effects ofSe is known to play a key role in carcinogenesis [24].

The common factor between both the soil and water was the detection of Sr. In soil and water, normal levels of strontium are 0.2 $mgkg^{-1}$and 0.3 Bq L^{-1} (ATSDR, 2004) [25]. In the present study, Sr levels in soil and water is 9.6 $mgkg^{-1}$ and 0.986 mg L^{-1} respectively. Elevated Sr levels have been reported in the hair samples of cancer patients from Malwa region of Punjab. In the same study, they pointed out on fertilizers being responsible for heavy metal burden in Punjab [26]. Sr has its lethal influence on bone growth as it mimics calcium. When Ca is not present than Sr adversely affect bone metabolism leading to weakning of bones [27]. IARC classify radioactive strontium as carcinogenic to humans.

Table 1 Total heavy metal content of soil and groundwater collected from Mansa, Punjab (India).

BDL is referred to be Below detection limit

MDL is referred to be Method detection limit

Heavy Metals analyzed	MOE limits for soil (mgkg^{-1})	Conc. In soil sample (mgkg^{-1})	MOE limits for ground water (mg L^{-1})	Conc. In groundwater sample (mg L^{-1})
Ba	210	92.4	0.61	0.066
Ni	37	47.7	0.014	BDL(MDL:0.005)
Cr	67	37.5	0.011	BDL(MDL:0.005)
Hg	0.16	23.8	0.0001	BDL(MDL:0.0005)
Se	1.2	21.1	0.005	0.006
Pb	45	15.6	0.0019	BDL(MDL:0.005)
As	11	8.1	0.013	BDL(MDL:0.005)
Cd	1	3.1	0.0005	BDL(MDL:0.001)
Sr	----	9.6	----	0.986
Fe	----	14000	----	BDL(MDL:0.010)
Al	----	10700	----	BDL(MDL:0.010)

Furthermore, we embarked upon analyzing the extent of pesticides (Aldrin, Chlordane, DDE-o,p', DDE-p,p', DDD-o,p', DDD-p,p', DDT-o,p', DDT-p,p', Dieldrin, Endosulfan (α and β), Endosulfan Sulfate, HCH (α, β, γ, δ), Heptachlor, Heptachlor epoxide, Chorpyrifos, Dimethoate, Ethion, Fenvalrate, Malathion, Monocrotophos, Parathion, Phorate, PhorateSulphoxide, PhorateSulphone, Cypermetharin (I, II, III and IV) in soil and groundwater samples. The mass spectra of the sample obtained by GC–MS, clearly demonstrated the presence of cypermetharin in soil sample when compared with spectra ofthe standard compounds. Concentration of all other pesticides is BDL. Fortunately, no pesticides were detected in water sample (Fig 2). Carcinogenic potential of cypermetharin has been reported previously [28]. Alpha-cypermetharin is shown to have genotoxic effects [29].

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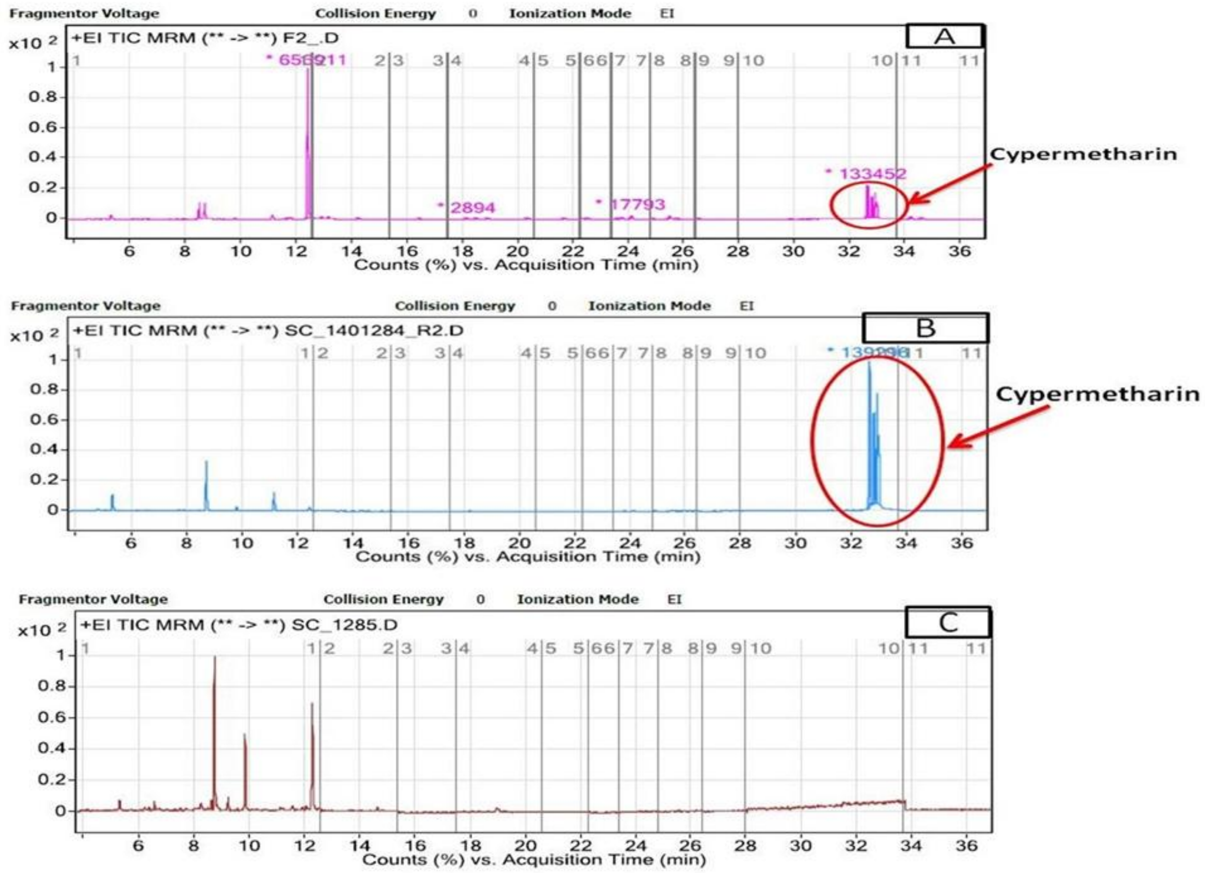

Figure 2GC-MSchromatograms of pesticides in soil and water compared with standard. (A) Standard (B) Soil (C) Water

III CONCLUSION

The present study outlined the heavy metal and pesticide profile in soil and groundwater samples of Mansa district. Due to modern agricultural practices, the presence of such pollutants was expected. The significantly high level of Ni, Hg, Se, Cd were observed in soil. High levels of Sr are observed in both soil and groundwater samples. Altogether, the results depict the poor quality of soil and groundwater in the area. These chemical inputs will definitely be having detrimental effects on human health as the incidence of cancer, asthma, kidney, skin, digestive tract diseases, heart ailments, male infertility, female reproductive disorders are increasing in Punjab. So, this type of study is a health alert to make people aware of what they are actually consuming and it is the right time that farmers should now move towards organic farming to improve the crop quality.

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