# Geochemical Distribution of Trace Metals in Water of Lower Gadilam River, Cuddalore District, Tamil Nadu, India

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## Abstract

The concentration of eight trace factors, Fe, Cr, Mn, Ni, Cu, Pb, Zn, Cd and physico chemical parameters have been assessed in water samples of Gadilam River, from mouth of river towards Panruti of Cuddalore District. Water samples were collected from seventeen areas and elements determined using Atomic Absorption Spectrophotometer (AAS) and standard prescribed analytical method for physico chemical parameters. The parameter quality reaches as pH (8.1-9.5), Ec (240-1415), TDS (168-991) and the samples investigated were in the order of magnitude as by Fe>Cu>Zn>Cr>Pb>Ni>Mn>Cd is existence range of trace metals in water samples.. The most noteworthy grouping of Fe were found all through the stream and took after by Cu>Zn>Cr>Pb>Ni>Mn>Cd and the variation of metals in Gadilam River because of the including of modern wastage and un-characterized anthropogenic impacts. The consolidated and aggregate outcomes are a genuine danger to the whole estuarine environment.

Keywords: Heavy metal, Water, Gadilam River, Cuddalore, Tamil Nadu, India.

## Introduction

Industrialization and human activity for the development all over the world has changed the ecosystem of our environment. The adjoining area of our environment is considered as a dumping site for generated waste materials. Thus, the discharged waste is directly or indirectly harmful to man and other living beings<sup>1</sup>. The toxic substance accumulated into water bodies are through the unpracticed common lifestyle of public, and additionally by confinement initiates the growth of microorganisms<sup>2,3</sup>. It is said that River pollution all over the world is the major environmental problem, which affects the aquatic ecosystem by numerous stress that deteriorate biodiversity. This extraordinary deterioration is accomplished by human beings for the death of aquatic ecosystems. Tempest water overflow and flow of sewage into streams, which are two regular ways that different supplements and different poisons enter the oceanic biological systems bringing about contamination<sup>4,5</sup>.

Heavy metals are firmly joined with ecological decay and the nature of human life, and in this way have fortified concern everywhere throughout the world. More nations have marked bargains to screen and lessen overwhelming metal contamination<sup>6</sup>. Substantial metal pollution especially the unnecessary components may have upsetting impacts on the natural equivalence of the beneficiary sea-going environment with a various creatures including fish. The present work is to evaluate the geochemistry of Gadilam waterway water to set up the likelihood of supporting contamination of the stream water,

which helps us to focus the impacts of overwhelming metal because of characteristic and anthropogenic impacts.

Geology and Geomorphology of Study Area: The present study area (Gadilam river) lies between 79°40' and 79°45' East longitude; and between 11°40 and 11°45' North latitude. It lies in SOI toposheet No. 58M of survey of India. The river originates near Sankarapuram and flows through the Cuddalore and Villupuram districts and drains at Bay of Bengal at Cuddalore, the area coverage of Gadilam River is about 181.315 Sq. Km. (Figure-1). The district is noted with different geological formations of Archaean rocks to recent sediments. Specifically the study area is covered by Quaternary formations consisting of marine, sandstone with clay, fluvial flood plains and fluviomarine (Figure-2). Generally, the Quaternary landforms of East coast of India generally denote features of emergence characteristics, while that of west coast are mostly dominated by features of submergence characteristics.

The geomorphology of district is broadly occupied by Western Pedi plains, deep buried pediment and pediments. The other part of the coastal plain is found with floodplain of fluvial origin developed by the influence of Ponnaiyar, Vellar and Coleroon river systems. In coastal region marine sedimentary plains are found in between marine sedimentary and fluvial flood plains. It is also said that sand dunes and back swamps are marked with the signature of fluvio marine deposits<sup>7</sup>. Particularly, geomorphic features of the study area can be categorized into alluvial plain, coastal plain, flood plain, pediplain and the remaining part are made of upland (Figure-3).

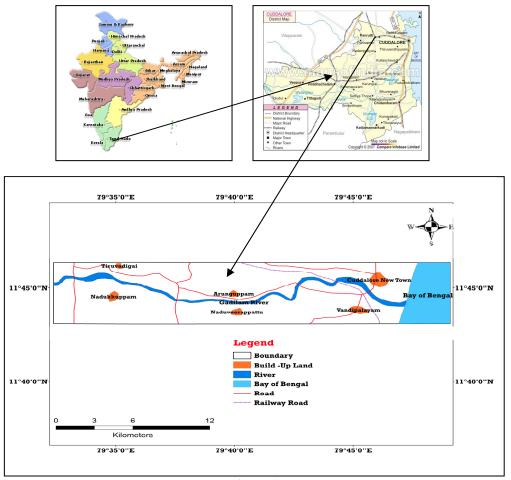


Figure-1 Study area location map

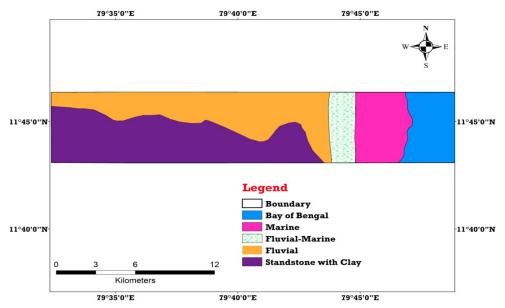


Figure-2 Geology map

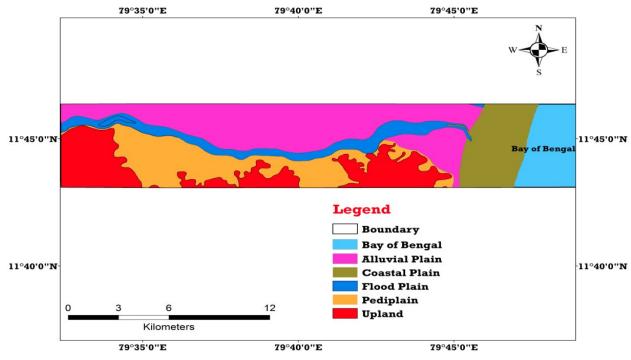


Figure-3 Geomorphology map

#### **Materials and Methods**

In the study area, almost seventeen sampling points were identified and collected randomly from mid-stream to downstream side within the study area. At each sample distribution point water samples are collected in clean rinsed polyethylene bottles. The physical parameters like pH and temperature water samples are monitored during the field survey. A pre-calibrated portable multi parameter kit PC TESTER 35(Multi-Parameter) was used for pH, Temperature and Electrical Conductivity (EC) measurements. Total Dissolved Solids (TDS) were estimated according to the suggested standard analytical methods<sup>8</sup> (Table-1). The examples were processed before the specimens were subjected to examination for the determination of trace metals utilizing AAS with particular fire and wavelength Atomic Absorption Spectrometer (Elico) (Table-2).

## **Results and Discussion**

Physical parameter of the study like pH varied from 8.1- 9.5 in post-monsoon periods, which lies in the range of acidic. The pH values of the study area are not within the limits of BIS and WHO drinking water standards<sup>9,10</sup>. It is understood that river waters with pH of 5.5 and below are hazard and the pH is predominantly resolved by the amount of dissolved carbon dioxide, which converts to carbonic acid in water and by decaying of flora and the dissolution of sulphide minerals to organic acids<sup>11-13</sup>. The higher concentration of ions in the

groundwater is due to weathering of silicate rocks and also from anthropogenic activities. Moreover evaporation leads to the concentration of ions thereby increasing the chemical budget of groundwater. EC values of the study area ranged from 0.240-1415 mhos/cm in post-monsoon period. The highest conductivity in downstream station is due to the flooding of sea water from Bay of Bengal during sea level rise<sup>14</sup>. The least possible conductivity may be due to the intensity of rain water. On the other hand, the change in conductivity in all locations was statistically insignificant. Total dissolved solids (TDS) in the study area are comparatively more during post-monsoon period, values range 168-991mg/L.

According to Kumar M. and Kumar R. 15, groundwater samples of Cuddalore during pre-monsoon and post-monsoon periods belong to brackish type (TDS>1,000 mg/L). It is reported that the considerable decrease in the concentration of ions in groundwater during post-monsoon period is due to dilution and discharges into the river water body. The absorption of heavy metals in water samples is systematically given as Iron (4.46-5.667mg/l), Chromium (0.78-2.44 mg/l), Manganese (1.03-1.71 mg/l), Cobalt (1.28-1.92mg/l), Nickel (0.31-1.87 mg/l), Copper (1.01-2.76 mg/l), Lead (1.06-1.96 mg/l), Zinc (1.12-2.67 mg/l) and Cadmium (0.05-0.58mg/l). This metal concentration leads to recognize the nature and pattern of distribution of these metals in the aquatic environment. The variation of metal distribution in aquatic environment is predominantly by anthropogenic activities and drastic changes in monsoon (Figure-4).

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Cadmium (Cd): Cd in surface water is contributed by various industrial practices found along the river. The average Cd concentration in water samples was found to vary between 0.05mg/L upstream and 0.56mg/L in downstream of the river (Figure-5). The values attained were found to be extremely higher than the permissible limit of 0.01mg/L set by WHO<sup>16</sup> and according to USPH standards. Higher Cd in waste water samples suggest that the elevated level of pollution is due to dyes, paints and pigments production industries around Cuddalore industrial area where the untreated water is discharged into the ocean and river. The instability of metals in samples sites of river is also attributed by other industrial and anthropogenic sources.

The dissimilarity of heavy metal absorption in both untreated and treated effluents was due to decreasing effectiveness of primary and secondary treatment of the Effluent Treatment Plant (ETP). In downstream side of the study area, it is observed that high concentration of metals identified, when compared to midstream. This indicates that the dilution effect of river water is also one of the factors other than anthropogenic inputs.

Copper (Cu): The mean concentration of Cu in river water ranges with 1.01 mg/L in downstream and 2.76mg/L mid stream close to main wastewater discharge point signifying an anthropogenic input Cu. The observed values are above the permissible limit of 0.05mg/L put by WHO and 1.0mg/L as per the USPH standards. The Cu concentration in the vicinity is amplified two times when compared to the outlet that is recognized as the reason of anthropogenic activities, agriculture runoff, sludge from publicly owned treatment works (POTWs) and municipal and industrial solid waste dumped into the river water.

Table-1 Comparison of pH, EC, and TDS values

| Loc. No | рН  | EC EC  | TDS |  |  |
|---------|-----|--------|-----|--|--|
| 1       | 8.2 | 1400.0 | 980 |  |  |
| 2       | 8.3 | 1364.3 | 955 |  |  |
| 3       | 8.1 | 1371.4 | 960 |  |  |
| 4       | 8.2 | 1415.7 | 991 |  |  |
| 5       | 8.6 | 1302.9 | 912 |  |  |
| 6       | 8.1 | 357.1  | 250 |  |  |
| 7       | 8.4 | 310.0  | 490 |  |  |
| 8       | 9.2 | 263.0  | 304 |  |  |
| 9       | 8.2 | 367.0  | 690 |  |  |
| 10      | 8.7 | 528.0  | 825 |  |  |
| 11      | 8.9 | 307.1  | 215 |  |  |
| 12      | 8.4 | 571.4  | 400 |  |  |
| 13      | 8.5 | 321.4  | 225 |  |  |
| 14      | 8.1 | 460.0  | 322 |  |  |
| 15      | 8.3 | 415.7  | 291 |  |  |
| 16      | 8.7 | 551.4  | 386 |  |  |
| 17      | 9.5 | 240.0  | 168 |  |  |

Table-2
Heavy metal concentration in water (Gadilam River) (mg/l)

| Loc. No | Fe   | Cr   | Mn   | Ni   | Cu   | Pb   | Zn   | Cd   |
|---------|------|------|------|------|------|------|------|------|
| 1       | 5.11 | 1.79 | 1.31 | 1.87 | 1.22 | 1.96 | 1.76 | 0.56 |
| 2       | 5.35 | 0.99 | 1.39 | 1.01 | 1.22 | 1.06 | 2.67 | 0.58 |
| 3       | 5.25 | 1.57 | 1.27 | 1.52 | 1.01 | 1.21 | 1.12 | 0.4  |
| 4       | 5.22 | 2.42 | 1.27 | 1.42 | 2.54 | 1.43 | 1.81 | 0.43 |
| 5       | 5.34 | 1.32 | 1.32 | 1.11 | 1.99 | 1.51 | 1.69 | 0.09 |
| 6       | 5.56 | 1.69 | 1.46 | 0.92 | 1.78 | 1.29 | 1.72 | 0.13 |
| 7       | 5.21 | 1.72 | 1.71 | 0.84 | 2.34 | 1.66 | 1.94 | 0.23 |
| 8       | 5.67 | 1.03 | 1.62 | 0.31 | 2.76 | 1.72 | 1.37 | 0.12 |
| 9       | 5.34 | 0.78 | 1.53 | 1.32 | 2.55 | 1.63 | 1.52 | 0.05 |
| 10      | 5.12 | 1.34 | 1.69 | 1.54 | 1.95 | 1.24 | 1.91 | 0.07 |
| 11      | 5.15 | 1.86 | 1.41 | 1.66 | 1.66 | 1.29 | 1.67 | 0.09 |
| 12      | 4.98 | 2.44 | 1.28 | 1.73 | 2.13 | 1.81 | 1.82 | 0.11 |
| 13      | 4.67 | 1.45 | 1.23 | 0.99 | 1.84 | 1.32 | 1.66 | 0.13 |
| 14      | 4.83 | 1.23 | 1.19 | 0.85 | 1.77 | 1.45 | 1.37 | 0.37 |
| 15      | 4.61 | 1.07 | 1.11 | 0.77 | 1.54 | 1.66 | 1.73 | 0.16 |
| 16      | 4.59 | 1.02 | 1.03 | 0.81 | 1.43 | 1.34 | 1.42 | 0.08 |
| 17      | 4.46 | 1.15 | 1.07 | 0.94 | 1.59 | 1.28 | 1.33 | 0.15 |

Copper is also discharged in to water as a result of natural weathering of soil, as outfall from industries and sewage treatment plants<sup>17,18</sup>. Cu concentration in midstream shows higher impact than the raw effluent Cu concentration. It is recognized that the domestic sewage and run-off from extensive farmed areas is also one of the factor<sup>19</sup>. It is also proven washed out copper compounds used in electroplating industries like cupric sulphate and cupric acetate. in fertilizers industries like copper naphthenate, paint industries such as cuprous oxide, ceramics and glass industries as cupric acetate, cuprous and cupric oxides and for making glass used as pigments were discharged through the treated industrial effluents. The occurrence of copper may also be due to spraying of fungicides, insecticides, herbicides in agricultural field. The prominent concentration of copper is also due to high alkalinity of water, when it is precipitated. This natural occurring element is extensively distributed in soils, rocks, in rivers and the sea.

Lead (Pb): Lead contribution in water samples shows a fluctuation of 1.06mg/L and 1.96mg/L in downstream area where river mixes with sea. Exposure to lead causes a variety of health effects, particularly affects children. Water is rarely an important source of lead exposure except lead pipes in old buildings. The proximity concentration of Pb at the sampling sites of river water could be recognized due to less solubility of Pb containing minerals in natural water, which is diluted through the dilution effect of the water<sup>20,21</sup>. The overall concentration of Lead in the study area is higher than other Indian rivers. It is summarized that the Pb has multiple source of input furthermore higher Pb concentration in the study area indicates the presence of contamination through various industrial effluents and local anthropogenic inputs. Lead is not often found in source water, but enters through the tap water by corrosion of plumbing materials. Lead toxicity is induced by lead ions reacting with free sulfydryl groups of proteins, such as enzymes.

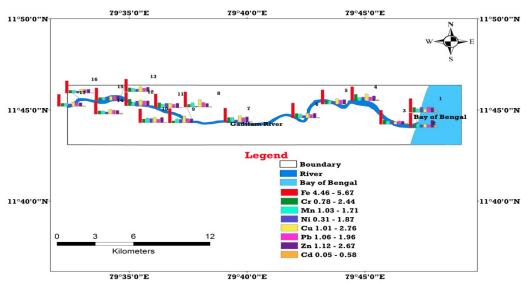


Figure-4 Heavy metal concentrations

**Zinc** (**Zn**): The Zn concentration throughout the study area ranges between 1.12 mg/L – 2.67mg/L. These metals can also be introduced into water naturally from minerals of rocks and soil by erosion. However, zinc ores are slightly soluble in water, even though little amount of zinc are normally found in nature. Further, zinc is also emitted through effluents of numerous commercial industries during mining and smelting (metal processing) actions, urban runoff, and municipal sewages are considered as the source of zinc in water<sup>22,23</sup>. The variation of zinc among these samples attributed to natural contribution from earth's upper continental crust, human activity, weathering of soils and rocks and most important are the presence of clay minerals, organic matter in sediments and the use of yield crop fertilizers.

Manganese (Mn): In the present study, Mn concentration throughout the study area ranges from 1.03mg/L in upstream and 1.71mg/L in mid-stream. Mn concentration is slightly higher in mid-stream area due to industrial and municipal wastages, which is recognized as the reason lack off plants<sup>24, 25</sup>. The manganese element is present in over 100 familiar salts and mineral compound that are generally found in rocks, in soils and on the lakes and oceans. Industrial discharge holding manganese oxides are the prime source of manganese in the atmosphere. The higher amount of Mn in certain localities in water and sediment are related to high levels of manganese in the adjacent ore bearing landmass and when the rivers flows through the ore bearing terrain picks up the element<sup>26</sup>, Zingde M.D.<sup>27</sup> has observed a decrease in concentration of Mn in water at the river mouth.

**Iron (Fe):** Iron is the most abandoned metals in earth crust. In the study area the concentration of Fe is 4.46mg/L in upstream end and 5.67mg/L in mid-stream side of the study area. It is reported that in natural fresh water the concentration of iron level ranges from 0.50 to 50 mg/l, it is also considered as a

fundamental element in human nutrition<sup>28</sup>. As per Rickwood C. et. al.<sup>29</sup> the accepted concentration level of Fe in drinking water is below 0.3 mg/l, but in the study area Fe concentration level was found around 5 mg/L. This indicates that the higher concentration of Fe in the study area is due to anthropogenic source of agricultural or urban runoff, municipal wastage<sup>30</sup>. However, contamination of anthropogenic origin cannot be excluded, since the Fe content is attributed by weathering of soil and rocks by various activities of mining high fertilizers for agricultural products<sup>23</sup>.

Chromium (Cr): In the study area Cr ranges from 0.78mg/L (mid-stream) to 2.44mg/L (River mouth), which is higher than the permissible limit of 0.05mg/L set by WHO standards. The higher concentration is due to lithogenic sources, industrial wastages and anthropogenic activities. The acceptable range of chromium in river water is 0.05mg/l<sup>31</sup>, it is found naturally in rocks, soil, plants, and animals. It also occurs with the combination of other elements as chromium salts, some of which are soluble in water. The pure metallic form rarely occurs naturally, it does not evaporate, does not degrade nor can it be destroyed. Chromium is an important element in metallurgy and used as a constituent in stainless and in "Chrome plating" as pigments. The high Cr compounds are also used as pigments, dyes in the textiles and tannery factories. The sources of Cr in the surface waters are from municipal wastes, laundry chemicals, paints, leather, and road run off due to tire wear, corrosion of bushings, brake wires and radiators and probably from anthropogenic sources<sup>32</sup>. Cr is generally more toxic at higher temperatures and its compounds are known to cause cancer in human<sup>33</sup>.

**Nickel** (**Ni**): Nickel concentration in water is estimated as 0.31mg/L in mid-stream and 1.87mg/L at downstream or mouth of the river. The tolerance limit in water as per BIS standard is 0.02mg/L and 0.1mg/L set by WHO. But in the study area the

tolerance limits is more than prescribed limits and below the permissible limit of 5.5mg/L as per USPH standard. In the study area, the higher amount of nickel in water is because of lithogenic sources, industrial wastages and anthropogenic exercises, it is also accumulated by both sulfide and oxide minerals. Nickel is a toxic component, the unpredictable compound like nickel tetra carbonyl Ni (CO) 4, which is utilized for the extraction of the component. Ni is not a toxic on human and but rather long haul presentation can bring about decreased body weight, heart, liver harm and skin irritation<sup>34</sup>.

# Conclusion

The maximum pH of Gadilam river water is 9.5, the maximum EC value is 1415  $\mu$  mhos/cm @ 32.5°C and the maximum TDS value is 991 mg/L. The low pH value may be due to the influence of fresh water influx, dilution of sea water, low temperature and organic matter decomposition.

The identified trace metals concentration in surface water of Gadilam river are slightly higher than other rivers in India, the elemental concentration all metals show slight elevated concentration in river mouth and mid-stream. This indicates the

study area is highly affected by industrial waste, municipal waste and in some places anthropogenic activities. In general, the concentrations of cations and anions are higher in the premonsoon ground water indicating excessive evaporation, silicate weathering and anthropogenic activities. Considerable decrease in concentration of cations and anions are found in the post monsoon water samples indicate that the dilution factor predominates over the leaching factor.

The trace metal concentration like Fe, Cu, Ni, Cr, Pb, Mn, Cd and Zn showed the influence of organic wastes from municipal sewage, industrial waste enters into the river of marine environment, there are various factors involved in the metal leaching into the water<sup>41</sup>. Some of the most important factors include the natural processes of releasing metals from minerals, physical characteristics of sediments, biogeochemical processes in the sediments, mine tailings, sewage sludge and dredge spoils and the effects of water characteristics (temperature, salinity, pH and DO). In future, additional studies are to be carried out with extensive sampling and analysis methods to measure all possible environmental geochemistry of the riverine ecosystem and put forwarding a management plan for stalk holders for protection.

Table-3 Comparison of dissolved metal concentration with other Indian River ( $\mu$ g/L)

|                     | 0011  | pur mon or |      |        | 1101 0001011 11 1011 |      |      | · <del>o</del> · / |               |
|---------------------|-------|------------|------|--------|----------------------|------|------|--------------------|---------------|
| Rivers              | Cd    | Cu         | Pb   | Zn     | Mn                   | Fe   | Cr   | Ni                 | References    |
| Mahanadi<br>River   |       | 5.9        | 2.68 | 11     | 96.9                 | -    | -    | -                  | 35            |
| Achankovil<br>River | 6.0   | 224        | 72   | 415    | 699                  | -    | -    | -                  | 36            |
| Ganga River         | 5     | 10         | 120  | 60     | 260                  | -    | -    | -                  | 37            |
| Damodhar<br>River   | 300   | 3950       | -    | -      | -                    | -    | -    | -                  | 38            |
| Brahmani<br>River   | 4     | 4.7        | 27   | 80.1   | 102                  | -    | -    | -                  | 39            |
| Uppanar River       | 36.08 | 191.5      | 98.5 | 201.38 | 273.93               | -    | -    | -                  | 40            |
| Gadilam River       | BDL   | BDL        | 320  | 70     | -                    | -    | BDL  | BDL                | 41            |
| Gadilam River       | 580   | 2760       | 1960 | 2670   | 1710                 | 5670 | 2440 | 1870               | Present study |

<sup>\*</sup>BDL (Below Detection Level)

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