
TRACE ELEMENTS CONCENTRATION DETERMINATION IN WATER FROM KEANA MINE AREA USING THE INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY (ICP – OES)

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ABSTRACT

Water samples across Keana Salt mine area of Nasarawa State were subjected to elemental analysis by Inductively Coupled Plasma Optical Emission Spectrometry technique, with the aim of building upon the information in the database of trace element concentration in water from the area and to assess the extent of environmental hazard or otherwise. The analysis was carried out at the department of Geology and Mining of the University of Jos. A total of 8 water samples were drawn from sources across the study area, comprising of 4 Stream samples and 4 Borehole samples. Analysis was carried out for a total of seven (7) elements which included As, Cd, Cr, Sr, Pb, Zn and Th. Arsenic (As) was detected in all the samples at a mean concentration of $(0.19 \pm 0.02 \text{ mg/L})$ which is very high when compared with the recommended maximum permissible value of 0.010 mg/L by the Environmental Protection Agency. The mean concentration of Sr in the samples was $(0.76 \pm 0.02 \text{ mg/L})$. The maximum permissible concentration for this element vary from 0.8 – 5.0 mg/L, therefore the concentration detected may just be acceptable. These observations suggest that water from the study area should be closely monitored to reduce its harmful effects on the environment and health of the inhabitants.

KEYWORDS: *Mining, Inductively Coupled Plasma Optical Emission Spectroscopy, Trace Elements, Elemental Concentration.*

INTRODUCTION

Mining activities have been carried out in Nigeria since the beginning of last century and some of the mines have been listed by Adetunji et al (2005) to include:- tin mining, coal mining, uranium mining, clay mining, salt mining and so on. Exploitation of mineral resources has assumed prime importance in several developing countries including Nigeria and have contributed immensely to the national wealth with associated socio-economic benefits to the host communities (Adetunji et al 2005). Mineral resources are an important source of wealth for a nation but before they are harnessed, they have to pass through the stages of exploration, mining and processing (Adekoya, 2003; Ajakaiye, 1985). Each of these stages has both health and environmental implications (Aigbedion and Iyayi, 2007). These desirable effects are overshadowed by the adverse effects that have been listed by Olaleye and Oluyemi (2010). Aigbedion and Iyayi (2007), Mokobia et al (2006) and Mokobia and Balogun (2004) to include ecological disturbances, destruction of natural flora and fauna, pollution of air, land and water, instability of soil and rock masses, landscape degradation and radiation hazards development (Aigbedion and Iyayi, 2007). H₂O (two parts hydrogen and one part oxygen) is a substance also known as water and is one of the most essential elements to health. It is a recognized reality that clean water is completely essential for healthy living. When the quality of water is altered by the presence of toxic waste or when there is variation in the natural composition, it tends to

cause harm to life, and environment if ingested. The toxic waste or foreign materials are called pollutants. Drinking water can become contaminated at the original water source, during treatment, or during distribution to the home. Many investors are mindless of the environmental consequences of their mining activities so long as it does not disrupt production at their factories. A plan of action to ameliorate some of these effects can only be effective if there is information on the elemental composition of the mineral deposit that is been mined. Such information can be generated by highly technical procedures. Amodu (2010) has listed some of these techniques to include the Atomic Absorption Spectrometer (AAS), X-Ray Fluorescence (XRF), Particle Induced Gamma Ray Emission (PIGE), Instrumental Neutron Activation Analysis (INAA) and Particle Induced X-ray Emission (PIXE). This study aims in building upon the information in the database of trace element concentration in water from the area and to assess the extent of environmental hazard or otherwise. The analysis was carried out using the Inductively Coupled Plasma Optical Emission Spectroscopy at the department of Geology and Mining of the University of Jos. Some of the examples of the application of ICP – AES include: The determination of trace elements geochemistry of the Keana brines field (Lar and Sallam, 2005), metals in wine (Aceto et al, 2002), Arsenic in food (Benramdane et al, 1999) and trace elements bound to proteins (Ma et al,2004). ICP – AES is often used for the analysis of trace elements in soil and it is for that reason it is often used in forensics to ascertain the origin of the soil samples found at crime scenes or on a victim. It is fast becoming the analytical method choice for the determination of nutrient levels in agricultural soils. This information is used to calculate the amount of fertilizer required to maximize crop yield quality.

MINING ACTIVITIES IN THE AREA

Mining activities is carried out here on a large scale and small scale. The operations are carried out by hand, by hydraulic dredging and by dredging depending on the scale of the operator. The first stage of salt mining in this area is the extraction of the material from the ground, which results in the exhumation of naturally occurring radioactive materials buried into the soil to the surface soil layer. A treatment plant separates the minerals from the impurities. These impurities also known as mine tailings (waste associated with sand and soil) are not confined to a point but rather dumped in heaps all over the environments. These uses of the tailings in whatever form provides another source of exposure in the environment, which may cause health hazard for the members of the public.

LOCATION

The specific areas of study are all indicated on figure 1.1

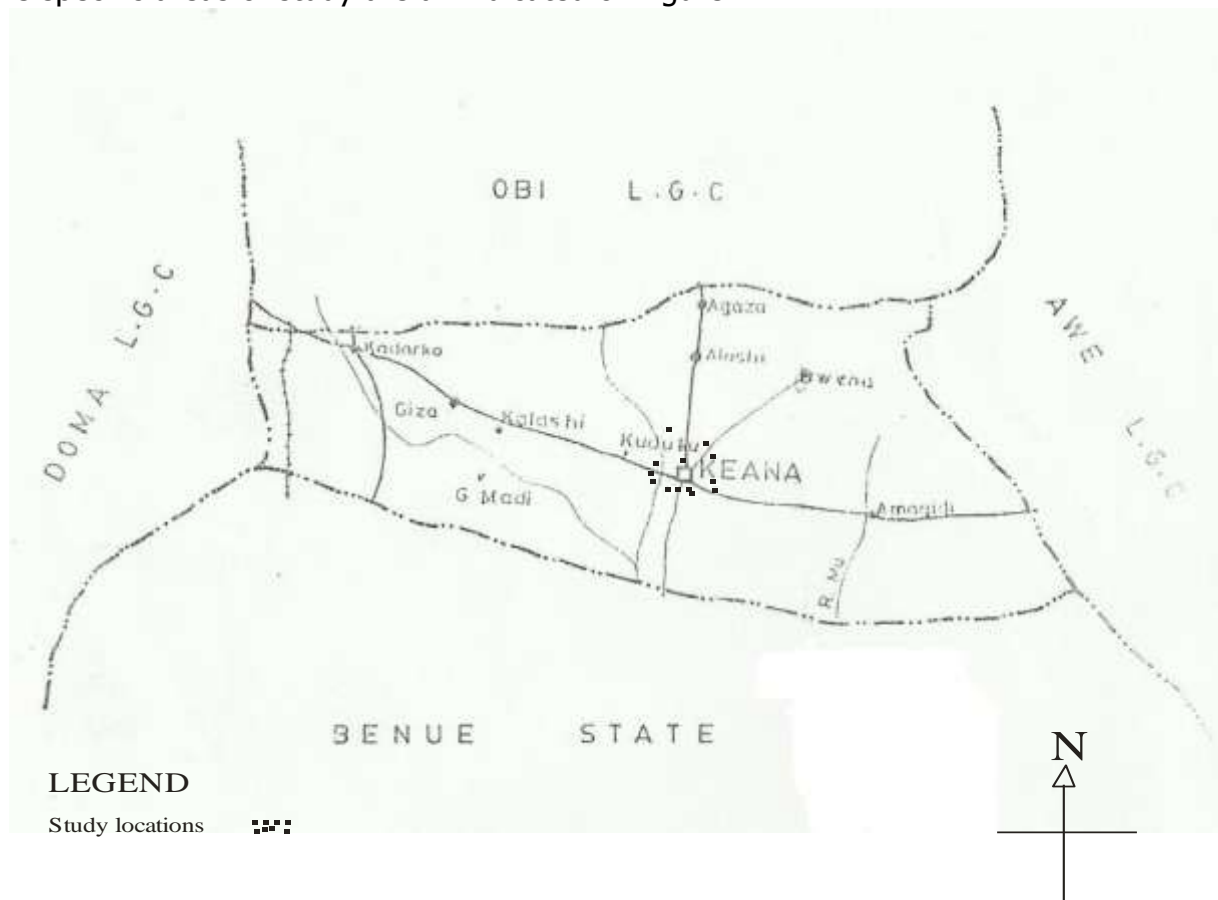


Figure 1.1: Political Map of the Study Area.

MATERIALS AND METHODS

Sample Collection

The sample was collected at Keana mine of nasarawa state, both within and around the immediate physical environment of Keana mine. The details of its location, climate, relief, as well as geology of the area had previously been discussed (Obaje et al, 2007).

A total of eight (8) sampling locations comprising of four (4) Bore Hole (BH) and four (4) streams (ST) were selected based on population distribution and degree of usage. The sample collection sites and specific locations are shown in Figure 1.1. The sample collection was done during the dry season. Generally the samples were collected in such a way that there is adequate representation of the whole study area. Each sample were collected in a 250ml container which had been thoroughly washed with dilute H_2SO_4 , rinsed with dilute water and dried. Each container were firmly sealed to prevent cross contamination. Water from the wells were done by employing the usual manual procedure for collection by the local users. Before collection of water from the borehole, the faucet was first turned on at full speed for several minutes to purge the plumbing system of any water which have been there for some time. The faucet was thereafter turned down to a low flow rate to reduce turbulence.

Sample Preparation

The following methods were used in sample preparation prior to measurement. The samples collected were acidified at point of collection. This is to stabilize the metals so as not to lose some of the elements (metals). The samples were then taken to the laboratory of the department of geology and mining where the water was first filtered and the machine is calibrated with the metals of interest which are As, Cd, Cr, Sr, Pb, Zn and Th. The sample is then introduced via the peristaltic pump to the nebulizer of the ICP – OES machine for analysis. In this system an aqueous sample was introduced into the ICP by a peristaltic pump (Perkin-Elmer) at a constant rate of 1.0 ml per minute. This solution stream was nebulized into a Scott type spray chamber by a cross-flow nebulizer and then introduced into the plasma. Argon was used as the nebulizing gas. The computer system was used for data acquisition and data reprocessing. The software used to control the Optima 3000 XL is Perkin-Elmer Winlab (version 1 .06). The data were manipulated using commercially available software (Microsoft Excel 2003) for results.

INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROSCOPY (ICP-OES)

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) or Inductively Coupled Plasma Atomic Emission Spectrometry (ICP – AES) is an analytical technique that performs elemental analysis with excellent sensitivity. The ICP-OES can simultaneously measure most elements in the periodic table and determine analyte concentrations down to the sub nanogram per liter, or parts per trillion (ppt), level. It can perform qualitative, semiquantitative, and quantitative analysis, and compute isotopic ratios on water samples, and in waste extracts and digests. It is a type of emission spectroscopy that uses the Inductively Coupled Plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element (Stefansson et al, 2007, Mermet, 2005).

Principle of Operation

The ICP – AES is composed of two parts: The ICP torch and the optical spectrometer. When the torch is turned on, an intense electromagnetic field is created within the coil by the high power radio frequency (RF) signal flowing in the coil. Argon gas is typically used to create the plasma. The argon gas flowing through the torch is ignited with a Tesla Unit that creates a brief discharge arc through the argon flow to initiate the ionization process. Once the plasma is ignited, the tesla unit is turned off. The argon gas is ionized in the intense electromagnetic field and flows in a particular rotationally symmetrical pattern towards the magnetic field of the RF coil. A stable high temperature plasma of about 7000K is then generated as the result of the inelastic collision created between the neutral argon atoms and charged particles. A peristaltic pump delivers an aqueous or organic sample into the nebulizer where it is changed into mist and introduced directly inside the plasma flame. The sample immediately collides with the electrons and charged ions in the plasma and is itself broken down into charged ions. The various molecules break up into their respective atoms which then lose electrons and recombine repeatedly in the plasma, giving off radiation at characteristic wavelength of the elements involved. After the radiations are separated into its different wavelengths (colours), their intensities are measured with a photomultiplier tube or tubes physically positioned to view the specific wavelength for each element line involved or in more modern units. The separated

colours fall upon an array of semiconductor photo detectors such as charged coupled devices (CCDs). In units using these detector arrays, the intensities of all wavelength (within the system range) can be measured simultaneously allowing the instrument to analyse for every element to which the unit is sensitive at once. Thus, samples can be analyse very quickly. The intensities of each line is then compared to previously measured intensities of known concentrations of the elements and their concentrations are then computed by interpolation along the calibration lines.

RESULTS

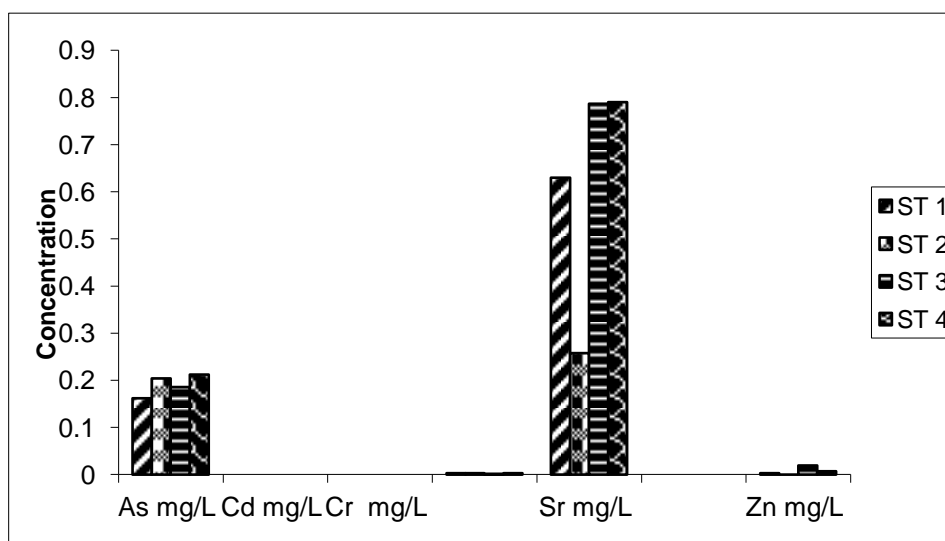
Results of Elemental Concentration of Stream Samples Across The Study Area:

The results from ICP-OES analysis of stream samples across the study area is shown in table 4.1 while a bar chart showing distribution of elements and their concentrations from well samples across the study area is shown in Fig 4.1.

Table 4.1 Results from ICP- OES analysis of stream samples across the study area

| Samples | As (mg/L) | Cd (mg/L) | Cr (mg/L) | Pb (mg/L) | Sr (mg/L) | Th (mg/L) | Zn (mg/L) |
|---------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| ST 1 | 0.162 | 0 | 0 | 0.003 | 0.630 | 0 | 0.003 |
| ST 2 | 0.204 | 0 | 0 | 0.003 | 0.258 | 0 | 0.001 |
| ST 3 | 0.186 | 0 | 0 | 0.002 | 0.787 | 0 | 0.019 |
| ST 4 | 0.212 | 0 | 0 | 0.003 | 0.790 | 0 | 0.007 |

Fig 4.1 A bar chart showing distribution of elements and their concentrations from stream samples



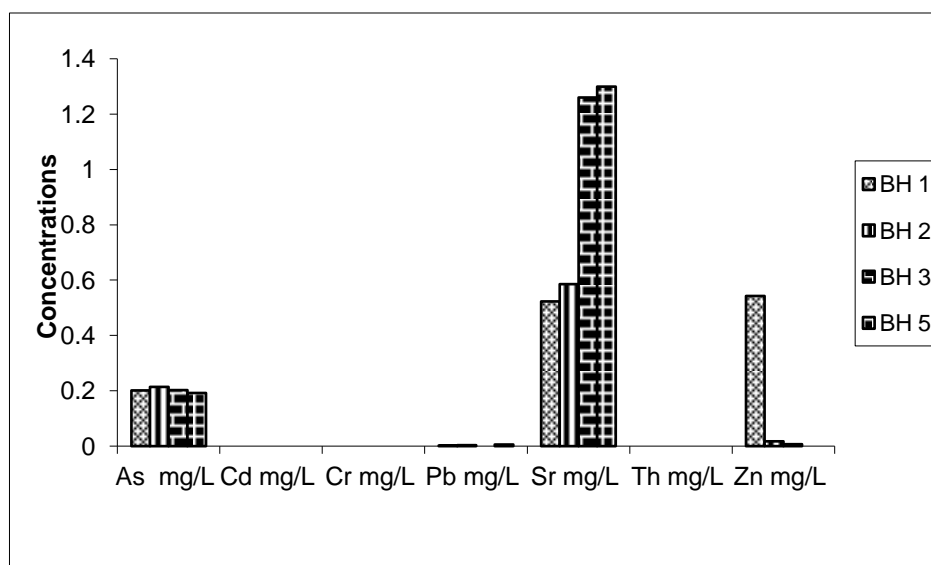
Results of Elemental Concentration Of Borehole Samples Across The Study Area:

The results from ICP-OES analysis of borehole samples across the study area is shown in table 4.2 while a bar chart showing distribution of elements and their concentrations from borehole samples across the study area is shown in Fig 4.2.

Table 4.2 Results from ICP- OES analysis of borehole samples across the study area

| Samples | As (mg/L) | Cd (mg/L) | Cr (mg/L) | Pb (mg/L) | Sr (mg/L) | Th (mg/L) | Zn (mg/L) |
|----------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| BH 1 | 0.201 | 0 | 0 | 0.003 | 0.523 | 0 | 0.543 |
| BH 2 | 0.214 | 0 | 0 | 0.004 | 0.585 | 0 | 0.018 |
| BH 3 | 0.202 | 0 | 0 | 0.000 | 1.26 | 0 | 0.007 |
| BH 5 | 0.192 | 0 | 0 | 0.006 | 1.299 | 0 | 0.000 |

Fig 4.2 A bar chart showing distribution of elements and their concentrations from Borehole samples across the study area.



DISCUSSION

Bar graph for elemental concentrations from stream samples across the study area:

A bar chart for the distribution of elements and their concentration in stream samples is shown in fig 4.1 from the study area.

- The concentration of Arsenic (As) ranged from 0.162 – 0.212 mg/L.
- The concentration of Lead (Pb) ranged from 0.002 – 0.003 mg/L.
- The concentration of Strontium (Sr) ranged from 0.630 – 0.790 mg/L.
- The concentration of Zinc (Zn) ranged from 0.001 – 0.019 mg/L.
- The concentration of Chromium (Cr), Cadmium (Cd) and Thorium (Th) were undetected in all the samples.

It is clear from the above values that:

1. Arsenic (As) had high mean concentration of 0.191 mg/L since the recommended safety value is 0.010 mg/L of 01-03-2006 by the EPA.
2. Lead (Pb) had low mean concentration of 0.002 mg/L since the recommended safety value of concentration is 0.015 mg/L.WHO (2011).
3. Strontium (Sr) had low mean concentration of 0.616 mg/L since the recommended safety value of concentration is 0.8 – 5.0mg/L.WHO (2011).
4. Zinc (Zn) had low mean concentration of 0.007 mg/L since the recommended safety value of concentration is 5 mg/L by the WHO (2011).

Bar graph for elemental concentrations from borehole samples across the study area:

A bar chart for the distribution of elements and their concentration in borehole samples is shown in fig 4.2 from the study area.

- The concentration of Arsenic (As) ranged from 0.192 – 0.214 mg/L.
- The concentration of Lead (Pb) ranged from 0.000 – 0.006 mg/L
- The concentration of Strontium (Sr) ranged from 0.523 – 1.299 mg/L
- The concentration of Zinc (Zn) ranged from 0.000 – 0.543 mg/L
- The concentration of Chromium (Cr), Cadmium (Cd) and Thorium (Th) were undetected in all the samples.

It is clear from the above values that:

- Arsenic (As) had high mean concentration of 0.202 mg/L than the recommended value of 0.010 mg/L of 01-03-2006 by the EPA.
- Lead (Pb) had low mean concentration of 0.003 mg/L since the recommended safety value of concentration is 0.015 mg/L.WHO (2011).
- Strontium (Sr) had low mean concentration of 0.916 mg/L since the recommended safety value of concentration is 0.8 – 5.0mg/L.WHO (2011).
- Zinc (Zn) had low mean concentration of 0.142 mg/L since the recommended safety value of concentration is 5mg/L by the WHO (2011).

RESEARCH SUMMARY

The presences of some trace elements were determined in all the water samples under the study area. The study made certain findings which are summarized below:

1. The concentration of As across the whole study area ranged from 0.068 – 0.214 mg/L.
2. The concentration of Pb across the whole study area ranged from 0.000 – 0.006 mg/L.
3. The concentration of Sr across the whole study area ranged from 0.349 – 1.299 mg/L.
4. The concentration of Zn across the whole study area ranged from 0.000 – 0.543 mg/L.
5. The concentrations of Cd were detected in only well 1 sample of 0.001 mg/L while Cr and Th were undetected in all the samples.

The main concern is the concentration contribution of some of this trace elements of water studied. There is however no justifiable basis for comparing the intake levels of

different studies since there are variations in consumption rates. The dietary intakes are probably normal within the countries and regions for which they are determined.

CONTRIBUTION TO KNOWLEDGE

The concentration rates of as are high in all the samples and the risk of health effect to a limit concentration of 0.010 mg/L (which is the international acceptable standard for the general public) and above is high.

This work has provided scientific data on the concentration of some of these trace elements in these areas, which can be used by the health experts to confirm and take vital decisions regarding possible health and the environmental hazards in these areas.

RECOMMENDATIONS

The following recommendations are made for future research work and the protection of the health of the inhabitants in the area:

- Investigation of the trace elements concentration in the water samples during the rainy season should be carried out.
- The trace elements concentration of food items grown in the area should be carried out.
- Blood samples of the inhabitants of those living around the mine area should be carried out to determine the ailment suffered by them as a result of these high concentrations of some trace elements from mining activities.
- Raise public awareness and strengthen community organizations to combat illegal mining activities.
- The government should establish a mechanism to observe and follow up whether permit procedure is efficient and controlled.
- Banning of Mining in sensitive and vulnerable areas by the government authorities should be done.
- Government should enforce law in an efficient and unbiased way.
- The community should restore damaged and affected natural environment using natural barriers such as tree plantations.
- The community should stop political and other interferences when issuing permits and enforcing law.

CONCLUSION

Based on the findings from this work, the concentration rates of some trace elements in the study area were determined. The concentration rates of as were found to be above the recommended standard rates acceptable for the general public. This study shows that there is the need therefore to protect the environment for adequate health and well being of the people as well as to conserve and use sustainable environment and natural resources for the benefit of the present and future generations.

APPENDIX : A - E**WATER CONTAMINATION LIMIT DECREED BY THE ENVIRONMENTAL PROTECTION AGENCY (EPA)****APPENDIX A: Micro – Organisms**

| Contaminants | MCL or TT (mg/L) | Potential Health Effects from Ingestion of Water | Sources of Contaminant in Drinking Water |
|--|-------------------------|---|---|
| Cryptosporidium | TT | Gastrointestinal illness (e.g., diarrhea, vomiting, cramps) | Human and fecal animal waste |
| Giardia lamblia | TT | Gastrointestinal illness (e.g., diarrhea, vomiting, cramps) | Human and animal fecal waste |
| Legionella | TT | Legionnaire's Disease, a type of pneumonia | Found naturally in water; multiplies in heating systems |
| Total Coliforms (including fecal coliform and E. Coli) | 5.0% | Not a health threat in itself; it is used to indicate whether other potentially harmful bacteria may be present | |

APPENDIX B: Disinfectants

| Contaminant | MRDL (mg/L) | Potential Health Effects from Ingestion of Water | Sources of Contaminant in Drinking Water |
|---|--------------------|--|---|
| Chloramines (as Cl ₂) | MRDL= 4.0 | Eye/nose irritation; stomach discomfort, anemia | Water additive used to control microbes |
| Chlorine (as Cl ₂) | MRDL= 4.0 | Eye/nose irritation; stomach discomfort | Water additive used to control microbes |
| Chlorine dioxide (as ClO ₂) | MRDL = 0.8 | Anemia; infants & young children: nervous system effects | Water additive used to control microbes |

APPENDIX C: Disinfection By-products

| Contaminant | MCL or TT(mg/L) | Potential Health Effects from Ingestion of Water | Sources of Contaminant in Drinking Water |
|-------------------------|------------------------|--|---|
| Bromate | 0.010 | Increased risk of cancer | Byproduct of drinking water disinfection |
| Chlorite | 1.000 | Anemia; infants & young children: nervous system effects | Byproduct of drinking water disinfection |
| Haloacetic acids (HAA5) | 0.060 | Increased risk of cancer | Byproduct of drinking water disinfection |

| | | | |
|-------------------------------|-------------------------|--|--|
| Total Trihalomethanes (TTHMs) | 0.100 ----- 0.080 | Liver, kidney or central nervous system problems; increased risk of cancer | Byproduct of drinking water disinfection |
|-------------------------------|-------------------------|--|--|

APPENDIX D: Inorganic Chemicals

| Contaminant | MCL or TT (mg/L) | Potential Health Effects from ingestion of Water | Sources of Contaminant in Drinking Water |
|----------------------------------|-------------------------|--|---|
| Antimony | 0.006 | Increase in blood cholesterol; decrease in blood sugar | Discharge from petroleum refineries; fire retardants; ceramics; electronics; solder |
| Arsenic | 0.010 as of 01/23/06 | Skin damage or problems with circulatory systems, and may have increased risk of getting cancer | Erosion of natural deposits; runoff from orchards, run off from glass & electronics production waste |
| Asbestos (fibre >10 micrometers) | 7 MFL | Increased risk of Developing benign intestinal polyps | Decay of asbestos cement in water mains; erosion of natural deposits |
| Barium | 2 | Increased in blood pressure | Discharge of drilling wastes; discharge from metal refineries; erosion of natural deposits |
| Beryllium | 0.004 | Intestinal lesions | Discharge from metal refineries and coal – burning factories; discharge from electrical, aerospace, and defense industries. |
| Cadmium | 0.005 | Kidney damage | Corrosion of galvanized pipes; erosion of natural deposits; discharge from waste batteries and paints |
| Chromium (total) | 0.1 | Allergic dermatitis Short term exposure: Gastrointestinal distress | Discharge from steel and pulp mills; erosion of natural deposits |
| Copper | TT; Action Level = 1.3 | Long term exposure: Liver or kidney damage People with wilsons Disease should consult their personal doctor if the amount of copper in their water exceeds the action level | Corrosion of household plumbing systems; erosion of natural deposits |

APPENDIX D: Inorganic Chemicals Continued

| Contaminant | MCL or TT (mg/L) | Potential Health Effects from ingestion of Water | Sources of Contaminant in Drinking Water |
|---------------------------|--------------------------|--|---|
| Cyanide (as free cyanide) | 0.2 | Nerve damage or thyroid problems | Discharge from steel/metal factories; discharge from plastic and fertilizer factories |
| Fluoride | 4.0 | Bone disease (pain and tenderness of the bones); Children may get mottled teeth | Water additive which promotes strong teeth; erosion of natural deposits; discharge from fertilizer and aluminium factories. |
| Lead | TT; Action Level = 0.015 | Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilities Adults: Kidney problems; high blood pressure | Corrosion of household plumbing; erosion of natural deposits |
| Mercury (inorganic) | 0.002 | Kidney damage | Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands |

APPENDIX D: Inorganic Chemicals Continued

| Contaminant | MCL or TT (mg/L) | Potential Health Effects from ingestion of Water | Sources of Contaminant in Drinking Water |
|--------------------------------|-------------------------|---|--|
| Nitrate (measured as Nitrogen) | 10 | Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue – baby syndrome. | Runoff from fertilizer use; leaching from septic tanks, sewage; erosion of natural deposits. |
| Nitrite (measured as Nitrogen) | 1 | Infants below the age of Six months who drink water containing nitrite in excess of the MCL could seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue – baby syndrome. | Runoff from fertilizer use; leaching from septic tanks, sewage; erosion of natural deposits. |
| Selenium | 0.05 | Hair or fingernail loss; numbness in fingers or toes; circulatory problems. | Discharge from petroleum refineries; erosion of natural deposits; discharge from mines. |
| Thalium | 0.002 | Hair loss; changes in blood; kidney, intestine, or liver problems. | Leaching from ore – processing sites; discharge from electronics, glass, and drug factories. |

APPENDIX E: Radionuclides , Potential Health Effects and Sources of Contamination in Drinking Water.

| Contaminant | MCL or TT¹ (mg/L)² | Potential Health Effects from Ingestion of Water | Sources of Contaminant in Drinking Water |
|--------------------------------------|---|---|---|
| Alpha particles | 15 (pCi/L) | Increased risk of cancer | Erosion of natural deposits of certain minerals that are radioactive and may emit a form of radiation known as alpha radiation |
| Beta particles and photon emitters | 4 millirems per year | Increased risk of cancer | Decay of natural and man-made deposits of certain minerals that are radioactive and may emit forms of radiation known as photons and beta radiation |
| Radium 226 and Radium 228 (combined) | 5 pCi/L | Increased risk of cancer | Erosion of natural deposits |
| Uranium | 30 ug/L as of 12/08/03 | Increased risk of cancer, kidney toxicity | Erosion of natural deposits |

SOURCE: EPA 816 – F – 02 – 013

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