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The Occurrence of Perchlorate Contamination in the Aquatic Environment of Kerala

Divya, P.S.[1*] and Benno Pereira, F.G.[2]

[1]*PG and Research Department of Zoology, Sree Narayana College, Kollam.*
[2]*Department of Zoology, University of Kerala, Trivandrum, Kerala.*
**Email: divyanu111@gmail.com*

Abstract
Environmental contamination of perchlorate (ClO_4^-) is becoming a serious health concern due to its widespread distribution in both ground and surface waters and its impairment of thyroid gland functioning (Isobe *et al.*, 2012). The current health advisory level for ClO_4^- based on the reference dose recommended by the National Academy of Sciences is 56ìg/L (USEPA, 2019).The perchlorate (rocket fuel) contamination in water sources collected from a community pond around an ammonium perchlorate production plant is located in Kerala is reported in this study.Water samples were collected from the different site of the pond for a period of one year (2014 June -2015 May) and analyzed for perchlorate. The perchlorate concentration ranged from 6000 ìg/L to >10,000 ìg/L. In our study, water samples collected from a contaminated perchlorate site revealed that a high concentration of ClO_4^- was present in the water samples collected from the contaminated area, which is much higher than the International guidelines.This report points out the need for close monitoring of ClO_4^- contamination in Kerala and also for implementing regulatory measures for controlling the environmental release of ClO_4^- in Kerala or India as a whole.

Keywords: Freshwater, Ecosystem, Pollution, Kerala

1. Introduction

Perchlorate (ClO_4^-) has been identified as a persistent pollutant which causes detrimental health effect and is acting as an endocrine disruptor (Wu *et al.*, 2010). Perchlorate is a naturally occurring and man-made compound, whereas anthropogenic source are the leading cause of contamination of aquatic ecosystem (Trumpolt *et al.*, 2005; Morrison *et al.*, 2006). The primary mechanism of perchlorate toxicity is associated with the thyroid gland and thyroid hormone production.The fate and effect of perchlorate in an aquatic environment are of immense concern because perchlorate salts are soluble, stable and persistent in water (Urbansky and Shock, 1999). Due to high stability and low reactivity, ClO_4^- transport readily in surface waters and through soils to groundwaters (Sparks, 1995). In an aqueous medium, perchlorate anion readily dissociates from its various cation and remains stable for an extended period under normal environmental conditions (Urbasky, 1998). Perchlorate present in groundwater can be transported and might reside for decades (Flowers and Hunt, 2000; Morrison *et al*. 2006). Due to these properties, aquatic organisms are most susceptible to perchlorate toxicity.The important health effect of perchlorate in humans and other ecological receptors are the inhibition of iodide uptake and subsequent thyroid hormone synthesis (Wolff, 1998; Clark, 2000).

Perchlorate contamination was reported from various food materials such as rice, fruits, leafy vegetables and breast milk. Presence of perchlorate was continuously reported from multiple water sources such drinking water, groundwater, surface water, seawater, snow and rainwater (Martinelango *et al.*, 2006; Ye *et al.*, 2013) from various countries (Dasgupta *et al.*, 2005; Munster *et al.*, 2009, Kannan *et al.*, 2009; Isobe *et al.*, 2013).The potential source of environmental contamination of perchlorate was mainly from its manufacturing, storage, testing, disposal sites and from military installations (USEPA, 2008).ClO_4^-, toxicity study was reported from animals such as rats, deer mice, amphibians,birds,lizards,fishesand mammals (Sharma and Patino., 2013).

Perchlorate contamination generated considerable concern for human health due to its endocrine disruption property. The main mechanism of perchlorate toxicity is related to the thyroid gland and thyroid hormone production. The thyroid gland secretes two hormones, thyroxin (T_4) and triiodothyronine (T_3) and iodine is a key component of both. Thyroxin ($T_{4)}$ and triiodothyronine (T_3) regulate the growth, maturation of tissues and cell respiration. Thyroid tissues selectively concentrate iodide from the blood. The molecule that is responsible for the transport of iodide into thyroid is called sodium – iodide symporter (NIS) (Dohan *et al.*, 2003). Perchlorate can act as a strong inhibitor of the sodium iodide symporter (NIS), and it competitively inhibits with iodide and blocks iodide uptake across the basolateral membrane of thyroid follicle which reduces the production of thyroid hormones (Clark, 2000; Yu *et al.*, 2002). Wolff (1998) reported that perchlorate has a great affinity (30-fold greater) to sodium – iodide symporter as compared to Iodine. Besides thyroid, the NIS appears in the mammary gland, salivary gland, gastric mucosa and placenta (Tazebay *et al.*, 2000). Perchlorate inhibits the NIS present in the mammary gland and interferes with the secretion of iodide into breast milk.

Perchlorate present in food and water is the primary pathways of human exposure (ATSDR 2008). Perchlorate absorbed through the gastrointestinal tract and has 6 to 8 hours half-life in humans. Approximately 95% of

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perchlorate is excreted within 72 hrs through urine (Eichler. 1929). Perchlorate was mainly adsorbed through oral exposure, and it migrates from the stomach and intestines to the bloodstream (ATSDR, 2008). In the human body, the thyroid gland is the primary target organ of perchlorate toxicity. High level of perchlorate exposure can interfere with the iodide uptake into the thyroid gland and disrupt thyroid hormones synthesis (ATSDR 2008).Thyroid hormone regulates a significant role in metabolism, normal growth, development of the foetus, infants and young children. The thyroid hormone level in infants has found to be adversely affected by ClO_4^- exposure, however low level of ClO_4^-exposure does not cause serious health effects in adults (Brechner *et al.,* 2000; Buffler *et al.,* 2004). Previous studies reported that during lactation human mammary gland actively secretes perchlorate into breast milk and in infants; the primary route of exposure of perchlorate is through breast milk (Tazebay *et al*., 2000).

Among fishes perchlorate toxicity study was mostly done in Zebra fish (*Danio rerio*) (Mukhi and Patino., 2007; Schmidt *et al.,* 2012), Fathead minnows (*Pimephales promelas*) (Crane *et al.,* 2005); Eastern mosquito fish (*Gambusia holbrooki*) (Bradford *et al*., 2006), threespine stickle back (*Gasterosteruss aculeatus)*(Bernhardt *et al.,*2011; Furin *et al.,* 2015; Petersen *et al.,* 2016). These studies reported that perchlorate cause morphological deformities (Mukhi and patino., 2007; Bernhardt *et al.,* 2006 and Bernhardt *et al.,* 2011) reproductive abnormalities (Park *et al*., 2006; Bernhardt and Von Hippel., 2008) altered thyroid hormone, disruption of thyroid follicles (Schmidt *et al.,* 2012; Petersen *et al*., 2016). In fishes, the route of perchlorate exposure is through gills, integuments and gastrointestinal tract (Theodoraki *et al*., 2006).

Due to the toxicological and potential effects of perchlorate, numerous states and agencies proposed enforceable standards and guidance levels for perchlorate. In 1998 perchlorate was added to the Contaminant Candidate List (CCL) for drinking water by USEPA (USEPA, 1998). In 2002 the USEPA published a reference dose (RfD) of perchlorate in drinking water level (DWEL) of approximately 1µg/L (USEPA, 2008). In 2005, U.S. EPA established an oral reference dose (RfD) of perchlorate was 0.0007 milligrams per kilogram body weight per day and drinking water equivalent level (DWEL) of 24.5 ìg/L. According to USEPA (2008), ClO_4^- is set as 15ìg/L based on the reference dose recommended by the National Academy of Sciences (NAS).The current health advisory level for ClO_4^- based on the reference dose recommended by the National Academy of Sciences is 56ìg/L (USEPA, 2019). Various states in the United States have implemented guidelines for perchlorate, ranging from 1 ìg/L to 18 ìg/L in drinking water and 1 to 72 µg/L in groundwater. The World Health Organization (WHO) established provisional maximum tolerable daily intake (PMTDI) of 0.01 mg/kg body weight for ClO_4^- (WHO, 2010). The maximum contaminant level (MCL) of perchlorate in drinking water was 6 and 2 ìg/L as proposed by California Department of Health Services (CDPH, 2007) and Massachusetts Department of Environmental Protection (2006) respectively. Ministry of Health, Korea (2010) added ClO_4^- in the pollutant list and set an advisory level of 15ìg/L. However, India does not publish standard guidelines or regulations for the level of perchlorate yet.

As an emerging environmental pollutant perchlorate requires utmost concern, and its contamination report seeks global attention in the current world. Perchlorate contamination was continually reported from various countries such as Canada (Backus *et al*., 2005; Kosaka *et al*., 2007), Japan (Munster *et al*., 2009), Korea (Kim *et al*., 2009), China (Quin *et al*., 2014) and India (Kannan *et al*., 2009; Isobe *et al*., 2013 and Nadaraja *et al*., 2015). At the same time,widespread occurrence of ClO_4^- was mainly reported from USA (Dasgupta *et al*., 2005) Insights from the extensive studies on ClO_4^- contamination that has been carried out in various countries of the world. Natural occurrences of perchlorate salts were reported from different countries such as New Mexico, Canada and Bolivia. The high concentration of perchlorate was mainly associated with Chilean nitrate fertilizers and potash ore (Orris *et al*., 2003). A studyreported that substantial reservoir (up to 1 Kg/ha) of natural ClO_4^- was found in unsaturated zones of arid and semi-arid regions in the South-West states of USA (Rao *et al*. 2007). Perchlorate contamination due to long-term atmospheric deposition was observed in Northwest Texas, Eastern and Central New Mexico in USA (Parker *et al*., 2008). Similarly, widespread occurrence of natural ClO_4^- was reported from Texas and New Mexico at different concentration levels (<4µg to 200µg) (Rajagopal *et al*., 2006). A recent study from Northern Chile reported that high concentration (290 ± 1 µg/kg to 2565 ± 1 µg/kg) of ClO_4^- was present in soil and water samples collected from a different region. The high concentration of Perchlorate (4 to 31,438 µg/L) was detected in water samples collected from Harrison Bayou and INF pond located near Longhorn Army Ammunition plant in central Texas (USA)(Smith *et al.* 2004). Another study reported that perchlorate contamination was reported from Colorado River (USA) and around 20 million peoples were exposed to ClO_4^- through drinking water drawn from this river. Smith *et al*. (2004) pointed out that among the US states, ClO_4^- contamination was mainly reported from Las Vegas and Nevada area with high concentration (from 630 mg/L to 3,700 mg/L). Moreover, ClO_4^- contamination was reported from Harrison creek and South Bosque River located near the naval weapons industrial plant in McLennan country, Texas (Theodorakis *et al.,* 2006). According to USEPA report over 60 Department of Defence (DOD) facilities from 35 states in the USA has detected to ClO_4^- from soil, drinking water, groundwater and surface water (USEPA, 2008). Backus *et al*. 2005 reported that ClO_4^- was detected in water samples collected from the Great Lake Basin in Canada mainly at the site related to the firework. A study conducted in Japan pointed out that high concentration of ClO_4^- was detected (340 and 2300 µg/L) in the Tone River and its tributaries as well as from tap water samples (>10 µg/L) (Kosaka *et al*., 2007).

The high concentration of ClO_4^- (34.1µg/L and 411µg/L) was found in tap water and river water samples collected from Korea (Kim *et al.,* 2009). A study reported that of

ClO_4^- and ClO_3^- were detected from lakes, streams and other surface bodies of the Antarctic region (Jackson *et al.*, 2012). perchlorate was detected from the rainwater samples collected from China (0.35 – 27.3 ng/mL), and precipitation may act as an important source of rain water contamination(Qin *et al.* 2014). A recent report of a multinational survey suggested that high concentration of ClO_4^- was found in indoor dust samples collected from 12 countries including USA, Colombia, Japan, Korea and India and the highest concentration (104µg/L) was reported from China (Wan *et al.*, 2015). A recent study reported that perchlorate is vulnerable to thyroid-blocking populations. (McMullen *et al.*, 2017). Cao *et al* (2019) reported that perchlorate showed worldwide occurrence and origin in waters.

Perchlorate contamination was also reported from South India**.** A study reported that, water samples collected from six states in India, ClO_4^- was detected in76% of the total water samples and the mean concentration of ClO_4^- in groundwater, drinking water, bottled water, surface water and rainwater was 1.0, 0.1,<0.02, 0.05 and <0.02µ/L respectively (Kannan *et al.*, 2009). Besides,in the present study also reported that $ClO_4^-$was present at different concentrations (0.2 µg/L - 4.7µg/L) in human saliva samples collected from three states in India. A report pointed out that ClO_4^- was present in ground water (< 0.005 -7690 µg/L), surface water (<0.005- 30.2 µg/L) and tap water (0.063- 0.393 µg/L) samples collected from Sivakasi and Madurai in Tamil Nadu (Isobe *et al.*2013). Perchlorate contamination was reported from various districts of Kerala. Perchlorate was reported from groundwater samples collected from 27 locations in Kerala showed that 58 % of the samples had perchlorate above the detection limit (2 µg/L) and the highest concentration was found at Ernakulam district (7270 µg/L)(Nadaraja *et al*. 2012). Among surface water samples, the highest value was reported from the Periyar River (355 µg/L). ClO_4^- was present in 51 rice samples (below the detection limit to 1.79 ± 0.39 µg/kg) purchased from a local market and seven samples (0.38 ± 0.1 to 3.23 ±0.47 µg/kg) collected from the Nakdong River watershed area of South Korea (Kim *et al*. 2014).

2. Materials and Methods

2.1 Study area

The present study was carried out in an area covering 5 km around of an ammonium Perchlorate production unit located at Keezhumadupanchayath in Aluva, Ernakulam district, Kerala, India. The location map of the study area is given in Fig. 1. The Ammonium Perchlorate Experimental Plant (APEP) of ISRO was located in Keezhmadu panchayath in Aluva. (10°05’43.74" N 76°23’25.17"E). The annual production capacity of the APEP is around 800 tons, where ammonium perchlorate is manufactured.

2.2 Sampling sites

Water samples were collected from a pond present in the contaminated area (Fig 2). Water samples were also collected from five different sites (S1 - S5) in a community pond (Kulakkadu pond) which covering 640 m^2 area, average depth 5 M, located ~600 m from the production unit. The residents use the pond water for feeding cattle, washing and other domestic purposes. A narrow stream has ~2 feet wide and ~2 feet depth flowing into the pond close to site 4. Water samples from this stream were also collected for ClO_4^-analysis.

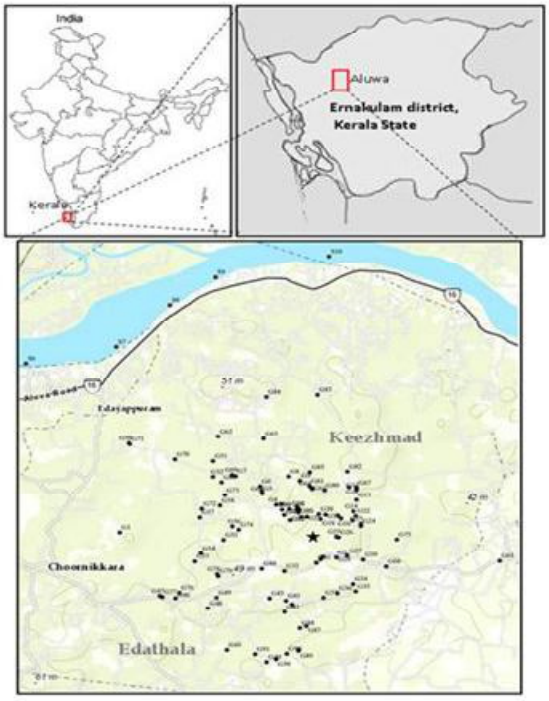

Fig. 1. Study site : Keezhmad panchayath

2.3 Water sample collection

In the present study, an extensive analysis of ground and surface water samples was done on a basis for a period of one year from June 2014 to May 2015. Water samples were collected withpre-cleaned 50 ml polythene vials just below the water surface. Three samples (50 ml) were collected from each study site. The samples were appropriately labelled before they are transported to the laboratory. The collected samples were brought to the laboratory and filtered immediately using 0.2ìm filters (Millipore), and stored at 4 °C till analysis.The physic chemical parameters were analyzed by using standard protocol (APHA,2005).

Fig. 2. Kulakkadu pond

2.4 Perchlorate analysis

2.4.1 Instrumental analysis

Perchlorate in the water samples was analyzed using ClO_4^- ion-selective electrode (ISE) with a lower detection limit 500 ppb (Cole Parmer, USA) and Ion Chromatography system (IC-1100, Thermo Dionex). The field samples were initially screened with ISE and subsequently diluted (if necessary) to ppb (µg/L) level for accurate analysis with the IC system. The IC was equipped with a self-regenerating anion suppressor (ASRS 300) and a conductivity detector. The Ion Pac AS 16 column specific for ClO_4^- ion with a lower detection limit of 2 ppb (µg/L) is used in this study in combination with AG 16 guard column (USEPA methods 314.0 and 314.1). The eluent used was 50 mM Sodium hydroxide (NaOH) at a flow rateof 1.5 mL/min. The injection volume was 1000 µL. All reagents were purchased from Sigma Aldrich, and standards were prepared in ultra-pure water (Millipore).

2.5 Quality control and Quality assurance (QC/QA)

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 ClO_4^- with the AS16 column and analytical condition was 100±10%.

3. Results and Discussion

Distribution of perchlorate in the area

The distribution of the toxic ClO_4^- in water sources during a period of 12 months was assessed based on ClO_4^- concentration in a water sample collected from the pond present in the contaminated area. Perchlorate concentration and water quality parameters in five different sampling points every month in the pond is given in Fig. 3 and Table 2. The result showed highest ClO_4^- concentration was reported from site 4 (29±1.5 mg/L) and lowest from site 1 (<2 mg/L) during the study period (Table1).

Perchlorate concentration in a small stream running into the pond near to site 4 was up to 10 mg/Lduring the rainy season.The stream arises from near the APEP. This stream water was containing ClO_4^- leach out from the soil in the premises of the production unit and this is the possible source of ClO_4^- contamination in the pond. Therefore the stream inflow can be the potential source of ClO_4^- contamination of the pond.

Table 1. Perchlorate concentration of water samples collected from the pond

Pond sites	Min: concentration (mg/L) (mean ±SD)	Max: concentration (mg/L) (mean ±SD)
1	1.3 ± 1.8	7.91 ± 1.74
2	1.9 ± 1.5	7.71± 1.42
3	8.3 ± 0.87	17.74 ± 1.1
4	10.3 ± 1.41	29 ± 1.5
5	4.8 ± 1.98	19.3 ± 1.91

The highest ClO_4^- concentration detected in the present study (29±1.5 mg/L) was ~5 times higher than concentration detected from a well water sample from this region (Nadaraja *et al*., 2015). This indicates continuous leaching of ClO_4^- from the source and accumulation in the water bodies. The South-West monsoon period in the state is from June to September, and the total rainfall in Ernakulam district during 2014 was 2376 mm (normal 2065 mm). The possible source of ClO_4^- contamination in the pond can be due to leaching of ClO_4^- from contaminated soil in the premises of the production unit. The soil contamination can be from ClO_4^- containing effluent spillage during bulk handling or by wash water drained from ClO_4^- storage facility. The movement of ClO_4^- in the soil is mostly a function of the amount of water present. ClO_4^- poorly adsorbs to soil and when released to the soil, they will readily dissolve in the available water. Then it will be completely leached from the soil based on sufficient infiltration. In dilute concentrations as in groundwater, ClO_4^- behaves conservatively, with the centre of mass of the plume moving at the same average velocity as the water (USEPA, 2008). The leachate from contaminated soil by rainwater can be the reason for the high level of ClO_4^- during July when maximum rainfall is obtained in the region.

Fram and Belitz conducted a study to investigate the distribution of ClO_4^- in deep groundwater under natural conditions and suggested that leaching of ClO_4^- and uranium from sediments in the unsaturated zone by

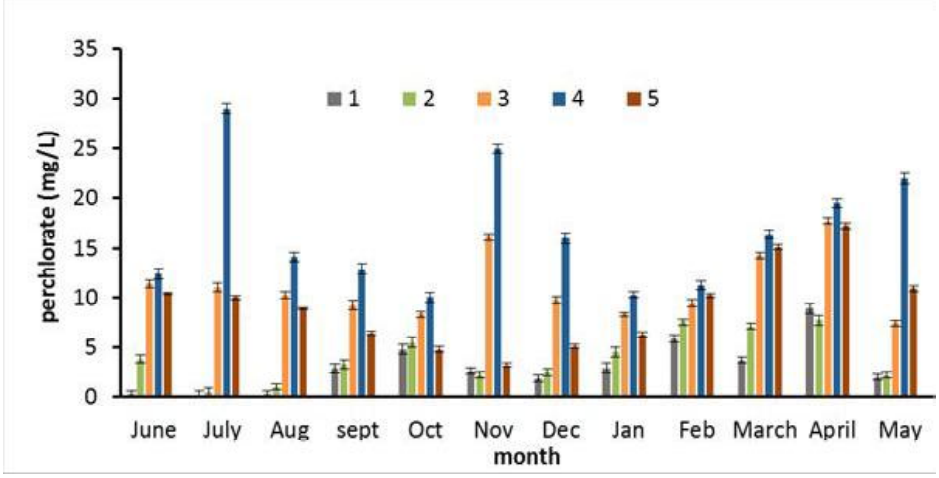

Fig. 3. Graph showing of ClO_4^- concentration water samples collected from five sites of pond during June 2014 to May 2015.

Table 2. Water quality parameters of contaminated pond and control pond

Sampling point	Chloride (mg/L)	Nitrate (mg/L)	Phosphate (mg/L)	Sulphate (mg/L)	Perchlorate (mg/L)	Ammonium (mg/L)	pH
S1	8.7±0.07	8.51±0.01	0.13±0.004	0.73±0.05	0.13±0.05	0.072±0.004	7.23±0.2
S2	8.4±0.13	11.2±0.12	0.09±0.003	0.63±0.03	0.16±.05	0.069±0.005	7.36±0.25
S3	8.62±0.02	8.52±0.03	0.12±002	0.72±0.04	5±0.29	0.072±0.002	7.44±0.3
S4	10.51±0.08	11.35±0.09	0.07±0.001	0.49±0.01	29±1.3	0.094±0.001	7.83±0.2
S5	10.32±0.02	8.50±0.02	0.13±0.002	0.72±0.04	10±0.53	0.084±0.002	7.73±0.4
Control	**5.46±0.03**	**6.72±0.01**	**0.12±0.001**	**0.42±0.01**	**Nil**	**Nil**	**7.83±0.5**

irrigation (Fram and Belitz, 2011). This supports the present finding that leachate can be a possible source of ClO_4^- contamination in the water bodies surrounding the contaminated area. A study on the distribution of ClO_4^- in a river reported that water samples collected during summer and fall months showed higher concentration than from the winter and spring months (Impellitter *et al.*, 2011). In a recent study on the distribution of anions in the aquatic environment in China reported that ClO_4^- was ubiquitously present in wastewater, surface water, seawater, rainwater and surface runoff.

4. Conclusion

In conclusion, the present study underlines the need for close monitoring of ClO_4^- contamination in Kerala and also for implementing regulatory measures for controlling the environmental release of ClO_4^- in Kerala or India as a whole. The present study highlights the need for more rigorous control of the endocrine disruptor present in a natural ecosystem and thereby ensuring the protection of aquatic as well as human health. Indiscriminate discharge of such type of pollutant must lead to ecological risk and destruction of a natural ecosystem. So government policymakers should take effective management strategies to control such type of persistent pollutant found on the natural ecosystem.

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