



ASSESSMENT OF ARSENIC HEAVY METAL IN AGRICULTURAL SOIL NEAR TEXTILE INDUSTRY: DETRIMENTAL TO HUMANS

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ABSTRACT

This study aims to assess the values of arsenic in soil of different villages of malwa region especially in barnala district (Punjab,India) and their harmful effects on human health. Samples of soil were collected from agricultural fields of four different villages of barnala region such as Rure ke kalan, Gunas, Handiaya, and Cheema from five different layers (0-10cm; 10-20cm; 20-30cm; 30-40cm and 40-50cm depth).There are three industrial sites in barnala district and these four villages are

located near to these industrial sites. In this study,adverse effect of different industries on fields of these four villages were investigated. Handiaya village has high value of arsenic while Gunas village has lowest value of arsenic. The concentration of arsenic was determined by Flame Atomic Absorption Spectrometry. Arsenic enter into human body through water, soil and food. Due to high value of arsenic people may suffer from irritation of stomach and intestines, blood vessel damage, skin changes, and reduced nerve function.

Keywords- Heavy metal, Arsenic, soil contamination, Human health, Textile industries

Introduction-

Arsenic is a naturally occurring element that is widely distributed in the earth's crust. Arsenic is classified chemically as a metalloid, having both properties of a metal and a nonmetal; however, it is frequently referred to as a metal. Elemental arsenic (sometimes referred to as metallic arsenic) is a steel grey solid material. However arsenic is usually found in the environment combined with other elements such as oxygen, chlorine, and sulphur. Arsenic combined with these elements is called inorganic arsenic. Arsenic combined with carbon and hydrogen is referred to as organic arsenic. Arsenic cannot be destroyed in the environment. It can only change its form, or become attached to or separated from particles. It may change its form by reacting with oxygen or other molecules present in air, water, or soil, or by the action of bacteria that live in soil or sediment. Since arsenic is found naturally in the environment. Human beings can be exposed to some arsenic by eating food, drinking water, or breathing air. Children may also be exposed to arsenic by eating soil. The

concentration of arsenic in soil varies widely, generally ranging from about 1 to 40 parts of arsenic to a million parts of soil (ppm) with an average level of 3-4 ppm. The concentration of arsenic in natural surface and groundwater is generally about 1 part in a billion parts of water (1ppb), but may exceed 1,000 ppb in contaminated areas or where arsenic levels in soil are high. Groundwater is far more likely to contain high levels of arsenic than surface water. Levels of arsenic in food range from about 20-140 ppb. However, levels of inorganic arsenic, the form of most concern, are far lower.

Soil pollution by heavy metals is a significant environmental problem worldwide (Alloway 1995). In particular heavy metal pollution of surface soils due to intense industrialization and urbanization has become a serious concern in many developing countries (Mireles et al. 2012; Wei and Yang 2010; Yaylah-Abanuz 2011). The accumulation of heavy metals in surface soils is affected by many environmental variables, including parent material and soil properties as well as by human activities, such as industrial production, traffic, farming, and irrigation. Large areas of land can be contaminated by heavy metals

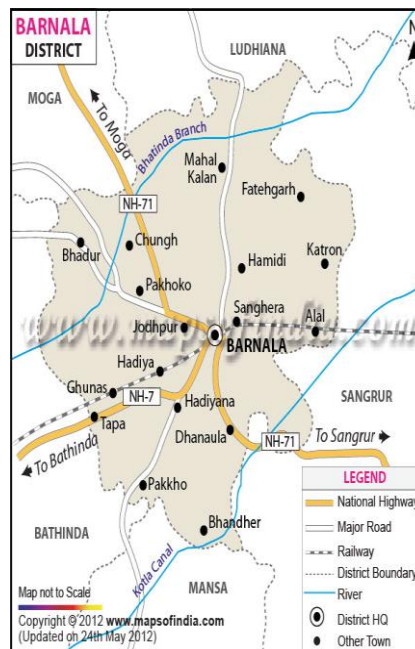
released from smelters, waste incinerators, industrial wastewater. Irrespective of their source in the soil, accumulation of heavy metals can degrade soil quality, reduce crop yield and the quality of agricultural products and thus negatively impact the health of human, animals and the ecosystem (Nagajyoti et al. 2010). It is important to identify the sources of heavy metals, besides quantifying their concentrations and spatial variability in the soils. The rapid industrialization and urbanization over the past three decades has brought significant environmental problems to the region.

MATERIALS AND METHODS-

Barnala (Punjab, India) is situated between 30° 23' North and 75° 33' East. It has a mean elevation of 227 meters (745 feet). It is located on the Bathinda-Chandigarh highway (no-7) and the Jalander-Rewari national highway (no-71), The Sirsa-Ludhiana state highway (no-13) are passes through it. It is 65 km from Bathinda and 85 km from Ludhiana. According to 2011 census, the total population of Barnala district is 595527. It was 526931 in 2001. Soil samples were collected from four different sites. 1st site is Rure ke kalan village which is at Barnala-Mansa Road in District Barnala 148107, Punjab. 2nd site is Gunas

village which is located in Barnala District 148108, Punjab. 3rd site is Handiaya village is located in Barnala District 148107, Punjab. 4th site is Cheema village is located in Barnala Tehsil of Barnala district 148103, Punjab, India.

MAP OF BARNALA DISTRICT-



Sample collection-

The sampling time was between 4:30 pm to 5:30 pm on 9th November, 2016. Plastic polythene bags were used to collect soil samples. Within 48 hours samples were carried to laboratory for testing in order to prevent the deterioration of soil samples. Testing was done in Environ Tech Laboratories (NABL Accredited Laboratory) Department of Science and

technology, India S.A.S nagar (Mohali), Punjab. Soil samples were collected from agricultural fields of four villages such as Rure ke kalan, Gunas, Handiaya and cheema which are present near to industrial sites. These four villages are located in Barnala district (Punjab, India). Soil samples were collected from five sampling depths 0-15 cm, 15-30 cm, 30-45 cm, 45-60 cm and 60-75 cm. Five sub-samples were taken within an area of 100 m² from each sampling location. About 1 kg weight of each sub-sample were collected. The collected soil samples were dried at 60 °C, sieved through a 2.0-mm Nylon sieve to remove sand, gravel, and plant debris, and stored in glass bottles at room temperature.

Samples (20 g) of dried soils were finely powdered by an agate ball-grinder and sieved to pass 0.15-mm Nylon sieve. The powdered samples (0.2 g) were then digested by trace metal grade acids (9.0 mL of HNO₃ and 3.0 mL of HF) using a microwave digestion system.

Determination of Arsenic heavy metal in soil by Tri-Acid Mixture Digestion Method using AAS-

1. Apparatus and Reagents

a) Tri-acid mixture:- Mix 10 parts of conc.HNO₃, 1 part of Conc.H₂SO₄ and 4 parts of HClO₄

b) Conical flask, 250 ml capacity

c) Hot plate

d) Whatman filter paper No.42

e) AAS

2. Preparation of sample

a) Take 5.0 gm of oven dried (105°C) sample thoroughly ground and sieved through 0.2 mm sieve in a conical flask

b) Add 30 ml tri-acid mixture, cover it with a small glass funnel for refluxing. Digest the sample at 200°C on a hotplate till the volume is significantly reduced with a whitish residue

c) After cooling, filter the sample with whatman filter paper No.42, make up to 100 ml in a volumetric flask with distilled water.

3. Analysis

In case of Arsenic, treat the sample with sodium boro hydride (NaBH₄) in hydride generation assembly attached to AAS.

4. Principle

The metals in different matrix wastes, in general, are digested in mineral acids, viz., nitric acid, hydrochloric acid, etc. and mixture of mineral acid.

The digested metal ions in solutions are estimated using atomic absorption spectrophotometer.

5. Apparatus and materials-

- a) Electric Hotplate
- b) Hot air Oven
- c) Porcelain Crucible 25,50 ml capacity
- d) Analytical Balance with 0.001 gm accuracy
- e) AAS with all necessary accessories for its operation
- f) Usual Lab. Glassware.

6. Reagents

- a) Conc. HNO₃ AR grade
- b) Conc. HCl AR grade
- c) H₂O₂ (30%) AR grade
- d) Double distilled water (DDW) with a conductivity less than 3 μS/cm
- e) Dil. HNO₃ (1:1) – Mix equal volume of conc. HNO₃ and DDW
- f) Dil. HCl (1:1) – Mix equal volume of conc. HNO₃ and DDW
- g) Reagent Blank Solution:- Slowly add 100 ml conc. HNO₃ to 250 ml DDW in 1 liter volume flask with constant cooling. Add 30 ml H₂O₂ followed by 50 ml Conc. HCl with cooling under tap water. Make up the solution to 1 liter with DDW.
- h) Stock Standard solution :- It may be prepared from high purity metals, metal oxide or non-hygroscopic reagent grade salts using HCl or HNO₃. All salts must be dried for one hour at 105°C, unless otherwise specified.

7. Sample Preparation

- a) weigh a representative sample of 1.0 to 2.0 g portion and transfer to 250 ml beaker.
- b) Add 10 ml of 1:1 HNO₃, mix the slurry and cover the beaker with a watch glass. Heat the contents of beaker to 95°C reflux for 10 to 15 minutes without boiling.
- C) Allow the sample to cool, add 5 ml Conc. HNO₃, replace the watch glass and reflux for 30 minutes.
- d) Allow the solution to evaporate to 2 to 3 ml volume of solution.
- e) Cool the sample, add 2 ml DDW and 3 ml of H₂O₂. Cover the beaker with watch glass and return the covered beaker to the hot plate for warming and to stall the peroxide reaction. Heat the beaker until the effervescence subsided and cool the beaker.
- f) Continue to add H₂O₂ in 1 ml aliquots with warming until the effervescence is minimal. Do not add more than 10 ml H₂O₂.
- g) Add 5 ml of Conc. HCl and 10 ml of DDW. Return the covered beaker to hot plate and reflux for an additional 15 minutes without boiling.
- h) After cooling, dilute to 100 ml with DDW. Filter the sample. The diluted digested solution contains approximately

5%(v/v) HNO₃. The sample is now ready for analysis by flame AAS.

8. Analytical Procedure

Prepare a series of working calibration standard metal solutions (minimum 5 working standards for each metal) in the working range. Follow the AAS operating instructions to operate the AAS instrument. Prepare and run the reagent blank along with the sample and standards.

9. Preparation of standard of Arsenic-

Dissolve 1.3203 gm of arsenious oxide (As₂O₃) in a minimum volume of 20% (w/v) KOH. Neutralize with HNO₃ to a phenolphthalein end point. Dilute to 1 liter with 1% HNO₃ to give 1000 ppm As solution.

10. Operation

1. Power on from UPS

2. Open gases and set out Pressure AIR = 2-4(3kg/cm²), Acetylene C₂H₂ = 1-1.5(3kg/cm²), Argon=3kg/cm²

3. Switch on main unit of AAS from Power button.

4. Switch on PC and double click on Icon "AAS 7000 SP Analysis System" on desk top of PC.

5. AAS Data Analysis System AA7000 asp work stat window will appear. Click on this window.

6. Initialize Device screen will appear and then disappears after 5 second.

7. Go to icon tool bar and click "Analysis" and click at set instrument Parameter (F7).

8. window "set instrument Parameters will appear. Select element HCl Lamp of interest. Set wavelength, method etc. Then Click at "Next" select element lamp screen will appear. When successes appear then click at "close"

9. Auto set parameters window will appear. Wait for 15-20 minutes for warm up the lamp.

10. Then click at "scan" when completed click "Adjust lamp", adjust lamp position screen will appear. Close the window 5 seconds after adjustment.

11. Click at "balance" screen "energy balance" will appear where status shows balance-4. Now click OK and then "Finish".

12. Now go to "file" at toolbar and click at new project. Window will appear, write "project name", "description" and "conc. Units" in their columns. Select measuring method as "standard curve" and calibration line as "crossing from origin", put 3 at measure time. Enter standards (0.5,1.0,2.0...) and click "Finish".

13. The window will appear. Then go to "control" at toolbar. And click at "set fuel gas flow rate. A window will appear, put

value 2.0 and click set. Then ignite the instrument by pressing ignition button till flame appears. Adjust flame by putting value 1.7 in place of 2.0 then click close.

14. Now inject double distilled water and click “Auto balance” on tool bar. Now go to “Analysis” then “auto zero”. Click “start” and blank and then inject

“blank”. Click 3 times in each case of blank or samples. Inject all samples one by one while putting distilled water between each sample as per PC demand. The window will appear with analysis date.

0-15	3.8
15-30	4.2
30-45	4.5
45-60	4.8
60-75	5.2
Mean ± S.D	4.5 ± 0.538

Table 4 of Site D

Depth of soil (cm)	Conc. Of Arsenic (mg/kg)
0-15	3.1
15-30	3.5
30-45	3.8
45-60	4.1
60-75	4.4
Mean ± S.D	3.78 ± 0.506

RESULTS AND DISCUSSION

Table 1 of Site A

Depth of Soil (cm)	Conc. Of Arsenic (mg/kg)
0-15	3.3
15-30	3.6
30-45	4.0
45-60	4.2
60-75	5.1
Mean ± S.D	4.04 ± 0.687

Table 2 of Site B

Depth of soil (cm)	Conc. Of Arsenic (mg/kg)
0-15	2.5
15-30	2.7
30-45	2.9
45-60	3.4
60-75	3.9
Mean ± S.D	3.08 ± 0.567

Table 3 of Site C

Depth of soil (cm)	Conc. Of Arsenic (mg/kg)
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In case of site A the values of Arsenic of the Soil samples ranged from 3.3 mg/kg to 5.1 mg/kg with an average value of 4.04 mg/kg (S.D = 0.687, N=5). The highest value of Arsenic was found in Depth of 60-75cm of soil and lowest value of Arsenic was found in soil sample taken from depth of 0-15cm.

In case of site B the values of Arsenic of the soil samples ranged from 2.5 mg/kg to 3.9 mg/kg with an average value of 3.08 mg/kg (S.D = 0.567, N= 5)

In case of site C the values of Arsenic of the soil samples ranged from 3.8 mg/kg to 5.2 mg/kg with an average value of 4.5 mg/kg (S.D = 0.538, N=5).

In case of site D the values of Arsenic of the soil samples ranged from 3.1 mg/kg to 4.4

mg/kg with an average value of 3.78 mg/kg (S.D = 0.506, N=5).

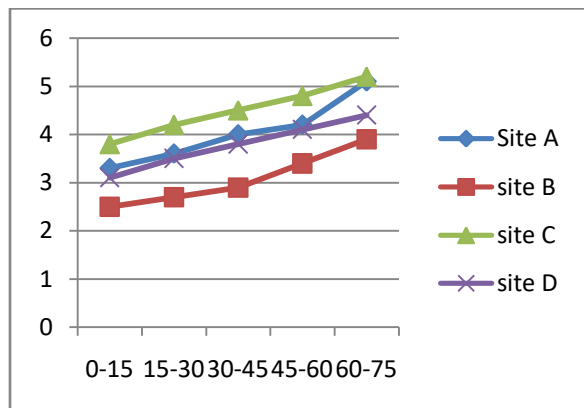


Table 5

Site	Absorption (X)	Conc. Of Arsenic(µg/L) (Y)
A	0.3033	14.8492
B	0.1841	8.6279
C	0.3409	16.8116
D	0.2655	12.8763

Statistical analysis:

The data obtained subjected to statistical analysis. In statistical analysis, a correlation developed between Absorption (nm) and Conc. Of Arsenic in µg/L by using KARL PEARSONS Coefficient of correlation.

Calculation of KARL PEARSON'S

Coefficient of correlation:

Correlation coefficient between Absorption (X) and Conc. (Y) calculated as

$$r = \frac{\sum xy}{\sqrt{\sum X^2 + y^2}} = 0.999$$

Where $x = X - \bar{X}$, $y = Y - \bar{Y}$, $X = \frac{\sum X}{n}$, $Y = \frac{\sum Y}{n}$

$$n$$

where n is the number of sites

For good correlation value of r should be between $-1 < r < 1$.

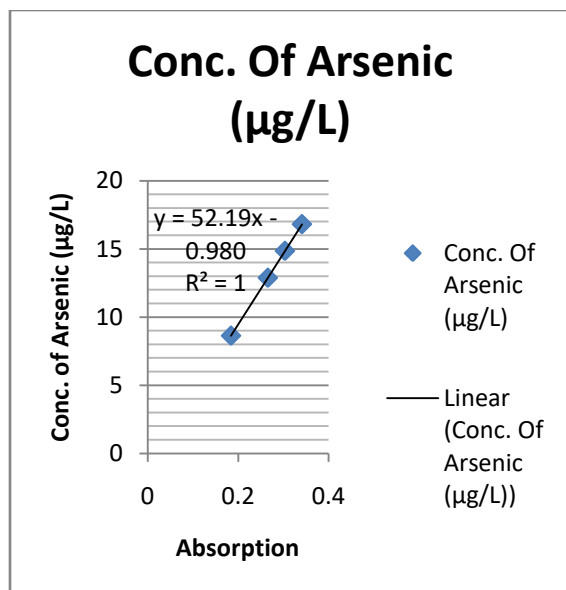
Calculation of Regression equation:

The term regression stands for some sort of functional relationship between two or more related variables. It measures the nature and extent of correlation and predicts the unknown values of one variable from known values of another variable. Following regression equation is used to established correlation between Absorption and Conc. Of Arsenic.

$$Y - \bar{Y} = byx (X - \bar{X})$$

The above equation called regression line equation of Y on X and byx called regression coefficient of Y on X and calculated as

$$byx = \frac{\sum XY}{\sum X^2}$$



Harmful effects of Arsenic-

Heavy metals released by textile industries reach the human body through water and crops. Heavy metal such as arsenic seep into the soil and underground water, when this underground water is used for irrigation of crops, these have harmful effect on human health due to eating these crops. Due to Increase of Conc. Of arsenic in human body, production of red and white blood cells may decreases. People may also suffer from abnormal heart rhythm, blood- vessel damage and high risk of cancer in skin, liver, lungs etc.

CONCLUSION

From the above results and discussion it is concluded that concentration of arsenic increases with increase in depth of soil.

When arsenic reaches human body through crops these may cause man suffer from cancer of skin, liver, lungs etc.

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