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# Attenuating Transition Metals/REE's by X- ray fluorescent Spectroscopy of Ground Water of the South Mahanadi Delta, India

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**Abstract :** Heavy/transition Metals and rare earth elements present in ground water have proved to be important for human growth. Some heavy and transition metals like cobalt, chromium, copper, iron manganese, selenium and zinc are nutritionally essential whereas mercury, cadmium and lead are toxic. Element like boron, silver, barium, arsenic and aluminum are noxious at high concentration in ground water and affect heart, kidney, lever, nervous and digestive system of people. The concentration of those transition metals present in ground water is gradually increasing due to increased industrial, agriculture and urban activities. The southern part of the Mahanadi delta includes Chilika lagoon of the Mahanadi system in Odisha India. After inception of Bhubaneswar city (1950) and high population growth in the south Mahanadi delta, the ground water is being polluted increasingly with metals and REE contaminants. Various methods like neutron activation analysis. X-ray fluorescent spectrometry, polarography, Gas chromatography Analysis, Anodic stripping voltammetry and atomic absorption spectrograph are used for ascertaining and quantizing the trace and different metals (heavy or trace) present in ground water. Versatility, unique properties of XRF spectrometer have urged to access the quantity of heavy metals and rare earth elements present in the ground water samples in the wells/bore wells of the south Mahanadi delta. It is observed that there is overdose of Phosphorous, Iron, Titanium, cobalt and tin in the water samples. Rare earth elements like samarium, europium, gadolinium, terbium, dysprosium, Erbium are present in ground water in traces were also found. Strategies have been proposed to ameliorate the concentration of higher dose of the heavy metals and the rare earth elements in the present study.
**Key Words** : South Mahanadi delta, XRF spectrometer, Ground water, heavy metals, REE.

## 1.0 Introduction

Over exploitation of ground water used human services have increased exponentially from the year 1980 onwards in India. People became conscious of the drop of water they consume. Bacterial and micro-organisms growth and some ground water related parameters like pH, DO, BOD, COD, dissolved solids, TSS were given weight while considering water supply schemes and satellite cities. Heavy metals are associated with medicines and industry. Ground Water (GW)became scarce and water bodies are contaminated with industrial and urban pollutants. The conversion of water bodies to concrete jungles in the south Mahanadi delta (SMD) could not recharge the underground aquifers. In the coastal areas the saline water intruded to GW inland

and made the aquifers brackish. Remediation of new heavy metals and plastics also joined the ground water table. The major source of ground water in India particularly in Odisha is the direct water drawn from wells or bore wells.

Heavy metals are elements whose specific gravity is 5 times the specific gravity of water. The toxic heavy metals that have specific gravity are arsenic, 5.7; cadmium, 8.65; iron, 7.9; lead, 11.34; and mercury, 13.546 (Lide 1992)[1].Heavy metals remain in ground water as total suspended solid (TSS or SPM) or total dissolved solid (TDS) which have positive/adverse impact on human health. Heavy metal free environment is **impossible**. Transition metals are also found in ground water in various ionic states i.e. as oxides, chlorides, nitrates and carbonates etc..Continuous exposure/consumption of some heavy metals is essential for biological metabolic functions but excess exposure or consumption can affect health. The metals promising for human health are Lead (Pb), Cadmium (Cd), Cobalt (Co), Zinc (Zn), Manganese (Mn), Copper (Cu), Chromium (Cr), Nickel (Ni), Arsenic (As) Iron (Fe), Fluoride (F) and Mercury (Hg) (Vaishaly et al., 2015)[2]. The modes of contact to heavy metals of the environment are through physical exposure, diet, intoxication, inhalation or drinking water. The vital organs affected are heart, brain, liver, kidney, lungs, pancreas and glands.

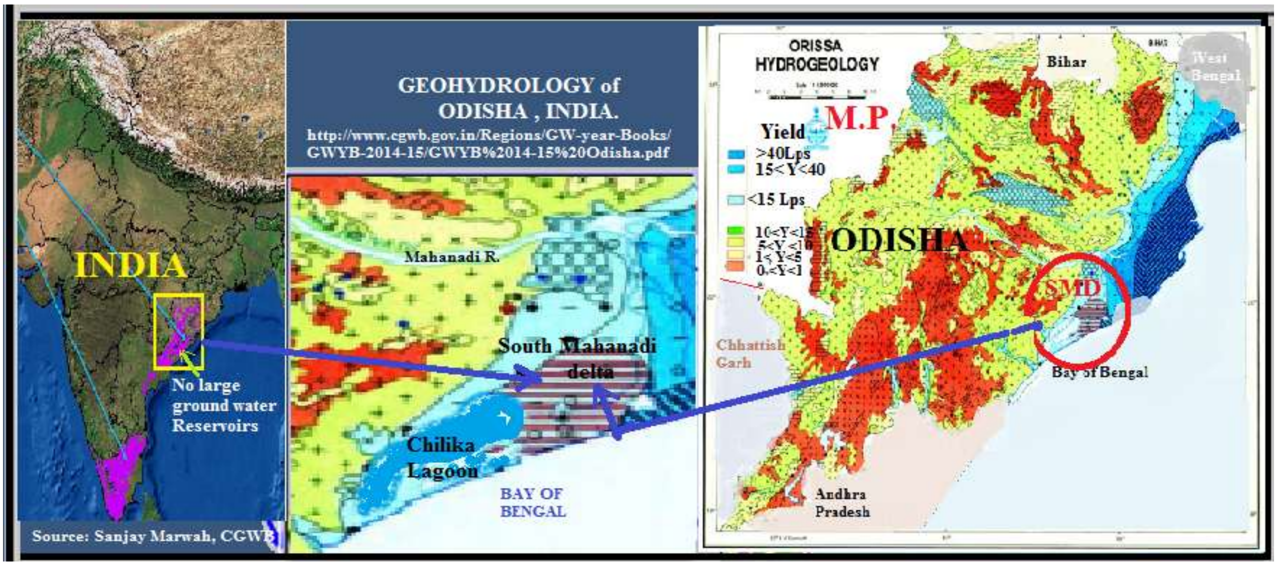


**Fig 1:Index map of the south Mahanadi delta: (Source Central Ground water Board, MOWR)**

The admission of heavy metals in GWis by infiltration or rock action, mining, milling processes, wastes, industrial effluents, pesticides, bio-solids, liquid and solid wastes, fertilizers. The contamination of GW has become expeditious and random for last 40 to 50years.Keeping pace with Anthropocene epoch and population explosion there is increased mining/milling, urbanization and industrialization actions. Anthropogenic activities have also increased the level of transion metals in GW. Wastes and industrial effluents /debris have polluted ground water at larger scale keeping pace with atmospheric pollution.

The main objectives of the proposed work is to collect samples from wells and bore wells in the south Mahanadi delta (SMD) and to evaluate the presence of heavy metals, quantizing them by XRF spectrometer method.

1. Tracing heavy metals/elements present in the collected sample.
2. Quantitative assessment as per standards.
3. Evaluating the levels of toxicity.
4. Magnitude of possible impact on health of these toxic elements of the people in SMD.
5. Relation between ground water quality and geology of the area and mining possibilities

**2.0 Review of literature:**

Nickel is a micronutrient for animals. Indian Ayurveda medicines are rich in Arsenic, lead and mercury (Lynch et al 2005)[3]. The order of heavy metals affecting human health are chromium (Cr), zinc ( Zn), copper (cu), cadmium (Cd), cobalt (Co), iron (Fe), aluminum (Al), nickel (Ni), titanium (Ti), zirconium (Zr), boron (Bo), silver (Ag), manganese (Mn), lead (Pb), lithium (Li) and silicon Si) available in groundwater. Children are the worst sufferers due to contaminants in Ground Water then the females and finally the adult males. Major affecting heavy metals are Silver, lead, nickel, cadmium and manganese(Vetrimurugan et al., 2016)[4]. All heavy metals by nature are toxic but some transition metals like iron, zinc, manganese, chromium, molybdenum and copper are good nutrition elements for human being (European medical agency, 2003)[5].The heavy metals are of density> 5 times high that of water (Tchounwou et al 2014)[6]. Alrakabi M et al., 2012[7]reported that uranium, bromine and strontium are found in high concentration in GW due to excess fly ass of coal based industries. The shallow ground water samples of Bhatinda city in Punjab are heavily contaminated.

Comparison was made between two types of tests by XRF and ICP-AES where heavy metals Pb, Zn, Ni, and Cu, gave better result for the XRF measurements whereas As, Cr, Cd, and Hg gave better results by ICP-AES experiment The order of reliability by the XRF measurements was Pb> Zn > Ni > Cu (Wu et al 2012[8]). On study of soil of Chilika lake at various zone concluded that textural parameters (clay +silt) and adsorption phenomenon increases trace metal ions in sediment of the Chilika lake and coefficient of variation were 3% for Cu & Cr and 4% for Zn Co and Ni (Panda et al., 2006)[9].The quantity of nonmetals and water quality parameters in coastal Odisha were within permissible limits(Mishra S. P, 2016)[10].

## 3.0 Method

The lifetime average daily dose LADD of the heavy metals through intake of water by a person (mg/kg/day) is calculated to find the hazard ratio of the GW contaminant in an area. Then the daily reference dose (RfD) for the heavy metal (mg/Kg) that a person is exposed or consume/day over his/her lifetime reto be known to avoid health hazards or any carcinogenic effects. The key heavy metals, threats to human health are lead, chromium, arsenic, cadmium, zinc, manganese, copper, mercury and nickel. Other than the heavy metals other nonmetals in ground water affecting health of human and plants are sodium, fluorine, calcium (Table 1).

### 3.1 Maximum permissible limits:

The maximum permissible limits and acceptable concentrations (mg/l) by Environmental Protection Agencies (US)and Indian standards are Table 2 (https://www.epa.gov/wqc/national-recommended-water-quality-criteria-human-health-criteria-table)

**Table 1: The MPL of non-metals, heavy metals and REE's present in ground water as per USEPA and IS norms**

| Sl No | Name of element | MPL(USEPA) mg/lIRIS/WHO | MPL (India) in mg/lit IS 10500 : 2012 | Reference |
|---|---|---|---|---|
| 1 | Silver (Ag) | 0.05 | 0.1 | Edwarde et al 1975[11] |
| 2 | Cadmium (Cd) | 0.01 | 0.003 No relaxation | IS 3025 (Part 41)/IS 10500/2012[12] |
| 3 | Mercury (Hg) | 0.005 | 0.001 | IS 3025 (Part 48)/U.S. EPA, 1997 |
|  | Plumbum (Pb) | 0.05 | 0.01- No relaxation | IS 3025 (Part 47)/IS 10500/2012 |
| 4 | Selinium (Se) | 0.01 | 0.5 - 1.0 | IS 3025 (Part 57)/IS 10500/2012 |
| 5 | Cupper (Cu) | 1.30 | 0.05- 1.5 | IS 3025 (Part 42)/IS 10500/2012 |
| 6 | Iron (Fe) | 0.3 | 0.3- No relaxation | IS 3025 (Part 53)/IS 10500/2012 |
| 7 | Manganese (Mn) | 0.05 | 0.1-0.3 | IS 3025 (Part 59)/IS 10500/2012 |
| 8 | Zinc (Zn) | 7.4 | 5-15 | IS 3025 (Part 49)/IS 10500/2012 |
| 9 | Silicon (Si) | 20–50 mg/day | 0.001 No relaxation | IS 3025 (Part 48) )/IS 10500/2012 |
| 10 | Aluminum (Al) | 0.2 mg/L/day | 0.03- 0.2 | IS 3025 (Part 55)/IS 10500/2012 |
| 11 | Magnesium (Mg) | 30mg/lit, WHO | 30-100 | IS 3025 (Part 46)/IS 10500/2012 |
| 12 | Calcium (Ca) | 75 (WHO) | 75-200 | IS 3025 (Part 40)/IS 10500/2012 |
| 13 | $CaCO_3$ | 75- 200 | 200-600 | IS 3025 (Part 21) )/IS 10500/2012 |
| 14 | Selenium (Se) | 0.17 | 0.01 | IS 3025 (Part 56)/IS 15303 |
| 15 | Fluoride(F) | 4.0 | 1.0- 1.5 | IS 3025 (Part 60) )/IS 10500/2012[12] |
| 16 | Nickel (Ni) | 0.61 | 0.02 No relaxation | IS 3025 (Part 54)/(IRIS) May 2002. |
| 17 | Arsenic (As) | 07 | 0.01- 0.05 | IS 3025 (Part 37) |
| 18 | Chromium (Cr) | 1.0 | 0.05 - No relaxation | IS 3025 (Part 52) |

### 3.1.1 Few terminologies:

The medical terms used in the ground water assessment for human health are**, MCL**:Maximum contaminant level; (Contaminant allowed): **MCLG**:Maximum contaminant level goal (below which no known risk to health);**TT**: Treatment technique, **MPL**: maximum permissible level;**IRIS**: Integrated Risk Information System; **TDI**: Tolerable daily intake,**IPCS** – International Program on Chemical Safety; (PDE)- The permitted daily exposure; (ADI): Acceptable daily intake; (IPCS)International Program on Chemical Safety,; MDD: Maximum daily dose; Concentration (ppm) = PDE/MDD; FSD – Food Standard Agency ; RfD – Reference Dose; US EPA – United States Environmental Protection Agency ; ESADDI – Estimated safe and adequate daily intake ; NOEL – No-observed effect level ; LOEL – Lowest observed effect level : CHMP: Committee for Human Medicinal Products,NOAEL:No Observed Adverse Effects Level

### 3.2 Hierarchy for human health

Nutritionally essential trace elements are Cobalt (CO), Chromium III (Cr), Copper (Cu), Iron (Fe), Manganese (Mn), Molybdenum (Mo), Selenium (Se) and Zinc (Zn) and with possible known beneficial effects are Boron (Bo), Nickel (Ni), Silicon (Si). Metals with unknown beneficiary effect on human health are Aluminum (Al), Antimony (Sb), Arsenic (As), Barium (Ba), Beryllium (Be), Silver (Ag), Strontium (Sn) and Thallium (Th). The heavy metals Lead (Pb), Mercury (Hg), Cadmium (Cd) are highly toxic (Grover et al 2004)[14]. Excess intake, overdose through medicine or exposure to heavy metals through GW is lethal. The heavy metals present in ground water, its impact on human health and the necessary reference doses are given in Table-2.

**Table 2:Heavy metals by consumption of Ground water, and reference dose and effect in human health.**

| # | Hheavy metal | Source that enter in GW | RfD: (mg/Kg/Day) | Effect on human, | Reference |
|---|---|---|---|---|---|
| 1 | Chromium (Cr)Group VIII**(Essential)** | Old mining, leaching, Fossil fuel burning,waste incineration multivitamin, food supplements | $3 \times 10{-}3$ mg /kg/dayIRIS from US EPA (2009) | powerful oxidant,need for glucose metabolism but high doses: carcinogenic/genetoxic properties, allergic dermatitis | www.ema.europa.eu/docs/en_GB/document_library/2009 |
| 2 | Zinc ( Zn), Group IIB (Essential) | Industrial waste, metal plating, and plumbing. | 15 mg/day for men/ 12 mg/day for women | Wilson disease, anemia,vomiting,dehydration , drowsiness, lethargy, electrolytic imbalance, abdominal pain, nausea, muscular dis-coordination, renal failure, lowers HDL raise LDL | Department of Health, 1991 (Europe) Vaishalyet al., 2015[2] |
| 3 | Copper (Cu), Group IB (Essential) | CuSO4, metal plating, industrial and domestic waste, mining, and mineral leaching | 0.005 mg Cu/kg/dayUS EPA CHMP,2007,https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=140917 | weight loss, bone disorders, microcytic hypochromic anemia, hypopigmentation, graying of hair and demyelination of nerves | US EPA: RfD[14], https:// water.usgs.gov/edu/groundwater contaminants. |
| 4 | Cobalt (Co) (Essential) | In GW, Vitamin B-12 (Treatment for Anemia) | No RfD( USEPA/ IS code)0.04-0.14mg/Co/day | Deficiency cause shortness of breath and low thyroid function | WHO - 2004[15], |
| 4 | Cadmium (Cd), (Toxic) | Batteries ,earth's crust @0.1mg/kg,, cigarette ,industrial discharge, | $5 \times 10{-}4$mg Cu/kg/day, IRIS from US | Osteomalacia, bronchitis , nausea,vomiting, muscle cramps, vertigo, shock, | Wou et al, 2009[8], Vetrimurugan |

| | | | | | |
|---|---|---|---|---|---|
| | | mining waste, metal plating, water pipes, battery, paints, plastic stabilizers, landfill | EPA (2009) | unconsciousness ,convulsion, gastrointestinal, kidney damage ,osteoporosis,,erosion, pulmo- nary, hepatic or renal injury | 2016[3] |
| 5 | Mercury (Hg) (toxic) | Industrial waste, mining, pesticides,coal, electrical equipment, batteries, lamps,switches),smelting, and fossil-fuel burning | 0.1µg/kg/day USEPA,1996, www.greenleft.org.au/content/mercury- | Paresthesia, blindness,nervous system and the kidney deafness,fetal death and abortion | https://water.usgs.gov/edu/groundwater-contaminants |
| 6 | Iron (Fe),Group VIII (Essential) | Both ferrous and ferric chloride) $Fe_2O_3$, Fe $Cl_3$,mining, industrial waste, and corroding metal | 1 mg/day in men and1.5 mg/day in women | Good for haemoglobin, myoglobin, Fe- based enzymes.but high dose is fatal (infants)gastrointestinal system | U.S. recommended daily allowance 1989 [14] |
| 7 | Aluminum (Al) Group III | Rocks and drainage from mines, Antacids, GW as aluminum oxide,& salts | Normal dose 0.2 mg/L/day(Toxic at high RfD) | Osteomalacia, Alzheimer's disease, turbidity or discolored water, normal renal dysfunction | https://www. atsdr. cdc. Gov /tox profiles/ tp22-c2. |
| 8 | Nickel Ni), Gr-VIIIB Toxic at high RfD | $Ni(NO_3)_2$, soils, groundwater, surface water. Electroplating, stainless steel and alloy products, mining, and refining. | 5 µg/day(Dept. of health Europe 1991), $2 \times 10^{-2}$ | Micronutrients but high dose toxic/carcinogenic/reproducetivetoxicity | (Kim et al. (2011)[17] |
| 11 | Boron (Bo),Toxic at high RfD | Boric acid, borax$Na_2B_4O_7 \cdot 10H_2O$ | $2 \times 10^{-1}$ mg /Kg/Day | Irritation in upper respiratory tract, nasopharynx, and eyes. | IRIS 2011, WHO/SDE/WSH/03.04/54[27] |
| 12 | Silver (Ag),toxic athighRfD | Fromore, mining,photography, electric & electronic equipt. Electroplating, alloy, solder. | 0.005 mg /Kg/Day | cellular necrosis, argyria10 g of silver can be the human NOAEL | http://www.who.int/water_sanitation_ |
| 13 | Manganese (Mn),Gr-VIIa(essential) | Mineral from sediment and rocks or from mining and industrial waste, Vitamins | 2.0 to 8.8 mg Kg/day | laundry stains,distastes water, , blackening plumbing fixtures. non-toxic to animals,toxic to plants at high dose, depression | WHO, 1973, |
| 14 | Lead (Pb), Corrodepipeline (Toxic) | From industry, mining, plumbing, gasoline, coal, and as a water additive., Ayurvedic medicines | $3.6 \times 10^{-3}$mg kg/day | Delays Children development Adults: Kidney damage; high blood pressure, lethargy, anemia, miscarriage, impotency Memory loss. | Viridor Waste Ltd(2009)[16], http://wwwdelloyd.50megs.com/hazard/water |
| 16 | Silicon (Si) Toxic at high RfD | Silica$SiO_2$,silicic acid , Silica gel ,insecticides and acaracides | No Observed adverse Effects Level (NOAEL) of 50,000 ppm (mg/L) | Bone/tendons/ aorta, liver and kidney deposits, Alzheimer's disease, affect bone formation , maintenance, Silicosis, chronicbronchitis; Lung | Martin K. R. 2007[18], https://archive.epa.gov/pesticides |

| | | | | | |
|---|---|---|---|---|---|
| | | | | cancer | |
| 18 | **Arsenic** Gr.VA Toxic at high RfD | insecticides, algicide, herbicide, sheep dips, fungicide, dye stuff, preservatives,(Treating yaws syphilis, amoebic dysentery, sleeping sickness) | 50 µg per day and it isubiquitous (single high dose 300 mg is fatal) | Toxic,Carcinogenic cardiovascular,dermatologic disease, nervous, hepatobilliary, renal, gastro-intestinal, respiratory systems, arsenic trioxide induces DNA damage | .WouTet al 2014[8] Grover et al 2004[13] |

**4.0 Testing methodologies:**

Different methods are used in the field and in the laboratory for finding the quantity of heavy metals in water. The different methods, techniques and methodologies are given in the Table - 3:

**Table 3: Various instruments/methodologies applied to ascertain/quantize heavy/ trace metals in ground water**

| **Instrument** | **Principle** | **Technology** | **Heavy metal quantized** | **Resources** |
|---|---|---|---|---|
| (XRF) X-ray fluorescence spectrometry | x-ray instrument | X-ray fluorescence technology | Studying fluids chemicals, minerals,sediments, non-destructive rocks | http://serc.carleton.edu/research_education/geochemsheets/ |
| Polarography | Dropping Mercury Electrode & other electrodes mostly solids:Voltammetry | Electroanalytical technique uses effect of potential of an electrode in an electrolysis cell current | Pb, Hg, As, Cd &Cr | https://www.engg.ksu.edu/HSRC/96Proceed/bundy1 |
| Atomic absorption spectrography (AAS) | analytical tech.to measures the conc. of elements | using the wave lengths of light absorbed by an element | Cd, Cu, Fe, Pb, Ag, Mn and Zn | http://www.liskeard.cornwall.sch.uk/images/Liskeard- |
| (ASV)Anodicstripping voltammetry | Electro rednbyHg electrode | sensitive analytical method | Cu, Cd, Mn, Hg, Pb, Zn | Edwards et al 1975[11] |
| Neutron activation analysis | standard method of analytical procedures | spectrometric techniques such as ICP-MS, ICP-ES and AAS | As, Cr, Hg, and Se, Cs, Co, Sc, Sb, Rb, Ce, La, Eu, and Yb | Mejia C. R., 2015[19] Mendoza P ei al., 2003[20] |
| Gas chromatography Analysis | Reduced in aqueous soln of hydrides of the metal. Using (KI+SnCl2) or (Mg+TiCl3), | separating “volatile” compounds taking changes in vapor pressures & hold to solid materials | As, Sb, Se, Bi, Ge, Te&Sn | http://www.oneonta.edu/faculty/viningwj/chem112/labs/gc_lab_2010.pdf |

**5.0 Study area:**

Proximity to sea, excess industrialization and over dose fertilizers in agriculture not only contaminates the drainage water but join ground water by interception in the south Mahanadi delta (SMD). The area is typically a peninsular delta comprising of denuded hills of Eastern Ghats Belt, Lateritic plains in the west, alluvial flood plains, young and old alluvial plains, paleo beach ridges, lagoon, swamps and anastomosed drainage channels. Puri, Satyabadi, Pipili, Jatni, Barang and Bhubaneswar are the major towns in SMD, which are susceptible to contamination of the ground water.

The south Mahanadi delta consists of 12 blocks of area 1777 $Km^2$, the Chilika lagoon (KrushnaPrasad block) in the southern corner has spread over of area 1532 $Km^2$ Fig -2 (Mishra et. al, 2015)[21].Theclimateishumid,tropical and the area are near to tropic of cancer.Temperature of the area ranges between 12-14$^0$C as minimum and maximum of 35-40 °C. The relative humidity is high (70 %) during August to April, and minimum humidity varies from 60 to 65 % between June and July. The normal rainfall of the area is 1451.2 mm. About 75% to 80% of rainfall is received from June to September during south west monsoon. Floods, droughts and cyclones are common natural disastersinthe area recurring almost every year of varying intensity(Mishra et al 2015)[22].

**5.1 Geo-hydrology of SMD**

The ground water of SMD has three regions. The upper deltaic reaches (Cuttack district) spread from Naraj (20 -29' N lat. and 86-47' E) to BBSR. The fresh water yield of the wells and tube wells in shallow stratum is less 1-5lps whereas for bore wells the capacity is 15-20lps in upper reaches of SMD. The yields of deep bore wells have range 3-75lps, drawdown 3-17m and hydraulic conductivity 50-150m/day. The soil of middle reaches extend from Khurdha, Jatni, Delang and up to Pipili (20 -24' N lat. and 86-57' E Long) consist either unconsolidated alluvium over Athgarh formation with alternated layers of sand, silt and clay. A part is bald EGB Hills with lateritic soil of Jatni and sedimentary rocks of Bhubaneswar.GWT is 4-6m below ground level (bgl). Mahallick 1996[23]has identified two confined aquifers one at 15-20mand other at 30m and 40m in the area. The lower marine marginal reach in the delta extends up to 25Km inland. Geologic formation is mixed igneous, sedimentary, and metamorphic rocks overlain by alluvium or sands or sandy alluvium. The depth of brackish water in GWT is at 3 to 10m(Mishra et al 2016)[24].Water enter the aquifer depending on the type of aquifers confined or unconfined and the geological properties of the soil. The aquifers in the upper south Mahanadi delta are generally deep aquifers except few shallow aquifers with fresh water. The aquifers in the middle and the coastal reaches extend up to 20 to 25Km inland. In the coastal areas there are prominent shallow aquifers containing brackish water due to salinity intrusion and underlain by a deep aquifer.

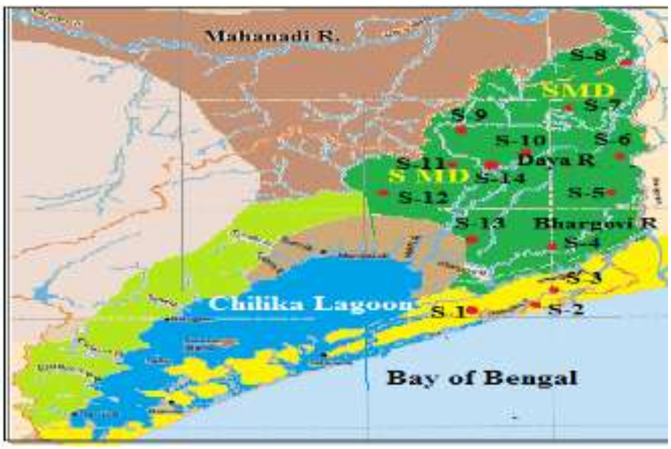


**Fig2: The sample collected from wells/bore wells in SMD**

**5.2 Methodology**

Sample bottles are usually glass or polyethylene. Polyethylene bottles are preferred to avoid adsorption of radioactivity elements. The bottles were cleaned thoroughly so that it cannot contaminate the samples. Dilute

$HNO_3$ or dil.HCl was used to thoroughly cleanse the bottle with shaking for one minute so that any metal in the interface of bottle shall react with the acid and shall be removed. The bottles after washing with detergent were kept24hrs and dried. To start with the observation wells and boring taps were selected distributing within the study area. The well cleaned one liter sampling polyethylene bottles were initially ringed by dil. HNO3. Again the bottles were ringed two to three times by the water to be used as sample bottles' and kept for 24 hours **Okoro et al, 2012**[25].

The samples, after collection from the wells or bore wells were filtered by 0.45 mm millipore filter membrane after cleansing it by. 1%dil. $HNO_3$ followed by rinsing with pure water before filtration (Meranger et al., 1979)[26]. Samples were there after refrigerated at 4°C in the laboratory prior to analysis by X-Ray fluorescent Spectrometer. X-ray fluorescence (XRF) spectrometry is a metal analyzer where individual atoms, are excited by an external energy. The emitted X-ray photons have specific wavelengths which estimate the quantum of heavy metals in a liquid sample.

### 5.3 The X- ray fluorescent Spectrometer

The X- ray fluorescent Spectrometer (Model: Epsilon 1 PAN alytical B. V., the Netherlands is used for quantizing the heavy metals, REE and nonmetals like composites, drugs, GW, soils, wastes and coins etc. made of sodium to americium..XRF Spectrometer is used for element and thin film analysis. It performs in three stages (i). X-Ray beam from 40-60KV, 50-300W (ii) versatile detection system for various uses (iii) Software package to inform the results of detection. The spectrometer is popular for its speed, long life and accuracy (www.eastern applied. com/XRF-Technology-Overview /utmexpid).

It can measure large varieties of samples of 1gm to larger block of solids, powers, liquids, beads, slurries granules, films and coatings. It can also analyses irregular blocks of maximum size 15cmx12cmx10cm. It is also used to detect a wide range of elements from Na (Z=11) to U (Z=92).

**Figure 3: Testing heavy metals by X-Ray Fluorescent spectrometer, Model –Epsilon 1PANalytical, B. V.**

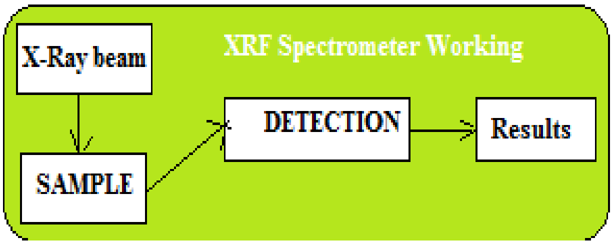


**Figure 4: Working of a XRF – Spectrometer, Epsilon-1**

### 5.3.1 Principle of XRF Spectrometer

The XRF spectrometer works on the principle that exciting individual atoms by external energy (X-ray photons) at specific energy or wavelength can count the quantity of photons emitted from the sample at each energy level so that the elements present can be identified and quantized or elements can be quantitated based upon the rate of emission of their characteristic X-rays from a sample that is excited ( http:/ /archaeometry.missouri.edu/ xrf_over view.html)

### 5.3.2 Superiority of XRF Spectrometer:

It is a cost effective, simple, versatile, rapid apparatus.It can analyze metals, nonmetals, minerals, solid, liquid, and thin-film sample.Thespectrometercan analyze soils (agriculture and dump lands),sorting scrap metal alloys and plastics for recyclable materials, geochemical mapping andlocating mineral deposits.It can also be used for environmental monitoring, the online control of industrial processes for the materials, archaeological studies and provenance of sculptures, paintings of cultural heritage(producing raw Gautin et al., 2012)[32].

## 6.0 The results

Fourteen stations (wells and bore wells) homogeneously distributed within the south Mahanadi Delta were taken whose ground water samples were studied. The stations from Stn-1 to station 14 were Gorual, back of Puri temple, back of Gundicha temple, Chandanpur, Satyabadi, Satasankh, Pipili, Bhubaneswar,Pahal, Tamando, Jatni (CUTM campus), Gambhari, Haripur, Talmal respectively. Water samples are collected as per norms stated above during 1st week of May-2017 ( summer). It is because the ground water level of the areas deplete to maximum before pre-monsoon. The samples were tested by the XRF Spectrometer and the results are tabulated in Table-3.

### 6.1 The nonmetals

Sodium, calcium and magnesium is universal in the ground water of the wells and bore wells of the south Mahanadi delta (Mishra et al 2016)[28].Similarly The maximum acceptable concentration of iron and manganese is limited to its taste, colour and turbidity and the water may not be toxic.The nonmetals, heavy metals and REE's found in the samples are in Table 3

**Table 3: The quantity of metals, minerals and rare earth metals present in ground water in SMD**

| | S-1 | S-2 | S-3 | S-4 | S-5 | S-6 | S-7 | S-8 | S-9 | S-10 | S-11 | S -12 | S-13 | S-14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Element** | **Gorual** | **PuriBadadanda** | **Gundicha** | **Chandanpur** | **Satyabadi** | **Satasankh** | **Pipili** | **BBSR** | **Pahal** | **Tamando** | **Jatni (CUTM)** | **Gambhari** | **Haripur** | **Talamal** |
| | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| Phosphorus | 827 | 548 | 661 | 854 | 513 | 807 | 511 | 526 | 530 | 554 | 528 | 541 | 530 | 506 |
| Sulfur | | | | 82 | 49 | | | | | | | 112 | 140 | |
| Chlorine | | | | 82 | 49 | | | | | 608 | | 112 | 140 | 415 |
| Potassium | 900 | 584 | 8 | 17 | 690 | 920 | 487 | 516 | 492 | | 414 | 0 | 0 | |
| Calcium | | 89 | 18 | | 21 | 69 | 28 | | | 220 | | 355 | 199 | 163 |
| Titanium | 284 | 239 | 248 | 393 | 190 | 347 | 204 | 224 | 189 | | 182 | 308 | 296 | |
| Vanadium | | | | | | | | | | | | 61 | 48 | |
| Iron | 0 | 0 | 0 | 0 | | 0 | 0 | 0 | | 15 | | 23 | 6 | 7 |
| Cobalt | 25 | 15 | 18 | 26 | 15 | 24 | 15 | 12 | 19 | 0 | 11 | 440 | 427 | |
| Zinc | 0 | | 0 | | 10 | | | | 0 | | 0 | | | |
| Tin | | | | 3 | | | | | | 48 | | 11 | 10 | |
| Samarium | 42 | 49 | 52 | 39 | 46 | 47 | | 51 | 48 | 23 | | 50 | 44 | |
| Europiu | | | | 0 | | 3 | | | | 0 | | 18 | | 2 |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| m | | | | | | | | | | | | | | |
| Gadolinium | | | | | | | | 23 | | 13 | | | | |
| Terbium | | | | | | | | 37 | | | | | | 43 |
| Dysprosium | | | 34 | | | | | | | | 40 | | | 37 |
| Erbium | 108 | | 79 | 100 | | | | | 72 | 66 | | | | |
| Rhenium | | | | | | | | 0.4 ppm | | | | | | |

**6.2 The nonmetals and transition metals:**

- **6.2.1 Phosphorous** is a nonmetal but essential for human health as it helps in formation of RNA to DNA. http://www.healthline.com/. The multivalent nonmetal is available in nature in allotropic forms as white, red and black phosphorous in phosphate form. White phosphorous in pure form is poisonous and cause nausea, stomach cramps and drowsiness and is fatal on consumption. Excess phosphorous also causes kidney damage, osteoporosis and, Hyperkalemia, Hyper-phosphatemia, problem of hypophosphatemia, weakening bones and teeth. Excess Phosphorous also causes Eutrophication. Human need of phosphorus depends upon age 100 mg to 1250 mg/day.In the SMD concentration of Phosphorous is below the RfD.
- **6.2.2 Vanadium**: It is a transition metal found in GW of swamps of the Chilika. High consumption/exposure of Vanadium pentoxide cause severe irritation of the eyes, skin, respiratory tract, pulmonary edema, and systemic poisoning.http://www.ojavanproducts.com/health_benefits.html
- **6.2.3 Tin (Strontium):Tin**in is a transition metal, toxic to human health.Tin supports the adrenals, and iodine supports the thyroid, with both subsequently affecting cardiac outputs. But the short term effects of tin are eye and skin irritations, headaches, stomachaches, sickness and dizziness, severe sweating, breathlessness, urination problems. The long-term effects are depressions, liver damage, malfunctioning of immune systems, chromosomal damage, shortage of red blood cells, brain damage (causing anger, sleeping disorders, forgetfulness and headaches)http://www.lenntech.com. Tin is found in GW at Tamandoand west bank of Chilika.
- **6.2.4 Titanium (Ti):** Titanium is abundant in the earth's crust and is used in various industrial processes. Titania (is used as Nanoparticles. it has two types of enzymes action. It creates lungs irritation and possibly carcinogenic. It is used for implant as it is nontoxic and inert. It interferes with the carbohydrate metabolism (Njoroge et al., 2014)[29].Titanium is found in almost all the samples except Talamal and Tamando. So the SMD is susceptible to carcinoma.

**6.3 The rare earth metals:**

**6.3.1 Dysprosium** is toxic and fatal only when a diluted 500gms dose is consumed. Insoluble Dysprosium salts are nontoxic (http://www.lenntech.com/periodic/elements/dy.html)
**6.3.2 Europium** has no known biological role. Standard limit is less than .001% in an average Human Body. Enhances normal cell growth and extends life. Europium salts could be mildly toxic by ingestion, but its toxicity has not been fully investigated (http://www.lenntech.com/periodic/elements/eu.htm)
**6.3.2 Samarium** is the fifth most abundant rare elements and four times as common as tin. It is not free in nature, but found added with monazite, bastnasite and samarskite. Samarium has no biological effect but in water causes skin and eye irritation,http://www.lenntech.com/periodic/elements/sm.htm .
**6.3.3 Gadolinium** is a Rare Earth Element (REE) with paramagnetic properties. gadolinium-based contrast agents (GBCAs) can develop nephrogenic systemic fibrosis (NSF) in patients with severe renal impairment (Rogosnitzky M, 2016).[30]
**6.3.4 Terbium** is a least abundant rare earth element (REE). The presence of this REE's in ground water have less impact.

**7.0 Management of Heavy metals in ground water of SMD**

The heavy/ transition metals present in soil depend upon the soil, rock stratum, pollutants, agriculture practices, management of industrial and urban wastes and anthropogenic activities of the area. Manage solid waste and prevent heavy metal contamination in ground water. The worst sufferers are the end users. The South Mahanadi covers two major cities (Cuttack and Bhubaneswar), three major urban townships (Puri, Khurdha and Jatni) and eleven block headquarters which is thickly populated. The end users of are the villagers consisting one billion whose prime source of drinking water is from wells or bore wells. Their primary concern is their health. The ground water is depleting continuously and is getting contaminated gradually and becoming unfit for human health. The approaches can be managed by augmenting recharge, isolating the source of pollution from water bodies, reducing toxicity at their origin and public awareness of their quality of water. Few points to ameliorate the concentration of the contaminants are:

a. **Isolation**: Urban liquid wastes and industrial effluents before releasing to the water bodies should be well treated. The pond walls created for isolation should be impervious so that the pollutants cannot access to ground water. Administrative frame work should implement to restrict release of the liquid wastes in the industrial cluster in between Cuttack and Bhubaneswar city.The isolations done by scrap collectors in different towns are not adequate.
b. **Solidification and stabilization**: Promoting separation/conversion of polluting solid matrixes and reutilization of the solid encapsulates for other uses are to be practiced. Waste management plants are to be established to manage wastes and debris. The plants existing at Puri and Bhubaneswar are inadequate. Each townships and blocks should be funded to construct solid waste disposal units on PPP mode.
c. **Segregation**: Segregation of metals, metalloids and plastics are to be dome at source before disposal can save the ground water and become raw materials for different industries. The scrap collection in the township has become a profitable business which should be encouraged throughout the area.
d. **Advanced technologies**: Bioleaching and Phytoremediation to be encouraged to collect heavy metals such as Cu, Pb, Zn, As, Cd, Cr and Ni (Vaishaly A. G., et al 2015)[2]
e. **Avoidance:** GW used for drinking should be avoided as far as possible and roof top water harvesting methods to be employed to become free from health hazards.
f. **Recharging of GW:** The over exploitation GW for drinking and irrigation in the SMD is regularly increasing without adequate recharge. The existing water bodies should be rejuvenated to increase the rate of recharge of ground water in the SMD.
g. **Check dams:** To provide incidental irrigation, drinking water, diverting water from perennial or semi-perennial sources and water storage for domestic and recreational uses, chek dams are presently 76 numbers have been constructed over drainage channels of SMD to recharge ground water and desalinization.
h. **Desalinization:** The lower marginal sectors of the delta, the ground water is brackish, the ground water possesses more rare earth elements, the human health and plants can be saved by using ground water after using advanced methods like reverse osmosis, desalination with system design, use of bio surfactants, membrane technology and Nano technology(Mishra S. P. 2017)[31]

## 8.0 Conclusion:

The ground water in the SMD, the concentration of nonmetals phosphorous, potassium, calcium, sulphur and chlorine was high in the samples but within RfD. The heavy metals widely available in ground water were titanium and cobalt but tin and iron in the periphery of the Chilika lagoon. The rare earth elements found in the wells were Samarium, Europium, Gadolinium, Terbium, Dysprosium, Erbium and Rhenium. The adverse effects of these REE’s are less reported. It can be concluded that only concern is with tin and iron in the coastal areas. The ground water is being polluted continuously which should be examined time to time in future by adopting proper management strategies. The stake holders and the government should institute to monitor the heavy metal /REE concentration in ground water of the south Mahanadi delta particularly the west bank of the Chilika.

The apparatus XRF spectrometer used to ascertain and quantify the heavy metals and REE’s in ground water of SMD is easy preparation of simple, versatile, minimum experiment time so that the risk of contamination is the least. The results can be directly obtained by use of software. So X-Ray Fluorescent spectrometer, Model –Epsilon 1 PANalytical, B. V. is a handy and beneficial tool to handle water pollution monitoring even the trace elements are scaled up to billion parts of a gram.

## References:


1. Lide, D. (1992). CRC Handbook of Chemistry and Physics, 73rd Edition 1992. Boca Raton, FL:CRC Press.
2. Vaishaly A. G., Mathew B. B. and Krishnamurthy N.B., 2015, Health effects caused by metal contaminated ground water, Int. Jour. of Advances in Scientific Research, 2015; Vol-1(02), pp- 60-64
3. Lynch E, Braithwaite R. 2005, A review of the clinical and toxicological aspects of 'traditional' (herbal) medicines adulterated with heavy metals. Expert Opin Drug Saf. 2005;4:76–78.
4. Vetrimurugan, E., Brindha, K., Elango, L. et al., Human exposure risk to heavy metals through groundwater used for drinking in an intensively irrigated river delta, Appl Water Sci (2016). doi:10.1007/s13201-016-0472-6
5. Lars Järup; Hazards of heavy metal contamination. Br Med Bull 2003; 68 (1): 167-182. doi: 10.1093/bmb/ldg032
6. Tchounwou P. B,Yedjou C. G., Patlolla A. K., and Sutton D. J., 2014, Heavy Metals Toxicity and the Environment, EXS. Author manuscript; available in PMC , US National Library of Medicine, National Institutes of Health. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4144270/
7. Alrakabi M., Singh G., Bhalla A, Kumar S., Kumar S., Srivastava A.,. Rai B., Singh N., Shahi J. S., Mehta D., 2012, Study of uranium contamination of ground water in Punjab state in India using X-ray fluorescence technique, Springer, JRadioanalNuclChem, 274(1), pp-1-9, DOI 10.1007/s10967-011-1585-
8. WuCheng-Mau, Hung-Teh Tsai, Kai-Hsing Yang & Jet-Chau Wen (2012): How Reliable is X-Ray Fluorescence (XRF) Measurement for Different Metals in Soil Contamination?, Environmental Forensics, 13 (2), pp- 110-121, http://dx.doi.org/10.1080/15275922.2012.676603
9. Panda, U. C., Rath, P., Sahu, K. C., Majumdar, S., and Sundaray S. K., 2006 "Study of geochemical association of some trace metals in the sediments of Chilika Lake: a multivariate statistical approach, Springer, Environmental Monitoring and Assessment 123: 125–150, , DOI: 10.1007/s10661-006-9187-8
10. Mishra S. P., 2016, Physico Chemical Indices of ground water and their geoponic management in Coastal Odisha, India, Engg. Management Research, Vol-5 (2),pp-47-62.
11. Edwarde K. W., Klusman R. W., 1975, Toxic heavy metals in ground water of a portion of a front range mineral belt, Thesis, Colorado state University, Series 67, Fort Collins, Colorado.
12. Bureau of Indian Standards, Ammendment No -1 to Indian Standard, 10500 - 2012 drinking water — specification, ( Second Revision ), 2015, ManakBhavan, 9 Bahadur shah zafarMarg, New Delhi 110002
13. Goyer, R. Golub M., Choudhury H., Hughes M., Kenyon E., Stifelman M., Issue paper on the human health effects of metals, Submitted to: U.S. Environmental Protection Agency Risk Assessment Forum, 1200 Pennsylvania Avenue, NW, by ERG, 110 Hartwell Avenue, Lexington, MA 02421, August, 2004
14. USEPA, 1989. Sediment classification methods compendium. Draft Final Report, U. S. Environmental Protection Agency, Watershed Protection Division, USA
15. WHO, 2004. Guidelines for Drinking Water Quality. 3rdEdn., World Health Organization, pp: 515.
16. Viridor Waste Ltd (2009). Viridor New England energy from waste project: Technical data for HHRA generic assessment criteria (402-0036-00350). Available from: http://www.devon.gov.uk/plandoc 259_4975.pdf.Volume 2011 (2011), Article ID 402647, 20 pages, http://dx.doi.org/ 10.5402/2011/402647
17. Kim KW, Chanpiwat P, Hoang TH, Phan K, Sthiannopkao S (2011) Arsenic geochemistry of groundwater in Southeast Asia. Front Med 5(4):420–433
18. Martin K. R., 2007, The chemistry of silica and its potential health benefits., PUBMED, J Nutr Health Aging. Vol;11(2): pp-:94-7.
19. Mejía, C. R., García, R. G., Longoria-G. L. C., López R. M. C., and Ávila P. P., 2015, Application of Neutron Activation Analysis for Determination of As, Cr, Hg, and Se in Mosses in the Metropolitan Area of the Valley of Toluca, Mexico, Journal of Chemistry, http://dx.doi.org/10.1155/2015/278326
20. Mendoza p., Ubillús M., Torres B., Montoya E. Bedregal P.,2003, Determination of trace elements in water samples by k0 based instrumental neutron activation analysis using Sodium as comparator,http://dspace.ipen.gob.pe/bitstream/ipen/240/1/_8-12
21. Mishra S. P., Dwebedy S., 2015, Geo-hydrology of South Mahanadi Delta and Chilika Lake, Odisha, International Journal of Advanced Research (2015), Volume 3, Issue 11, 430 – 445

22. Mishra S. P. and Jena J. G., (2015) “Analytical Study of Monsoon Rainfall South Mahanadi Delta and Chilika Lagoon, Odisha” International Journal of Engineering and Technology (IJET), ISSN : 0975-4024 Vol 7 No 3 , 985 – 996
23. Mahalik; N. K., Das, C., and MaejimaWataru (1996): “Geomorphology and evolution of Mahanadi Delta, India”,Jour. of Geosciences, Osaka City University, Vol. 39, Article. 6, p. 111 – 122 (March,1996)
24. Mishra S. P. and Dash Joykrishna (2016) Hydro–morphology of cuts in coastal rivers debouching Chilika ; South Mahanadi Delta, Odisha, India, International Journal of Advance Research, Volume 4, Issue 5, pp- 391-404
25. Okoro H. K., Adeyinka A., , Jondiko O. E., Bhekumusa J. X. and Kakalanga S. J., 2012, Assessment of heavy metals contamination in groundwater: A case study of central industrial district in Ilorin, Kwara State, Nigeria, International Journal of Physical Sciences Vol. 7(28), pp. 5078 - 5088,
26. Meranger, J.C., K.S. Subramanaian and C.A. Chalifoux, 1979. National survey for cadmium and magnesium, copper, lead, zinc, calcium and magnesium in Canadian drinking water supplies. Environ. Sci. Tchnol., 13: 707-711.
27. Integrated Risk Information System (IRIS) ,1988, Manganese; CASRN 7439-96-5, U.S. Environmental Protection Agency, Chemical Assessment Summary National Center for Environmental Assessment, 02-46 CPMP/SWP/QWP/4446/00 corr, 2007, European Medicines Agency , Pre-authorisation Evaluation of Medicines for Human Use, http://www.ema.europa.eu/docs/en_GB/documentlibrary/ Scientific _guideline/2009/09/WC500003587.pdf
28. Mishra S. P., 2016, Physico Chemical Indices of ground water and their geoponic management in Coastal Odisha, India, Engg. Management Research, Vol-5 (2),pp-47-62.
29. Njoroge B. N., Murigi I. P. and Ndunge D., 2014, Monitoring of Heavy Metals in Groundwater In Makuyu Division, Maragua District, International Journal Of Engineering And Science Vol.4, (2), PP 06-15
30. Rogosnitzky M. and Branch S., 2016, Gadolinium-based contrast agent toxicity: a review of known and proposed mechanisms, Bimetals. 2016; 29: 365–376, doi: 10.1007/s10534-016-9931-7
31. Mishra S. P., 2017, The apocalyptic Anthropocene epoch and its management in India, Int. Jour. Adv. Research, Vol, 5(3),pp. 645-663
32. Guthrie J. M.,”Overview of X-ray Fluorescence”, University of Missouri Research Reactor, Revised, August 2012, Jeffrey R. Ferguson, University of Missouri Research Reactor, http://archaeometry.missouri.edu/xrf_overview.html

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