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Surveillance of perchlorate in ground water, surface water and bottled water in Kerala, India

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Abstract

Background: Perchlorate is an emerging water contaminant that disrupts normal functioning of human thyroid gland and poses serious threat to health, especially for pregnant women, fetus and children.

Results: High level of perchlorate contamination in fresh water sources at places nearby ammonium perchlorate (rocket fuel) handled in bulk is reported in this study. Of 160 ground water samples analyzed from 27 locations in the State Kerala, 58 % had perchlorate above detection limit (2 µg/L) and the highest concentration observed was 7270 µg/L at Ernakulam district, this value is ~480 times higher than USEPA drinking water equivalent level (15 µg/L). Perchlorate was detected in all surface water samples analyzed ($n = 10$) and the highest value observed was 355 µg/L in Periyar river (a major river in the State). The bottled drinking water ($n = 5$) tested were free of perchlorate.

Conclusions: The present study underlines the need for frequent screening of water sources for perchlorate contamination around places the chemical is handled in bulk. It will help to avoid human exposure to high levels of perchlorate.

Keywords: Ground water, Ion chromatography, Kerala, Perchlorate, Thyroid disorders

Background

Perchlorate (rocket fuel) is an oxyanion (ClO_4^-), extensively used in arms and ammunition industries [1]. The chemical is reported as a potential thyroid disruptor by inhibiting iodide uptake causing hypothyroidism and associated health effects especially in infants, pregnant women and fetuses [2, 3]. A number of animal studies have reported ClO_4^- induced toxicities including delayed metamorphosis, haemolytic anaemia, thyroid tumor development etc. [4–6]. The current health advisory level for ClO_4^- is set at 15 µg/L based on the reference dose recommended by US EPA [7]. The World Health Organization (WHO) established provisional maximum tolerable daily intake (PMTDI) of 0.01 mg/kg body weight for ClO_4^- [8]. However, in many countries including India, drinking water/wastewater standard for ClO_4^- is yet to be defined. Detailed assessment and continuous monitoring of ClO_4^- in water sources have been reported from various countries such as USA [9], Canada [10], Europe and Middle East [11], Japan [12], Korea [13], India [14, 15] and China [16]. Perchlorate was detected in

several food samples at concentrations above the Reference Dose (RfD) of 0.053 µg/kg bw/day proposed by National Academy of Sciences [17]. In USA, ClO_4^- was detected in 39 infant formulas at concentrations ranging from <0.4–13.5 µg/L [18].

An earlier study has reported ClO_4^- in 76 % of water samples collected from 13 locations in six States/Union territory (Tamilnadu, Karnataka, Bihar, Maharashtra, West Bengal and Pondicherry) in India with concentrations ranged from <0.02–6.9 µg/L [14]. But, a more recent study has reported ClO_4^- in the range <0.005–7,690 µg/L in ground water samples from near cracker manufacturing industrial area (Sivakashi) in Tamil Nadu, India [15]. Unlike the states covered in previous two studies, Kerala has two known major inventories of ClO_4^- . One is the ammonium perchlorate experimental plant (APEP) at Aluva in Ernakulam district where this chemical is produced in bulk and other place is Vikram Sarabhai Space Research Centre (VSSC) at Thumba, Trivandrum district. A preliminary study conducted in our lab (in 2010) has revealed wide contamination of ClO_4^- in water samples from many districts in Kerala. In a different perspective, a study conducted in the coastal area of central Kerala revealed 10–15 % of iodine-sufficient population suffering from

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thyroid disorders [19]. Studies have also shown high incidence thyroid cancer in Kerala compared to major cities in India [20]. However, a proper reason for these serious health problems could not be identified yet. In view of this the present study focus on a detailed assessment of ClO_4^- in ground and surface water samples giving emphasis to places where this chemical is handled in bulk. The finding of this study underlines the need for regular screening of ground and surface water sources for perchlorate around places where this toxic chemical is handled in bulk.

Methods

Study area

Five sites in Kerala were selected in this study for detailed assessment of ClO_4^- contamination. One of the sites was near Ammonium Perchlorate Experimental Plant (APEP) at Aluwa in Ernakulam district. The second site was at Thumba, near Vikram Sarabhai Space

Centre (VSSC) in Thiruvananthapuram district. The other two locations were in Kannur and in Palakkad districts. Our preliminary study has revealed high ClO_4^- level in water samples from these four districts. Location map of the study area is presented in Fig. 1. A fifth site, Koorg (latitude 12.33749° and longitude 75.80691°) in the nearby State Tamilnadu was selected as a control site. This is a hilly region (altitude ~ 5000 feet above sea level) and a far off place from any known inventories of perchlorate. Sampling was done from 27 locations in Kerala.

Sampling

Sampling was done during March – May 2012. Hundred ml of sample was collected from each point and filtered using $0.2 \mu\text{m}$ filters (Millipore) and brought to laboratory and stored at 4°C till analysis. Repeated sampling was done from sites that showed high ClO_4^- values.

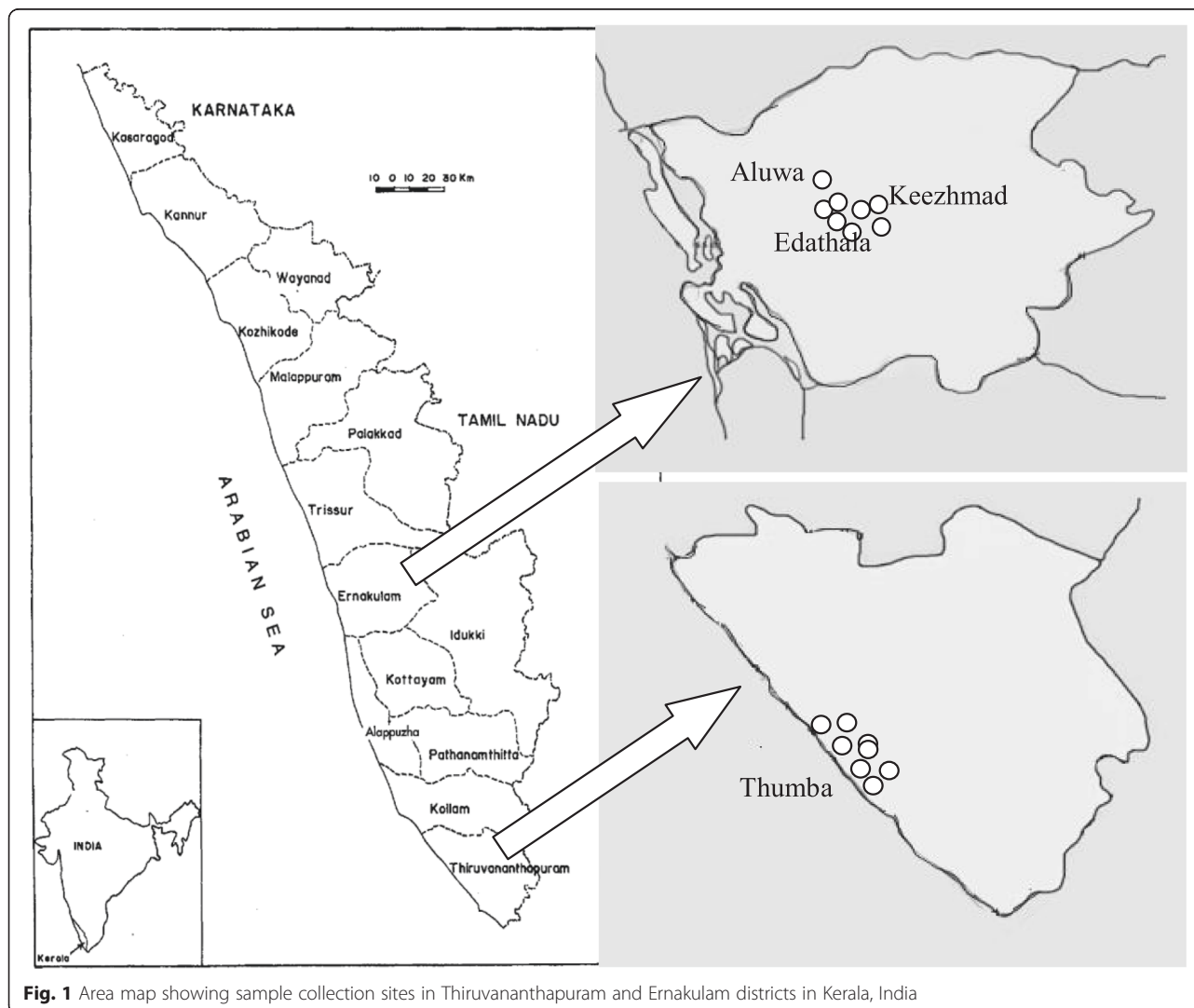


Fig. 1 Area map showing sample collection sites in Thiruvananthapuram and Ernakulam districts in Kerala, India

Perchlorate analysis in commercial drinking water

Perchlorate was also analyzed in 5 brands of bottled drinking water available in local market. These brands include Kinley, Aquafina, Neyyar aqua, Green valley and Surabhi.

Instrumental analysis

Water sample analysis was performed using an Ion Chromatography system (IC-1100, Dionex) with a separation column – Ion Pac AS 16 (2 × 250 mm and 4 × 250 mm), guard column – Ion Pac AG 16 (2 × 50 mm and 4 × 50 mm) and an anion self-regenerating suppressor ASRS 300 (4 mm). The Ion Pac AS 16 column is specific for ClO₄⁻ ion with a lower detection limit of 2 ppb (µg/L). This method for ClO₄⁻ detection in drinking water is recommended according to USEPA methods 314.0 and 314.1. The eluent used was 50 mM Sodium hydroxide (NaOH, Fluka) at a flow rate 1.5 mL/min. The injection volume was 1000 µL. Calibration standards of ClO₄⁻ was prepared with high purity KClO₄ (Sigma Aldrich) by diluting 1000 mg/L primary standard. All solutions were prepared in ultra-pure milliQ water (Millipore).

Quality assurance and quality control (QA/QC) for IC

Three sets of calibration curves were generated ranging from 5–30, 50–100 µg/L and 100–500 µg/L. Laboratory reagent blank and fortified samples were also analyzed for QC. The mean recovery of ClO₄⁻ with the AS16 column and analytical condition was 100 ± 10 %.

Results and discussion

Detailed assessment of perchlorate in water samples

The present detailed assessment of ClO₄⁻ was based on our preliminary study in the past. We have observed ClO₄⁻ contamination of water samples from public drinking, open well and surface water sources at few districts in Kerala and a maximum of 91.4 ppb ClO₄⁻ was observed in open well water (for drinking) from Thumba (near VSSC) [21]. More detailed screening of samples was done during this study. Perchlorate concentration in ground and surface water samples collected from different locations in Kerala is presented in Table 1 and 2 respectively. Of the 160 samples analyzed from 27 locations, 58 % had ClO₄⁻ above detection limit (2 µg/L). The highest concentration

Table 1 Perchlorate (µg/L) in ground water samples from different districts in Kerala

District	Sampling site	No. of samples	Highest value	Mean value	Median value	Geometric mean
Ernakulam	Aluva town	4	BDL	BDL	BDL	BDL
	Keezhmad	5	2.76	0.52±1.2	BDL	1.22
	Marampalli	4	4.7	1.2±2.3	BDL	1.47
	Kulakkad site 1	7	666	243±218	185	170
	Kulakkad site 2	2	7270	7230±49.5	7230	7230
	Nalammile	15	667	243±278	45.4	28.3
	Edathala site 1	3	6420	4270±3700	6400	345.2
	Vazhakulam	5	6.74	1.67±2.9	BDL	1.6
	Edathala site 2	8	BDL	BDL	BDL	BDL
	Kazhakutom	10	7.07	4.05±1.2	3.8	3.9
Trivandrum	Manavila	7	10.9	6.46±5.2	4.83	3.9
	Kumapuram	12	9.19	3.66±4	2.8	2.66
	Thumba site 1	7	155	85±40	75	77.3
	Thumba site 2	2	300	300±80	294.7	294
	Veli	5	17.7	9.88±7.3	12.32	6.87
Kannur	Kannapuram	4	20.10	13.65±4.9	13.2	12.9
	Morazha	3	17	5.67±9.8	BDL	2.57
	Kannur town	4	BDL	BDL	BDL	BDL
	Thalassery	2	BDL	BDL	BDL	BDL
	Arayal	4	17	10.15±8.3	11.8	6.64
Palakkad	Chittur	4	13.2	11.6±1.6	11.9	11.5
	Palakkad town	5	15.0	14±1.02	13.6	13.9
	Olarakode	2	8.2	7.19±1.4	7.19	7.12
Koorg (control site)	Koorg	2	BDL	BDL	BLD	BLD

Table 2 Perchlorate (ug/L) in surface water samples from different districts in Kerala

District	Sampling site	No. of samples	Highest value	Average	Median	Geometric mean
Trivandrum	Veli lake	2	19.6	16.4	16.4	16
Ernakulam	Periyar river	4	355	122	35.4	66.8
Palakkad	Sokanashini river	2	21	17.5	15.75	17.14
Kannur	Velli keel river	2	BDL	BDL	BDL	BDL

observed were 6420 µg/L and 7270 µg/L in samples from house hold open well at Edathala and from a public open well at Kulakkad respectively (both places are ~500 meters away from APEP). These values are ~480 times higher than drinking water equivalent level (DWEL), 15 µg/L established by USEPA. Perchlorate was detected in all the samples collected from Periyar river in the area with an average concentration 122 µg/L (n = 4) and the highest concentration observed was 355 µg/L. Periyar river (~3 km away from APEP) flows through the states of Tamil Nadu and Kerala, and it is one of the few perennial rivers in the region and provides drinking water to major town like Ernakulam in Kerala. Analysis of water samples from Trivandrum district also revealed high concentration of ClO₄⁻. The highest value observed was 300 µg/L in a house hold open well water from Thumba (near VSSC). The average ClO₄⁻ level in this region was 85 ± 45 µg/L (n = 7). The mean concentration of ClO₄⁻ in ground water samples from all the study area is given in Fig. 2. Ground water perchlorate level was high in Ernakulam and low in Kannur district. Fig. 3 shows a comparison of perchlorate in all ground water and surface water sources studied. Compared to surface water (mean = 773), the ground water (mean = 79) perchlorate level is almost 10 times higher.

Perchlorate was detected in 60 % samples (n = 18) from various places in Kannur district with a highest value of 20.1 µg/L. Perchlorate was also detected in all the samples (n = 5) from Palakkad district with a peak value of 15 µg/L in sample collected from a rock mining site. As

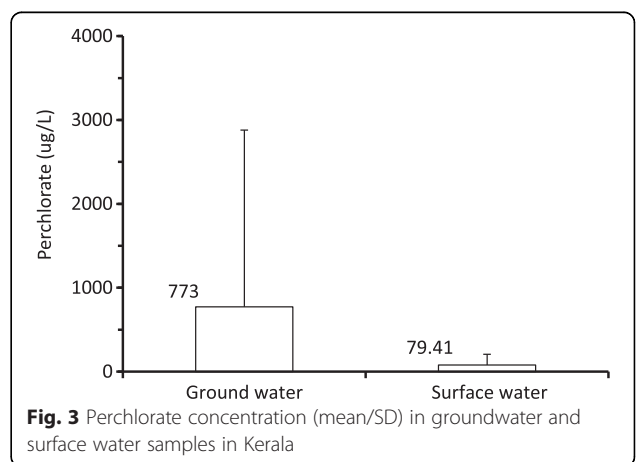
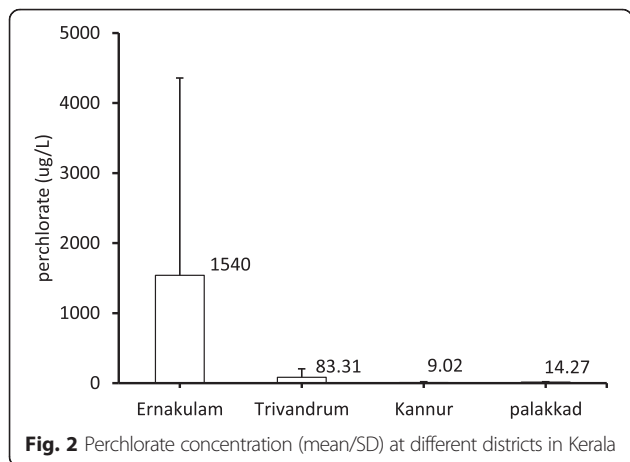
expected water samples from the public distribution system from Koorg had no detectable level of ClO₄⁻ due its geographical location.

Reports on perchlorate contamination in drinking water supplies from different countries in recent years indicate the growing concern about ClO₄⁻ contamination. Comparable to the high value (7270 µg/L) observed in this study, in a recent study 7,690 µg/L ClO₄⁻ was reported in ground water samples collected from fire cracker manufacturing sites Tamil Nadu, India [15].

USEPA has reported ClO₄⁻ analysis data collected from 3,865 public water supplies between 2001 and 2005 from several states and territories. It was found that, ~4 % of samples had at least one analytical detection of ClO₄⁻ at ≥4 µg/L and the maximum detected level was 420 µg/L.

Probable sources of ClO₄⁻ contamination in water sources in Kerala

The two inventories of ClO₄⁻ could be considered as the major sources of its contamination in Ernakulam and Trivandrum districts. The NH₄ClO₄ manufacturing and using places in Ernakulam and Trivandrum districts respectively in this state could be one of the potential sources of ClO₄⁻ contamination. Our preliminary study revealed high level of ClO₄⁻ (91.4 µg/L) and chlorate (ClO₃⁻) (177 µg/L) in water samples from Thumba, Trivandrum [21]. The present study also detected high level of ClO₄⁻ (300 µg/L) from household well water from Thumba. However, unlike the previous study, the



highest ClO_4^- concentration (7270 $\mu\text{g/L}$) was observed in public well water source located in close proximity to APEP in Ernakulam district. Ammonium perchlorate washout from these sources can be the potential source of high level contamination detected in ground water in this region. Isotope Ratio Mass Spectra (IRMS) analysis will provide more concrete information about the source of perchlorate in this region and other places in Kerala. Moreover, assessment of thyroid gland functioning of people around APEP will bring out health effects due to the exposure to high level of ClO_4^- in drinking water. Analyzing Thyroid gland functioning (TSH, T3, T4 etc. values) as well as Iodide and perchlorate level in urine samples will provide information about thyroid gland function and exposure level to perchlorate.

Perchlorate was also detected in water samples from the Northern districts, Kannur and Palakkad (20.11 and 15 $\mu\text{g/L}$) which are ~220 and ~150 km away from the APEP facility. The presence of ClO_4^- in these regions points to other possible sources like usage of ClO_4^- in fireworks, explosives etc. There are a large numbers of fire work display occurs in Kerala especially during April-May which is the festival season in the state. Several small scale fire work manufacturing units are operated during this period, however only few data about these industries are available as most of these are unauthorized. An increase in deposition of ClO_4^- by 18 fold was observed due to fallout from fireworks in USA [22]. In another study, surface water ClO_4^- level increase in the range of 24–1028 times was observed following fireworks display in Oklahoma Lake (USA) [23]. Perchlorate contamination due to firework production and display was also reported from China and Japan [12, 16]. As already mentioned, high levels of ClO_4^- was detected recently from ground water samples from a cracker manufacturing industrial area in Tamil Nadu [15]. A number of rocks mine operating in most of the districts in Kerala. The explosives used in these mines may include ClO_4^- salt also. Traces of ClO_4^- from these sites may also contribute to ClO_4^- contamination of waters in Kerala. This could be a potential source of ClO_4^- in the water sample from near rocks mining areas of Palakkad. No information is available on the consumption of ClO_4^- in rock mines, primarily due their unauthorized operational status similar to small scale fire-cracker industries. Perchlorate can also form naturally under rare environmental conditions like ozone oxidation of aqueous chloride or through electric discharging of chloride aerosol [24]. Natural ClO_4^- deposits were found at relatively high concentration in Atacama Desert in Chile [25]. High concentration of ClO_4^- (1000 mg/Kg) was detected in natural mineral ores like potash ore from places like New Mexico, Canada, Bolivia and California [26]. Stable isotope analysis of chlorine and oxygen in

ClO_4^- ($^{17}\text{O}/^{16}\text{O}$, $^{18}\text{O}/^{16}\text{O}$ and $^{37}\text{Cl}/^{35}\text{Cl}$) can distinguish the nature of ClO_4^- (synthetic or natural) present in environmental samples [27].

Screening of commercial drinking water for perchlorate contamination

Perchlorate was not detected in any of the bottled drinking water samples tested in this study. Previous report from India also had a similar observation where ClO_4^- was not detected in 5 of the branded of bottled drinking water analysed [14]. Perchlorate concentration was also very low (<0.002–0.22 $\mu\text{g/L}$) in bottled water from China [16]. However ClO_4^- was found in 10 of the 21 bottled water samples in USA with a mean concentration of 0.16 $\mu\text{g/L}$ [28].

Conclusions

The present study reveals high level ClO_4^- contamination in ground and surface water around places where ClO_4^- is handled in bulk. The contamination was more severe in ground water (max. value 7270 $\mu\text{g/L}$) compared to surface water (max. value 355 $\mu\text{g/L}$), both from Aluva in Ernakulam district, Kerala. Findings of this study points to the need for frequent monitoring of ground water samples around places where ClO_4^- is handled in bulk and necessitate epidemiological study in the contaminated area to assess the status of thyroid gland functioning. This study also underlines the need for defining water quality standards for perchlorate in India and also for controlling the environmental release of perchlorate especially from point sources like the manufacturing and using sites.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

AVN & PGP: Sample collection from field, chemical analysis and manuscript preparation. KKB Conceived the study, data analysis, interpretation of results and manuscript preparation. All authors read and approved the final manuscript

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