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Perchlorate in Ground Waters of Industrial Areas in Kerala, India

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Abstract

Perchlorate has been increasingly reported in ground waters of industrial Kerala. The Perchlorate (ClO4–), is a manufactured chemical used as the main ingredient of rocket fuel, safety flares, matches, fireworks, batteries and vehicle air bags. Presence of perchlorate in drinking water may damage the thyroid gland, which controls growth and metabolism. The objectives identified are to study the temporal variation of Perchlorate in ground waters of industrial areas in Kerala, variation in shallow and deep aquifers, aerial distribution of Perchlorate in ground waters of industrial areas in Kerala, find out the suitability of Perchlorate containing ground water in the area for various purposes and to compile the base line information on perchlorate in ground waters of all industrial areas in Kerala.

Keywords: Bioremediation; Ernakulam; Periyar; Temporal Variation; Aerial Variation

Introduction

Presence of Perchlorate in ground waters of industrial areas in Kerala, India has been reported in recent years. Perchlorate (ClO4–), is a manufactured chemical used as the main ingredient of rocket fuel, safety flares, matches, fireworks, batteries and vehicle air bags. The perchlorate anion consists of a tetrahedral array of oxygen atoms around a central chlorine atom. Perchlorate is usually found as the anion component of a salt most often associated with cations such as ammonium, sodium, or potassium [1]. It is an anion that originates from the dissolution of ammonium, potassium, magnesium, or sodium salts and mobile in ground water and surface water systems and can persist for many decades. Due to exceptional oxidizing capacity, perchlorate is used in the manufacture of munitions, explosives and fireworks, specific medicinal applications and has been used medically to control hyperthyroid conditions and Graves disease [2,3]. The principal health concern is that if perchlorate gets into drinking water it could damage the thyroid gland, which controls growth, development and metabolism. Perchlorate interferes with iodide uptake into the thyroid gland, and because iodide is an essential component of thyroid hormones, it disrupts how the thyroid functions. Impairment of a woman's thyroid function during pregnancy may impact the baby and result in delayed development and decreased learning

capability. Changes in thyroid hormone levels may also result in thyroid gland tumors.

Several types of point-of-use or point-of-entry treatment systems for homes, including exchange resins, reverse osmosis and distillation, can reduce perchlorate concentrations in well water. Some ion exchange resins remove all other anions before binding perchlorate, resulting in corrosive water that may need to have some hardness restored. Because perchlorate binds tightly to resins, high salt concentrations may be necessary for resin regeneration. Brine disposal could then be a problem because the perchlorate is concentrated and not destroyed. For contaminated site clean-up, many different technologies are under development, including biological treatment and large-scale ion (anion) exchange systems. Biological processes (bioremediation) may be the most cost efficient, and research continues with bioreactor treatment systems and with below ground in-situ treatment involving trenches filled with bio-barriers of organic material. The industrial area of the state is mainly Aluva in Ernakulam district and the area is noted for the manufacturing of pesticides, fertilizers, rocket fuel, safety flares, matches and fireworks. Some areas viz. Veli and Thumba in Thiruvananthapuram district are also noted for the manufacturing of pesticides, fertilizers, rocket fuel, safety flares, matches and fireworks. Another major industrial belt of Kerala is Kanjikode in Palakkad district engaged in the manufacturing of safety flares, matches, fireworks and many others.

Objective of the Work

The project objectives include

- To know the temporal variation of Perchlorate in ground waters of industrial areas in Kerala
- To know the aerial distribution of Perchlorate in ground waters of industrial areas in Kerala
- To compare the Perchlorate in ground waters of industrial areas in Kerala in the shallow and deep aquifers
- To know the controls and mechanisms of Perchlorate concentration in ground waters of industrial areas in Kerala
- To find out the suitability of Perchlorate containing ground water in the area for various purposes viz. domestic, irrigational and industrial
- It is high time to compile the base line information on perchlorate in ground waters of all industrial areas in Kerala.

Study Area

Kerala is a tiny strip of land, located in the southwestern tip of India between North latitudes 8° 18'and 12° 48' and East longitudes 74° 52' and 77° 22' (Figure 1), occupying 1.2 percent of India's land area and occupies an area of 38,863 sq.km, stretching 580 km in length and 30.13 km in breadth. In terms of area, though Kerala forms only 1.2% of the total area of India (32,863 sq. km), 3 percent of country's population inhabits the State. Kerala receives mean annual rainfall of more than 3000 mm, received mainly during the Southwest Monsoon period, extending from May to September, followed by the Northeast Monsoon in the months of November and December.

Age	Formation	Lithology
Recent	Alluvium	Sand, clay, riverine alluvium etc.
Sub-recent	Laterite	Derived from crystalline and sedimentaries
Tertiary	Warkali Quilon Vaikom Alleppey	Sandstone, clays with lignite Limestone, marl and clay Sandstone with gravel, pebbles, clay and lignite Carbonaceous clay and fine sand
Undated	Intrusive	Dolerite, Gabbro, Granites, Quartzo-feldspathic Veins
Archaean	Wayanad group Charnockites Khondalites	Granitic gneiss, Schists etc. Charnockites and associated rocks Khondalites suite of rocks and its associates

Table 1: Stratigraphic Succession of Geological Formations in Kerala.

The more than 88% of the State is underlain by crystalline rocks of Archaean age comprising schistose formations, Charnockites, Khondalites and gneisses. All these formations are intruded by dykes of younger age. The sedimentary formations of Tertiary age occurring along the western parts of the State comprise four distinct beds

viz. Alleppey, Vaikom, Quilon and Warkali. The crystalline and the Tertiary formations are lateralized along the midland area. Alluvial deposits of Recent origin are seen along the coastal plains and the stratigraphic sequence is compiled (Table1).

In hard rock terrain, comprising weathered crystallines and laterites, ground water occurs under phreatic conditions in the weathered residuum and the shallow fractures hydraulically connected to it, whereas it is under semi-confined to confined conditions in the deep fracture zones. In the alluvial terrain, ground water in the shallow aquifer systems is in phreatic condition. Granular zones in the Tertiary sedimentary formations at deeper levels form potential confined to semi-confined aquifers.

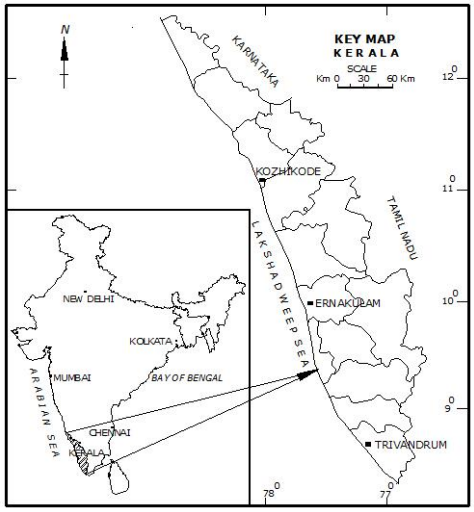

Figure 1: Location map of Kerala.

Background

The detailed hydrogeological studies carried out in the proposed study area by the CGWB, KR and the studies include systematic and reappraisal studies, special studies on industrial pollution, routine premonsoon qualitative analysis of ground water samples and Grounds Water regime studies through periodic monitoring of ground water level. Perchlorate is produced in bulk in the ammonium perchlorate experimental plant (APEP) at Kalamassery industrial area in Ernakulam district of Kerala and the area surrounding this Plant is reported to have been affected with perchlorate contamination. Studies in coastal areas of central Kerala have found that a considerable section of the population suffers from thyroid disorders as well as a high incidence of thyroid cancer compared to other states. However, there are no studies that have shown evidence of the presence of perchlorate contamination in the water and its connection to health disorders. The studies by Nadaraja, et al. (2015) in Kerala identified perchlorate contamination in surface and groundwater at four places viz. Aluva in Ernakulam district, Thumba in Trivandrum district and other two locations in Kannur and Palakkad districts. The ammonium perchlorate experimental plant (APEP) where this chemical is produced in bulk is the major source of the contaminant in Aluva and Thumba. Whereas the contaminant source in Kannur and Palakkad districts is mainly from possible sources such as usage of ClO_4^- in fireworks, explosives etc., The studies indicate a high perchlorate contamination in groundwater compared to surface water. To date, the Bureau of Indian Standards (BIS) has not established a maximum contaminant level or enforceable regulatory limit for perchlorate in drinking water. The World Health Organization has established a provisional maximum tolerable daily intake (PMTDI) of

0.01 mg/kg body weight for perchlorate. The main purpose of the present study was to identify the mobility of perchlorate ion in groundwater to develop a solute transport model in the aquifer system and the chemical reactions it undergoes within the system (if any) and its socio-environmental implications.

Data Collection

As part of the study, a reconnaissance survey was carried out in the above area, where perchlorate contamination is reported/ suspected. The main objectives of the reconnaissance survey were to understand the general hydrogeological set up, physiography, slope-hydrology relationships, and local ground water level scenario and also to interact with the local population on the health problems associated with perchlorate in ground water, if any.

Location Brief of Project Area

The study area falls around, the ammonium perchlorate experimental plant (APEP) at Aluva in Ernakulam district (Survey of India (SOI) to po sheet No.58B/8). The area has been identified for a detailed study on perchlorate contamination and its mobility in groundwater. The study area falls between N latitudes 10° 03' 46.7028" and 10° 07' 31.7028"; and E longitudes 76° 19' 4.93" and 76° 25' 22.93" covering an area of 80.056 sq.km. The ISRO-APEP, is located at a distance of 8 km SE of Aluva town and is approachable by Aluva-Munnar road (Figure 2). The study area is bordered by the Periyar River in the North, Vazhakkulam-MES canal in the South, Periyar and Muttar (Tributary of Periyar River) rivers in the East, and in the

West by a minor tributary of The Periyar River flowing towards North.

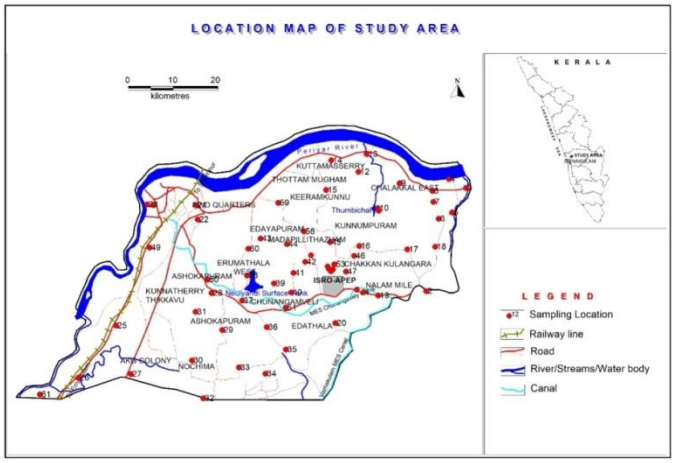

Figure 2: Location map of the study area.

Physiographic Setup

Physiographically, the study area falls in mid land division (7.6 – 76 m amsl) with undulating hills and valleys. The highest point in the study area is 55.6 m. amsl, located in the southern part of the study area, at about 800 m NE of Nochima on NAD road (Figure 3 and Figure 4). The area has got a plain to undulating topography with slope ranging from 0-15°. Geomorphologically, major part of the area is occupied by Lower Plateaus, and the remaining by valley fills and alluvial deposits of various geomorphological classes (Figure 5).

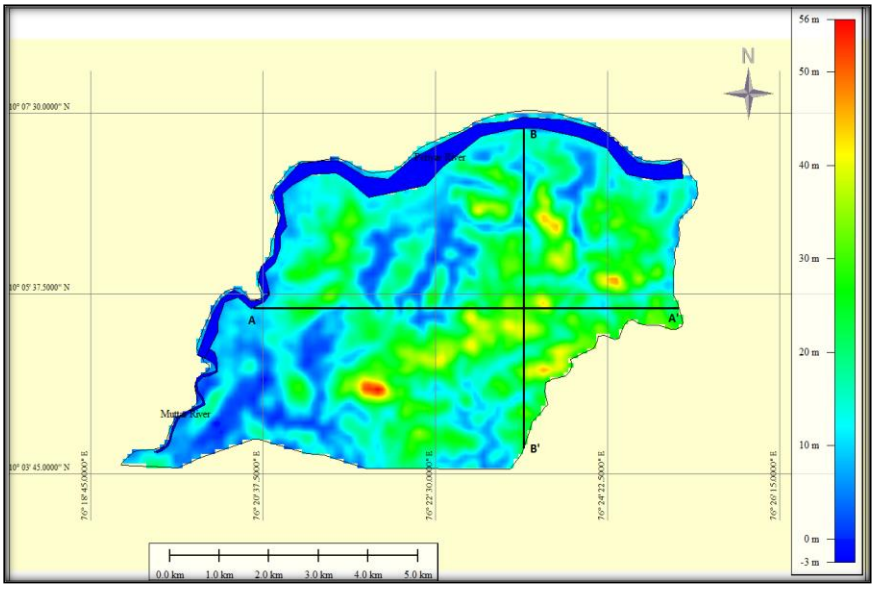

Figure 3: Digital Elevation Model of the study area.

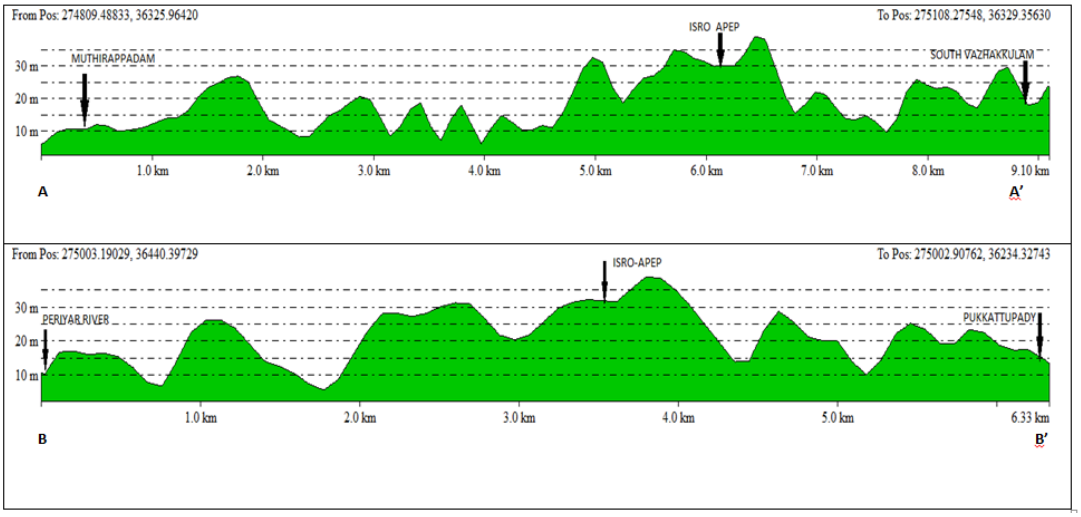

Figure 4: EW and NS topographic sections of the study area.

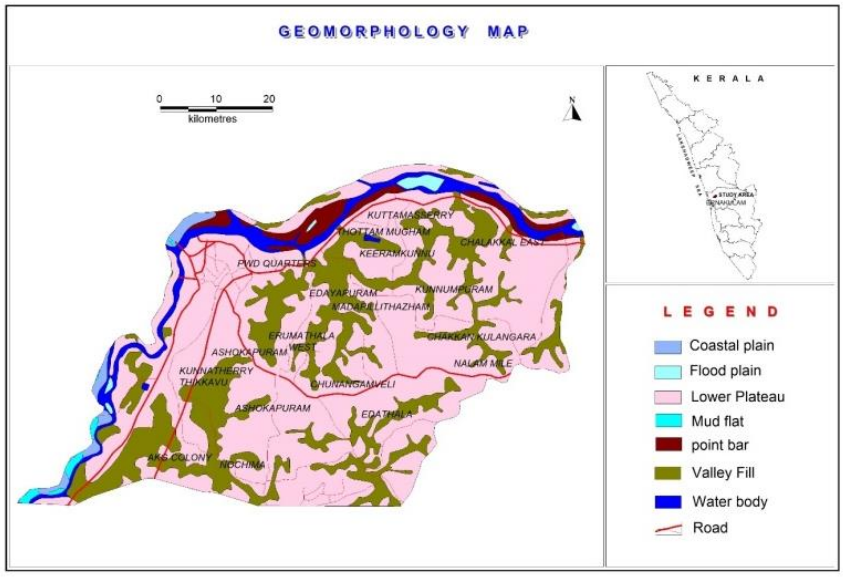

Figure 5: Geomorphologic map of the study area.

Soil Type

On the basis of morphological features and physico-chemical properties, the soils of the study area are classified as lateritic and riverine alluvium (mainly clay and clayey sand). The lateritic soil is the most predominant soil type of the area. These soils are well drained, low in organic matter and plant nutrients. The riverine alluvium is restricted to the banks of rivers and their tributaries. They are composed of sandy to clayey loam and are enriched in plant nutrients. It is suited for a large variety of crops like coconut, paddy, arecanut, pepper, vegetables etc (Figure 6).

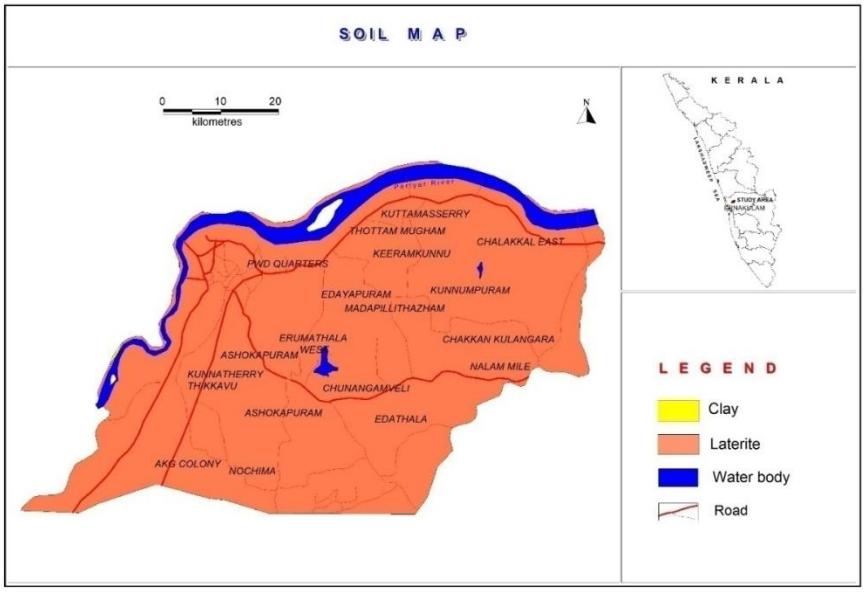

Figure 6: Soil map of the study area.

Hydrology

There exists many small surface tanks in the study area, out of which *Nediyandi,* in Chunangamvely West is the biggest with a perimeter of 1.93 km and area of 0.12 sq. km. followed by *Thumbichal,* at Kunnumpuram with a perimeter of 0.786 m and an area of 0.01783 sq. km. The study area is bounded in the North by Periyar River and in the East by Muttar, a tributary of Periyar. The drainage pattern is broadly dendritic with few minor tributaries contributing to the Periyar.

Geology and Structures

The geology of the study (Table 2) area has a direct influence on the hydrogeological and hydrochemical aspects of the area. The mode of occurrence of groundwater is as varied as the rock types in which they occur. A close correlation of the geology of the study area with the hydrogeological and hydrochemical data of the basin reveals that the geology of the area has high influence of the groundwater potential of the area. The Charnockites which is the dominant geological formation of the study area is a good aquifer for the development of groundwater.

Geologically, the study area has two distinct geological formations; crystalline rocks of Precambrian age, and the Recent alluvium deposits along the river course. The most widespread geological formations of the study area are the Precambrian crystalline rocks comprising Charnockites. The leading characteristics of the Charnockites are the granulitic texture and the invariable presence of rhombic pyroxene amongst the constituents. Charnockites in this area are both massive and foliated, showing strike in NNE – SSW to N – S direction with gentle dip towards West. Sub-Recent, laterites occur as a capping, above the Charnockites, with a lithomarge clay deposit in between. Quaternary formation is found at the entire stretch along the river course of Periyar and Muttar.

Age		Formation	Lithology
Quaternary	Recent	Alluvium	Sands, Clay
	Sub-Recent	Laterite	Laterite derived from Charnockites by Chemical weathering
Precambrian		Charnockites Group	Charnockites, intruded by felsic and mafic intrusives varying from Proterozoic to Tertiary periods

Table 2: Regional geological setting of the study area.

Hydrogeology (Groundwater Occurrence and Regime)

The groundwater generally occurs under phreatic condition in weathered (laterite) and fractured Charnockites, and unconsolidated river sediments along the courses of the Periyar and Muttar rivers in the study area. Ground water occurs under semi-confined to confined conditions in the deep-seated fractured aquifer of the crystallines rocks. The weathered laterite capping the Charnockites forms the primary phreatic aquifer in the study area. Lithology wise occurrence and movement of ground water is given below:

Hard Crystalline Formation

Groundwater occurs under phreatic condition in the shallow weathered portions whereas it occurs under semi confined to confined conditions in the deep-seated fractures of the crystalline formation. The hard rock formations in general lack primary porosity. The water is stored in the secondary pores developed as a consequence of weathering, fissures and joints etc. The movement of groundwater is controlled by the extent of the interconnection of the fractures. The depth of dug wells varies from 3.5-18.00 meters below ground level (mbgl) in the study area tapping the phreatic aquifer (Laterite) zone. The static water level in the wells tapping lateritic phreatic aquifers in the study area ranges from ranges from 3-15 mbgl. The laterites are highly porous and permeable. It is extensively developed by dug wells in the study area for domestic and to a limited extent for irrigation. The wells located on slopes and elevated areas go dry or have very small water column during the summer season.

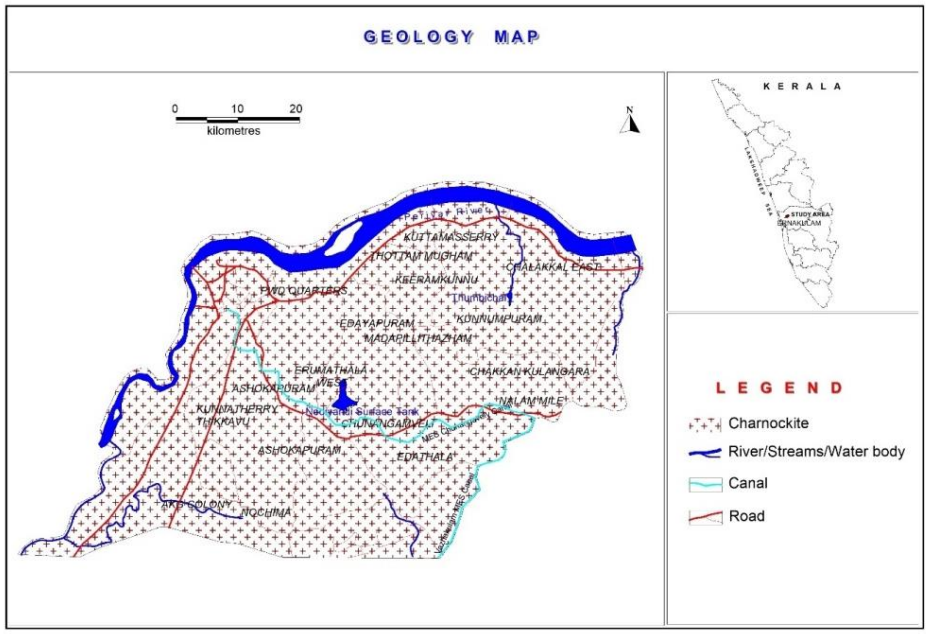

Figure 7: Geology of the study area.

Alluvial Formations

The thin beds of alluvial formation occur as the river/flood plain deposits in the study area along the courses of Periyar and Muttar. It forms aquifers in isolated pockets and the thickness of alluvium in such areas ranges up to a maximum of 10 m and is tapped by dug wells (having depth between 3-10 mbgl) and occasional filter points to meet domestic and other needs. The depth to water level in dug wells tapping alluvium ranges between 2 and 9 mbgl.

Ground Water Quality

The Ground water quality except for perchlorate in the study area is fairly good as observed during the preliminary survey. The electrical conductivity in laterite aquifers ranges between 30 and 270 µS/cm at 25 °C with pH in the range of 5.7-7.6, whereas in alluvium electrical conductivity ranges between 60 and 260 µS/cm at 25 °C with pH in the range of 5.6-6.4.

Groundwater Draft and Water Budgeting

Study under progress (detailed study will be carried out only after obtaining the financial approval for the study.

Status of R and D Activities

In addition to the main area around Aluva, certain samples were also taken from Thumba ERLS premises, Trivandrum and Puttingal village in Kollam district. A total of 92 samples for the analysis of perchlorate concentration and 51 samples to understand the hydro geochemical characteristics (major ions) of the aquifer were collected (Table 3).

#	Location/District	No. of Samples for Perchlorate analysis	No. of Samples for major ion analysis
1	Aluva/Ernakulam	61	37
2	Puttingal/Kollam	16	8
3	Thumba/Thiruvananthapuram	15	6

Table 3: Enumeration of samples collected as part of R&D study on perchlorate concentration.

Output and Outcome of the study

The expected output/outcome of the study include

- An effective scientific approach in the demarcation of areas affected by perchlorate contamination, evaluation of its concentration in the groundwater and understanding the chemical reaction and mobility of perchlorate in the aquifer system in space and time.
- Development of a predictive model of the solute (perchlorate) transport in the aquifer system so as to manage the groundwater resources in the area effectively.
- Assessment of socio environmental implications of perchlorate contamination and arrive at viable solutions to address the issue.

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