Final Project Report

Perchlorate Contamination of Drinking Water Resources in Kerala

DoECC/E2/R&D-59/2927/2014

Submitted to

Directorate of Environment and Climate Change
Government of Kerala

Principal Investigator

Dr. Mahesh Mohan
Assistant Professor

School of Environmental Sciences
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ABBREVIATIONS

%	:	Percentage
° C	:	Degree Celsius
µ	:	Microns
µg	:	Microgram
µL	:	Microlitre
µS	:	Micro Siemens
AB	:	Athirampuzha before fireworks display
AMON	:	APEP monsoon
AOPs	:	Advanced oxidation processes
APEP	:	Ammonium Perchlorate Experimental Plant
APOM	:	APEP post-monsoon
APRM	:	APEP pre-monsoon
ARPs	:	Advanced Reduction Processes
ATSDR	:	Agency for Toxic Substances and Disease Registry
AWWA	:	American Water Works Association
BDL	:	Below Detectable Limits
BF	:	Before fireworks
BIS	:	Bureau of Indian Standards
BW	:	Body weight
Ca^{2+}	:	Calcium
CE	:	Capillary Electrophoresis
Cl^-	:	Chloride
ClO	:	Hypochlorite
ClO_3^-	:	Chlorate
ClO_4^-	:	Perchlorate
cm	:	Centimeter
CW	:	Chemical concentration in water
d	:	Day
DEP	:	Department of Environmental Protection
EA	:	Edathua after fireworks display
EB	:	Edathua before fireworks display

EC	:	Electrical Conductivity
ED	:	Exposure duration
EPA	:	Environmental Protection Agency
FACT	:	The Fertilisers and Chemicals Travancore Limited
FCA	:	Fireworks control after fireworks display
FCB	:	Fireworks control before fireworks display
Fe^{2+}	:	Iron
g	:	Gram
G	:	Ground sample
H	:	Hydrogen
H_2O	:	Water
HCl	:	Hydrochloric acid
hrs	:	Hours
IC	:	Ion Chromatography
IQ	:	Intelligence Quotient
IR	:	Intake Rate
ISRO	:	Indian Space Research Organization
K^+	:	Potassium
kg	:	Kilogram
kHz	:	Kilo Hertz
KMON	:	Kottayam monsoon
kms	:	Kilometers
KPOM	:	Kottayam post-monsoon
KPRM	:	Kottayam pre-monsoon
L	:	Litre
LC	:	Liquid Chromatography
LCMS	:	Liquid Chromatography Mass Spetrometry
LoQ	:	Limit of Quantification
m/z	:	Mass/charge
MA	:	Manarcad after fireworks display
MB	:	Manarcad before fireworks display
MDL	:	Method Detection Limit
mg	:	milligram

Mg^{2+}	:	Magnesium
min	:	Minute
ml	:	Millilitre
mM	:	MilliMolar
mol	:	Mole
MON	:	Monsoon
MS	:	Mass Spectrometry
Na^{+}	:	Sodium
NAS	:	National Academy of Sciences
NASA	:	National Aeronautics and Space Administration
NH_4^{+}	:	Ammonium
NIS	:	Sodium Iodide Symporter
NO_3^{-}	:	Nitrate
O	:	Oxygen
OC	:	organic carbon
^{o}C	:	Degree Celsius
P	:	Pond water sample
PA	:	Palakkad after fireworks display
PB	:	Palakkad before fireworks display
PbO_2	:	Lead oxide
pH	:	Potential of hydrogen
PMON	:	Paravur monsoon
PO_4^{3-}	:	Phosphate
POM	:	Post-monsoon
ppb	:	parts per billion
ppm	:	Parts per million
PPOM	:	Paravur post-monsoon
PPRM	:	Paravur pre-monsoon
PRM	:	Pre-monsoon
psu	:	Practical salinity unit
Pt	:	Platinum
R	:	River water sample
RfD	:	Reference Dose

S	:	Sample number
s	:	Soil sample
S_2O_8	:	Persulfate
SAL	:	Salinity
SCMON	:	Seasonal monsoon
SCPOM	:	Seasonal control post-monsoon
SCPRM	:	Seasonal control pre-monsoon
SD	:	Standard deviation
SIM	:	Selective ion mode
$SO_4^{\bullet-}$	:	Sulfate radical
SO_4^{2-}	:	Sulfate
sq. mtrs	:	Square meters
sq.km	:	Square kilometer
T3	:	Triiodothyronine
T4	:	Thyroxine
TA	:	Thrissur after fireworks display
TB	:	Thrissur before fireworks display
TDS	:	Total Dissolved Solids
TERLS	:	Thumba Equatorial Rocket Launching Station
TMON	:	TERLS monsoon
TPOM	:	TERLS post-monsoon
TPRM	:	TERLS pre-monsoon
TSH	:	Thyroid Stimulating Hormone
UCMR	:	Unregulated Contaminant Monitoring Rule
US	:	United States
USA	:	United States of America
USEPA	:	United States Environmental Protection Agency
UV	:	Ultra violet
VSSC	:	Vikram Sarabhai Sapce Center
W	:	Water sample
WHO	:	World Health Organization
Wt	:	Weight

Executive summary

Perchlorate, an emerging pollutant, is an oxy anion of chlorine. Salts of perchlorate like sodium and potassium perchlorates are used in fireworks and ammonium perchlorate is used in rocket propellants. The soluble and persistent perchlorate salts can enter the water bodies, soil and air and then reaches various life forms. Toxicity of perchlorate is mainly confined to hypothyroidism and the major victims are infants and women. Drinking water sources, soils, food etc. are found to be contaminated with perchlorate. Primary route of exposure of perchlorate for animals and plants is drinking water. The health protective dose of perchlorate is 0.7 ppb which equals a drinking water equivalent of 24.5 ppb. More than this perchlorate results in thyroid disorders and more risk to infants as the thyroid deficiency can lead to irreparable nervous disorders. Perchlorate contamination was reported from various parts of the world Kerala is a centre for fireworks and rocket testing facilities. No extensive study on perchlorate contamination in Kerala, its effects etc is reported. Hence the present study is highly significant.

Perchlorate is detected and quantified using Liquid Chromatography Mass Spectrometry (LC/MS) (EPA method 331.0). Perchlorate in drinking water (well, bore well, tap water) from different parts of Kerala, bottled water, rain water samples etc are collected and analyzed for perchlorate. District wise and region wise data has been generated. Well water was contaminated than bore well water and tap water. During pre-monsoon contamination has followed the pattern well water> bore well water> tap water; during monsoon it was well water> bore well water (perchlorate BDL in tap water); and in post monsoon well water> tap water (perchlorate BDL in bore well water).

Seasonal sampling of perchlorate around rocket manufacturing site, rocket testing facility and firework manufacturing sites were done. All the sites have showed perchlorate contamination except the control site during these seasons. Highest mean perchlorate was observed in site 1 (APEP) followed by site 2 (TERLS), site 3 (Paravur fireworks manufacturing site) and site 4 (Kottayam fireworks manufacturing site).Perchlorate is found maximum (concentration) during pre-monsoon and post monsoon seasons whereas wide spread contamination occurred during monsoon season.

The role of fireworks in environmental perchlorate contamination is assessed. Selected major firework display sites were analyzed for perchlorate contamination before and after the firework display and a continuous monitoring study after firework display has been done at a selected site. After fireworks soil samples were found to be more perchlorate contaminated than water samples. In selected sites water samples that were collected from wells or ponds within the site were contaminated with perchlorate. Variation of perchlorate in different sites owed to the variation in amount of perchlorate used spent or unused chemical, partial combustion of firework etc. Geographical factors also determined the rate of perchlorate contamination. Continuous monitoring study proved that perchlorate can reach groundwater through runoff or atmospheric deposition.

A health based survey was done in selected sites (where seasonal study and firework display study was carried out) to assess the health effects of perchlorate in the site. Perchlorate was found to be exceeding in drinking water samples at APEP, TERLS and Paravur fireworks manufacturing sites. At APEP, as the government provided drinking water, no thyroid disorder was reported. But at TERLS and Paravur average intake of perchlorate was far higher than the recommended dose and this might have resulted in hypothyroidism in humans. Women of conception age suffered the most in these two sites where as in all other sites the reported thyroid rate was less than the normal rate (except Manarcad fireworks display where majority was said to have hereditary thyroid disorder) and the women of post-menopausal age suffered from thyroid disorder. In short, some extra factors aided in inducing thyroid disorder at TERLS and Paravur and perchlorate might be the inducing factor. Along with perchlorate, other genetic, environmental factors also may add to the thyroid disorder.

Remediation study done with Advanced Reduction Processes indicated the inefficiency to degrade perchlorate completely. In sonochemical degradation maximum reduction obtained was 28.83%, with the addition of sulfite to perchlorate standard at acidic pH. Fentons reaction gave the highest reduction among the studied reduction processes. 32.25% reduction of perchlorate was shown in acidic pH under the addition of persulfate and iron (II) sulfate. Very low degradation of perchlorate was noticed with UV photolysis experiments.

The present study urges for detailed investigations on the contamination and remediation of perchlorate in our environment.

Introduction

Water is the most precious gift of nature, not only to the mankind but also to the whole organisms living in different segments of the ecosphere (Mandal, 2006). Water occurs about 71% of the global surface, so the water environment comprises a major part of the human environment (Connel, 2005). Pollution of air, water and land through wastes generated as a result of increasing population, urbanization and industrialization is a challenge of serious dimensions (Srivastava, 2002). Water pollution is a major problem in the global context. Generally speaking, water pollution is a state of deviation from the pure condition, whereby its normal function and properties are affected (Prabhu *et al.,* 2009). A lot of emerging contaminants are being reported worldwide from drinking water. Pharmaceuticals, personal care products like soaps, fragrances, cosmetics, steroids, plasticizers, etc. are a few of them (Arroyo, 2013; Petrie *et al.,* 2015). One such debating problem in the field of water pollution is perchlorate contamination in drinking water.

1.1 Perchlorate-Properties

Perchlorate is an oxy-anion of chlorine, where chlorine is in the +7 oxidation state. It is negatively charged and is composed of one chlorine atom surrounded by four oxygen atoms arranged in tetrahedral geometry. Molecular formula of perchlorate is ClO_4^- and has a molar mass of 99.451 g/mol. It is the least reactive oxidizer of the generalized chlorates and is the weakest oxidant among the four in water (Cotton and Wilkinson, 1988). It acts as a strong oxidizer in acidic conditions than in basic conditions.

The major perchlorate salts are sodium perchlorate, potassium perchlorate and ammonium perchlorate. These salts, made up of electropositive metals, are slow to react unless heated and this character renders it useful in pyrotechnics. Mixtures of perchlorate with organic compounds are more reactive.

Table 1.1 Properties of perchlorate salts

Properties	Ammonium perchlorate	Potassium perchlorate	Sodium perchlorate	Perchloric acid
Mol. Wt	117.49	138.55	122.44	100.47
Color/form	White orthorhombic crystal	Colourless orthorhombic crystal or white crystalline powder	White orthorhombic deliquescent crystal	Colourless oily liquid
Taste/odor	Odorless	Slightly salty	Odorless	Strong odor
Density/specific gravity	1.95 g/cm^3	2.53 g/cm^3	2.52 g/cm^3	1.77 g/cm^3
Solubility	200 g/L at 25°C	15 g/L water at 25° C	2096 g/L water at 25° C	Miscible in cold water
Sorption capacity	Very low	Very low	Very low	Very low
Volatility	Non volatile	Non volatile	Non volatile	Volatile
pH	5.5-6.5	6.0-8.5	7.0	Highly acidic

Perchlorate salts are highly soluble in water, kinetically inert to reduction and shows little tendency to adsorb to mineral or organic surfaces. Perchlorate anion persists in groundwater for a long time and its mobility in surface or groundwater is so high, hence it can move along with the flow of water (diffusion and convection controlled movement). Perchlorate in high doses can impair proper functioning of the thyroid gland.

Redox properties

Perchlorate anion is the +7 oxidation state of chlorine and its half-reaction is as follows:

$ClO_4^- + 8\ e^- + 8\ H^+ \Longrightarrow Cl^- + 4\ H_2O.$

It is unstable with respect to the evolution of oxygen from water. But it does not occur spontaneously at ambient temperatures. Perchlorate salts when compared with organic/other ions may cause explosions under specific conditions.

1.2 Sources of perchlorate

Perchlorate occurs in the environment as natural and man-made compound. Naturally occurring perchlorates are found in limited geographic locations with low concentrations where as the manufactured perchlorates are having high concentrations near the manufacturing sources (ITRC, 2005).

1.2.1 Natural sources

Natural sources of perchlorate are mainly confined to arid regions or arid environments. Perchlorate is found naturally in Chilean nitrate, evaporate deposits, sea weeds etc. It was once believed to exist naturally only in the Atacama Desert in Chile. It existed in mineralogical association with nitrate of sods caliche deposits that may have been derived in part from past volcanic activity (Ericksen, 1983; Schumacher, 1960). A very low lithospheric perchlorate was observed from Peru and Bolivia. These lithospheric deposits were used in the manufacture of fertilizer, gun powder, as feedstock to make nitric acid, explosives, fireworks and additional end products. These deposits are formed by evaporation and concentration in arid environments and include marine and non-marine deposits and consist of salts of bromine, boron and borates, gypsum and anhydrite, nitrogen compounds, potash, iodine, sodium sulphate and sedimentary phosphate (Lefond, 1975). The perchlorate observed from a specific area is a mixture of man-made and naturally occurring salts (Duncan *et al.,* 2005). These salts could be differentiated by fingerprinting detected perchlorate plumes using analytical forensic techniques.

Origin of natural sources of perchlorate

Natural atmospheric processes are expected to be the reason for natural origin of perchlorates. The theory suggests that chloride, possibly in the form of sodium chloride from sea or land-based chloride compounds blown in from the atmosphere, reacts with atmospheric ozone to create perchlorate. This process might occur in almost all regions of the earth and is analogous to nitrate formation in the atmosphere (Walvoord *et al.,* 2003). Another possibility for natural formation in the atmosphere is lightening (Dasgupta *et al.,* 2005; Jackson *et al.,* 2003). But these atmospheric processes are relatively slow. Once perchlorate is formed in the atmosphere, it deposits to the earth's surface through precipitation. In arid environments, where the rate of deposition exceeds the rate of

dissolution by ongoing precipitation, perchlorate can be accumulated in the soils/sediments over time (Orris *et al.,* 2003). Tropospheric perchlorate is found to be the result of electro-oxidation of chlorate (http://www.geocities.com/c apecanaveral/ campus /5361/chlorate /leaddiox/bedtime.html).

1.2.2 Anthropogenic sources

Perchlorate was first manufactured in commercial quantities in Masebo, Sweden, in the 1890s by Stockholms Superfosfat Fabrisk AB. Perchlorate production in US started in 1910, by Oldbury Electro-Chemical in Niagara Falls, New York and the major perchlorate compounds (>99%) produced were ammonium perchlorate, sodium perchlorate, potassium perchlorate and perchloric acid.

A two-step electrolytic process is used for the preparation of perchlorate in the laboratory. Sodium chloride is first oxidized to sodium chlorate which is subsequently oxidized to sodium perchlorate. Sodium chlorate is again treated with other chemicals to form potassium perchlorate or ammonium perchlorate. Production process requires high voltage and is done in an undivided cell with PbO_2 or Pt-coated material as anode and cell tank (bronze or 316 stainless steel) as cathode. To avoid undesirable reduction of chlorate, sodium dichromate is added.

Uncertain sources

Studies are going on about the potent environmental contaminant-perchlorate. To analyze perchlorate more aptly, the source must be well known. Most of the sources of perchlorate are uncertain. The apparent list of suspected perchlorate sources are growing. Confirmation and verification testing are to be done and researches in these areas are still continuing.

1.3 Uses of perchlorate

Perchlorate salts are used as energetic oxidants. Ammonium perchlorate is among the most important propellants because it has high oxygen content and decomposes to the gaseous phase products- water, HCl, nitrogen and oxygen, leaving no residue. Perchlorate is also used as an inert electrolyte as it is a non-complexing anion. Perchlorates are used in solid rocket propellants, fireworks, explosives, munitions, agriculture, laboratory etc (ITRC,2005).

Solid propellants

Ammonium perchlorate is widely used as solid propellant in rockets and missiles. Space shuttles, commercial satellite vehicles, small rockets attached to ejector seats for pilots, explosive bolts for separating missile stages or other components and oxygen generators for both civilian and defense aircraft uses perchlorate. Satellite launch vehicles use solid rocket motors with ammonium perchlorate propellant as strap on boosters to increase payload capacity. Many of these devices are replaced due to their degradation issues (ITRC, 2005). Disposal of perchlorate-containing debris, scraps of solid propellant and explosives and rejected rocket motors are done by burning in open burn/open detonation areas. Incomplete burning could permit perchlorate to be dissolved and may cause soil/water contamination. To prevent this, a new method is practiced by destructing propellants in burn pans. After the initial burn, a cleanup is performed and any unconsumed material is treated again (ITRC, 2005). Another process is 'hog-out process' or 'hydro-mining' in which the solid propellant is washed with high-pressure jets to enable reuse of rocket motor hardware. If the liquid waste from the hog-out process is discharged untreated to the ground surface or leaky lagoons, it will contaminate soil and water. Capturing and treating the waste stream prior to discharge can avoid the contamination. In order to demonstrate the viability of replacing ammonium perchlorate in large rocket or missile systems with an environment friendly alternative oxidizer, Green Missile Program has been launched. NASA announced a new paraffin-based solid propellant instead of perchlorate based fuel in space craft (NASA, 2003).

Munitions

Munitions contain perchlorate in varying amounts. Perchlorate containing munitions include training simulators, insensitive munitions, smokes or obscurants, pyrotechnics, grenades, signals and flares and fuses. Besides the use of munitions, its manufacturing, storage, disposal etc. can create environmental contamination. In the manufacturing of munitions, usually a hydraulic washout or hog-out process is conducted, and this makes opportunity for potential releases of perchlorate into the environment. Disposal of munitions were usually accomplished by burying on ranges. In course of time, these may corrode and the munitions' cases degrade and finally

results in the release of perchlorate into the environment. For example, a number of contaminated sites were reported from US, related to the use and disposal of munitions (GAO, 2005). Perchlorate contamination in the environment due to munitions proceeds in two ways. Either the munitions containing perchlorate or rocket motors do not function as intended through low-order detonator or if it completely detonates, the propellant may not be consumed completely and subsequent precipitation may give way to environmental contamination (ITRC, 2005).

Commercial explosives

Perchlorate is used as a sensitizing agent in modern commercial explosives. The commercial explosive products such as emulsions, water gels, delay elements in detonators and some seismic explosives mainly contain sodium perchlorate, ammonium perchlorate and potassium perchlorate. Perchlorate increases the shock initiation sensitivity of an emulsion or water gel product.

According to Material Safety Data Sheet (MSDSs), the perchlorate concentration varies with products. For example, seismic products contain 66-72%; bulk and packaged water gel products- 0-4%; packaged continuous water gel explosives- 0-7%; emulsion explosives- 0-30%; electric detonators- 0-0.5% and non-electric detonators- 0-0.89% of perchlorate salts. Explosive manufacturing industries use unlined ponds to collect production-derived wastewater and this may result in percolation of perchlorate into groundwater. Similar to munitions, if explosive detonation is incomplete, the blasting site may get contaminated. Misfires, undetonated explosive products after a misfire etc. may cause an increase in contamination.

Fireworks

Fireworks are an important source of environmental contamination. In fireworks, the chemical compounds are encased in cardboard cylinders or spheres called “shells”. In fireworks, potassium perchlorate is mixed with fine aluminium or magnesium powder to produce photoflash effect. During the process, perchlorate decomposes at high temperatures and release free chlorine. The released free chlorine combines with barium, strontium or copper to produce characteristic green, red and blue hues respectively (Conkling, 1990). In some firework shells, an oversupply of potassium perchlorate beyond the stoichiometric need is used to suppress the effects of certain

chemical elements during reactions. Fireworks based perchlorate residue can contaminate soil and water over a wide area. But the extent of contamination depends on the number of displays, types of fireworks involved, amount of misfiring and the duration of the display. Disposal of misfires is a major concern (MADEP, 2005).

Safety or hazard flares

Emergency and signal flares also use perchlorate salts. The chlorine from perchlorate and strontium from strontium nitrate combines to emit bright red light (Conkling, 1990). Almost 2000µg of perchlorate residue will be available from fully burned flares and even greater concentration of perchlorate than this from a partially burned flare. The leaching of residues may contaminate ground water (Silva, 2003).

Industrial uses

Perchlorate is widely employed in the manufacturing of many common products. Industrial processes like processing of rare earth element ores, medical devices manufacturing etc. uses perchlorate. Production, handling and usage of perchlorate may finally result in perchlorate contamination.

Laboratories

Perchlorates are used in research or analytical work in laboratories. Some detergent based laboratory glassware cleaning agents such as Alconox, Alcotabs, Liquinox and Neu Trad have been tested and shown to contain up to 2.5mg/kg perchlorate. For example, actinide research and high-explosive synthesis and testing at Los Alamos National Laboratory (LANL), USA had resulted in perchlorate contamination of groundwater (Hjeresen *et al.*, 2003).

Agricultural uses

In agriculture, perchlorate has been used as a component of certain fertilizers. Sociedad Quimica Y Minera De Chile SA (SQM), the sole mining and processing company of caliche-type deposits, marketed a fertilizer, Bulldog Soda, contains 0.03% perchlorate and is still applied to the croplands in US.

Medical/Pharmaceutical

The use of perchlorate in the medical field is undebatable one and perchlorate is applied for many therapies since many decades. Potassium perchlorate is widely used for the treatments. It is employed in medical field in three different ways

a. In the treatment of induced hypothyroidism or thyrotoxicosis resulting from the primary treatment of tachyarrhythmia or ischemic heart disease by the iodine-containing drug amiodarone.

b. To limit the uptake of sodium pertechnetate in the thyroid when pertechnetate is administered in the course of brain and blood-pool imaging and placenta localization.

c. Potassium perchlorate has been used as a diagnostic agent in the treatment of certain thyroid disorders.

Water and wastewater treatment

Sodium hypochlorite is used to disinfect water supplies, to treat pool water, to disinfect groundwater production wells, to treat waste water in publicly owned treatment works etc. Sodium hypochlorite in solution dissociates to form perchlorate ions.

Landfills

Landfills create problems when they are dumped with waste packaging of perchlorate and sometimes perchlorate as such. Perchlorate usually may dissolve in moisture and leach to groundwater.

Sodium chlorate manufacture

Perchlorate ion is produced as an unintended by-product, in the electrolytic cell process for manufacturing sodium chlorate. Sodium chlorate is widely used in agriculture, as a nonselective herbicide, as a defoliant, for desiccant purposes for crops and in non –agricultural fields like household and industrial bleaching, pulp and paper bleaching, food processing etc. (PMEP, 1995).

1.4 Environmental fate and transport

There are many processes responsible for the release of perchlorate into the environment. Most significant factors affecting fate of perchlorate in the sub-surface are likely to be dilution (as it migrates from the source), biological uptake, and possible degradation under anaerobic conditions (ITRC, 2005).

Perchlorate may be released into the environment either in the solid form or in the liquid form. The solid salts such as ammonium perchlorate, potassium perchlorate, sodium perchlorate etc. dissolves in water. The liquid form of perchlorate may be in the form of concentrated brine or as perchloric acid and this increases the potential as well as the speed of a spill reaching groundwater or surface water. When perchlorate is released into the soil, it will readily dissolve in the moisture present in the soil. It does not bind to soil particles appreciably and its movement is almost controlled by the amount of water present. However, at relatively high perchlorate concentrations, perchlorate may "salt-out" or precipitate with cations such as potassium because potassium perchlorate is relatively low soluble, thus decreasing its migration potential. The dissolution of perchlorate salts will release perchlorate anion which in turn percolate into ground water and moves with the gradient of groundwater flow. The presence of perchlorate in soil will be negligible since it gets dissolved in water. The roots of plants absorb water/moisture containing perchlorate and get accumulated in leaves, stem etc. Degradation of perchlorate depends on organic carbon, perchlorate-degrading anaerobic bacteria and reducing environment. However, it may not occur at ambient temperature/other environmental conditions. Features like high solubility, low sorption and low degradation makes perchlorate difficult to remediate.

In arid regions, crystallized perchlorate salts may accumulate at various horizons in the soil due to evaporation of infiltrating rain water that leached perchlorate from shallower depths. Perchlorate behaves conservatively, in dilute concentrations, with the center of mass of the plume moving at the same average velocity as the water. The contaminant front moves faster than the average velocity resulting in the dispersion. The perchlorate released from various processes/activities has negative charge and non-complexing nature with metal ions. This will render perchlorate to be poorly sorbed or retained by sediment minerals in the sub-surface. As it is highly soluble, its

mobility and fate are largely influenced by hydrologic and biologic factors (Urbansky and Brown, 2003).

Food and drinking water are the prime sources by which perchlorate enter human system. Women with low iodine levels who are exposed to perchlorate may have impaired thyroid function even when their exposure level is below the EPA safe dose. Methods are still in pending for the degradation or removal of perchlorate from food.

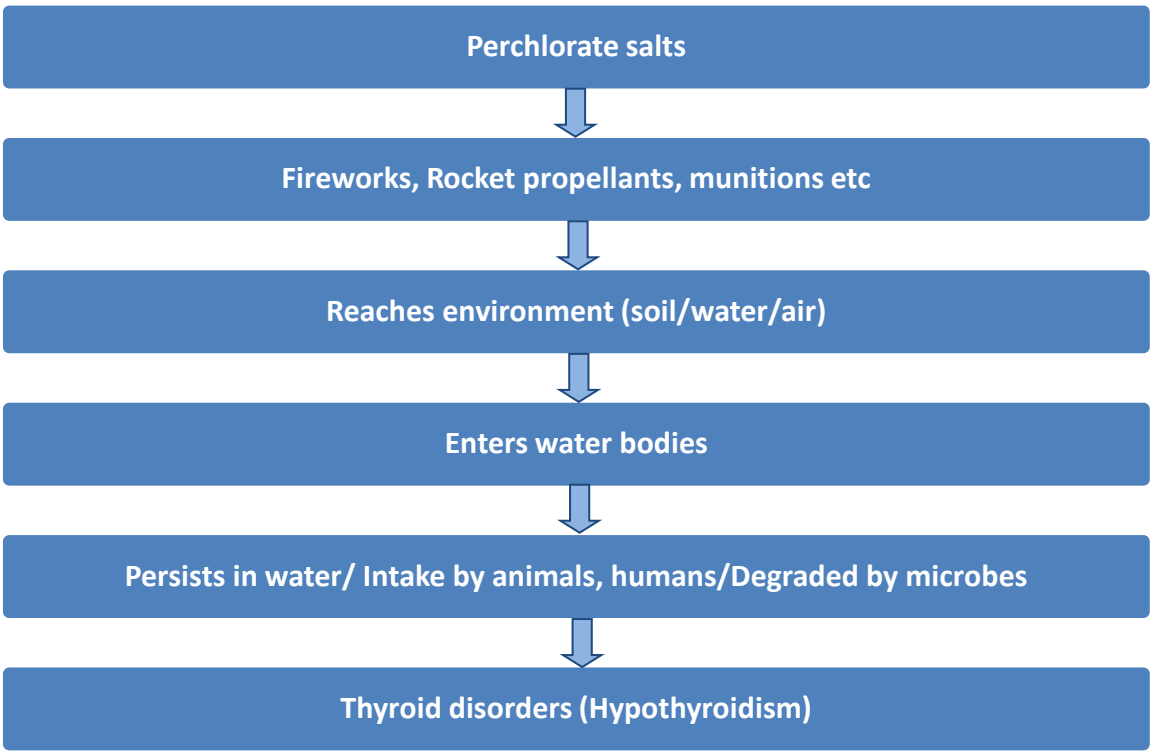


Fig. 1.1 Transport of perchlorate in the environment

1.5 Environment management

Release of perchlorate into the environment occurred in large quantities in past decades, since its impacts were unknown. The management plans were initiated only after the reports on the toxic effects of perchlorate got published. But it is not quite easy to manage perchlorate because of its high solubility, little attenuation, stability, persistence and the fact that a relatively small amount of perchlorate can contaminate a large amount of water. There is no risk of perchlorate air emissions, since perchlorate compounds and the perchlorate ions in water are not volatile (ITRC,

2005). Banning the use of perchlorate is not necessarily a solution as for some applications, replacement of perchlorate with any other compound is impossible and the only way left is the effective management of perchlorate. Effective management practices include spill contingency plans, secondary containment, waterproof storage, treatment of waste streams, zero discharge etc.

1.6 Toxicity of perchlorate

Perchlorate is a potent thyroid disruptor. It inhibits the uptake of iodide by thyroid gland, reducing the T3 and T4 levels in blood and thereby increasing the TSH levels, finally resulting in hypothyroidism.

The thyroid gland in mammals function as an ion-exchanger with a preference for large, poorly hydrated anions like perchlorate, iodide ion, pertechnetate and perrhenate anions. These anions have common characteristics like hydration energies, size, charge density etc. Perchlorate interferes with the thyroid's uptake of iodide, an essential component of thyroid hormones, and results in a dose-dependent decrease in hormone production.

Perchlorate actively inhibits the iodide uptake by thyroid gland and impairs proper functioning of the thyroid gland (NRCHIPI, 2005). The mode of action (MoA) for perchlorate identifies that perchlorate has a threshold for effects and that the degree of effects is dependent on the dosage. Perchlorates' ability to block the uptake of iodine by the thyroid has been exploited in medicine to treat patients who suffered from Graves' disease (Von, 1995) and hyperthyroidism (Godley and Stanbury, 1954). Accidental consumption of large doses of perchlorate may interfere with human and animal growth and development by interfering with the normal production of thyroid hormones (Wolf, 1998). The most sensitive life stage, for perchlorate, is fetal stage. Once fetal stage is affected by reduced thyroid hormones, it will end up in irrecoverable nervous and skeletal disorders. Perchlorate can even cross placenta and amniotic fluid, thereby adding to the toxicity.

Importance of thyroid hormone

Thyroid is a small gland located at the base of the throat and releases hormones that play a crucial role in the body's metabolism, skeletal growth and development,

reproduction, growth and function of the cardiovascular and central nervous systems, especially in fetuses and infants (Thompson and Potter, 2000; ITRC, 2005). Thyroid hormones also determine metabolic activity, control iodide levels in the blood stream and affect many organ systems. Ingested iodine is converted to iodide and is used for the synthesis of two key thyroid hormones- triiodothyronine (T3) and tetraiodothyronine (T4), also known as thyroxine, that are maintained within narrow concentration limits by an efficient regulatory mechanism. Thyroid hormone synthesis is regulated by a feedback control loop involving the anterior pituitary gland and the hypothalamus. Hypothyroidism is the most common type of thyroid disorder and occurs when the thyroid produces too little of the thyroid hormone that the body needs to function properly. Significant or sustained decrease in thyroid hormone levels in the blood streams have been found to result in effects ranging from a decrease in metabolism, dry skin, cold intolerance, tiredness, impairment in behavior, movement, speech, hearing, vision and intelligence (Felz and Forren, 2004). Hypothyroidism is more likely to affect women than men (Surks *et al.*, 2004). However, the perchlorate hazard depends on the extent, frequency and duration of exposure (Robles, 1999).

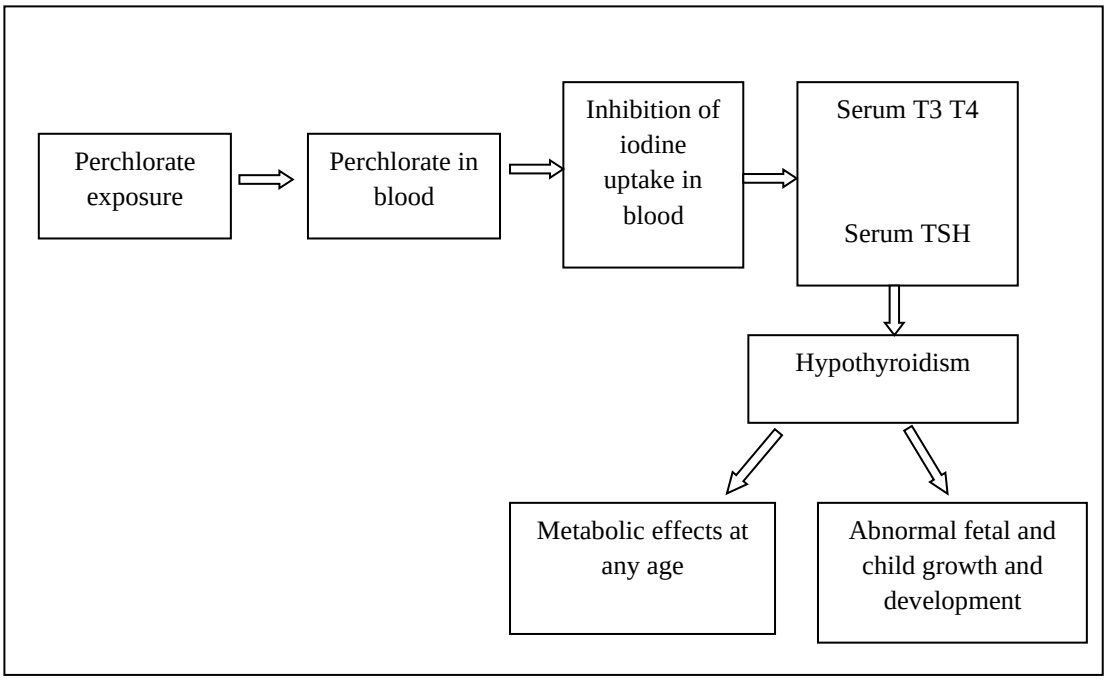


Fig. 1.2 Mode of action model for perchlorate toxicity (Adapted from NRC, 2005)

Various animal toxicity studies, epidemiological studies, clinical studies, ecological studies etc. were done to assess the toxicity of perchlorate on different spheres because effect of perchlorate varies widely with species, especially affecting thyroid gland. Iodide inhibition takes place because of the similarity of perchlorate anion with iodide, in size.

1.7 Remediation of perchlorate

Perchlorate remediation technologies are associated with many factors like concentration of perchlorate and other contaminants, and groundwater geochemistry. At low concentrations of perchlorate (<50µg/L), ion exchange is the most cost-effective method. Certain site-specific factors can influence the treatment technologies. For example, if the groundwater contains a large amount of common anions like nitrate, sulfate and bicarbonate, these can compete with perchlorate for binding sites on ion exchange resins, and can thus increase the cost of ion exchange. Low pH and high TDS have negative impacts on microbial perchlorate reduction. Perchlorate degradation is also negatively impacted by high levels of co-contaminants, such as heavy metals and organic solvents.

Co-contaminants

Co-contaminants are the contaminants that are usually found along with perchlorate and these affect the treatment of perchlorate. Nitrate and sulfate are the usual co-contaminants. Nitrate interferes with the efficient reduction of perchlorate anion but it is removed along with perchlorate, as most perchlorate-reducing bacteria are denitrifiers as well (Logan, 2001). Perchlorate is generally reduced before sulfate and thus sulfate poses little effect on perchlorate degradation. If the redox potential is too low, sulfate may become the electron acceptor (ITRC, 2005). Other identified co-contaminants are trichloro ethylene (TCE), N-nitrosodimethylamine (NDMA), 1,4-dioxane, volatile organic carbons, calcium, chlorate, explosive compounds, HMX, RDX etc. Presence of these contaminants makes perchlorate treatment systems more difficult to design. Better understanding of co-contaminants is necessary before selecting a perchlorate treatment technology.

Remediation technologies

Remediation technologies currently being used and commercially available fall into two broad categories-ion exchange and biological processes.

Ion exchange

Ion exchange is the most common physical method for treating contaminated ground water, where the negatively charged perchlorate ion is exchanged with another anion, typically chloride. The ion exchange takes place in a medium consisting of a polymer (ion exchange resin) containing a positively charged functional group like quaternary amine, with a strong preferential affinity to the perchlorate ion. Once the exchange resin gets ladened with perchlorate, it will be exposed to concentrated (sodium) chloride brine to reverse the equilibrium, thus displacing the perchlorate from the resin, resulting in the regeneration of spent resin. It can again be reloaded with chloride and can be used again for ion exchange. Common anions that compete with the perchlorate ion for the resin surfaces are sulfate, nitrate, bicarbonate, carbonate, bromide, chlorate, bromate, arsenate etc. High TDS values containing water hinders ion exchange effectiveness, making cost-prohibitive to treat (ITRC, 2005; CalEPA, 2004). After the regeneration of ion exchange resins, brine containing high levels of perchlorate is left out and it is a significant challenge to regenerate the brine concentrated with perchlorate, chlorides and other anions.

Biological processes

The presence of perchlorate in the environment is localized. Also the prevalence of perchlorate reducing bacteria is widespread in the environment. Earlier studies showed that the addition of an appropriate electron donor (i.e. energy source) to a site sample causes perchlorate degradation without the addition of exogenous bacteria (Coates *et al.,* 1999; Hatzinger *et al.,* 2002; Waller *et al.,* 2004; Tan *et al.,* 2004). The perchlorate degradation studies were very limited during earlier times (Hackenthal *et al.,* 1964) and started only after the report on perchlorate contamination in United States during mid-1990s.

A variety of perchlorate reducing bacteria are identified, most of them included in the genera *Dechloromonas, Dechlorospirillum* and

Azospira(Achenbach *et al.,* 2001; Xu *et al.,* 2003). Facultative anaerobes (organisms that can grow either in the presence or absence of oxygen) were able to degrade perchlorate in presence of proper nutrients. These bacteria use an organic substrate or, in some cases, hydrogen gas as an electron donor, for perchlorate reduction and use perchlorate molecule as a terminal electron acceptor. Perchlorate reduction is carried out in three steps, using two enzymes. In the first step perchlorate is reduced to chlorate and then chlorate is reduced to chlorite. Perchlorate reductase enzyme is used for this reaction. Finally, the enzyme chlorite dismutase disproportionate chlorite to chloride and oxygen (Coates *et al.,* 1999; van Ginkel *et al.,* 1996; Kengen *et al.,* 1999). To detect the presence of perchlorate reducing bacteria in the environment, an immunoprobe for chlorite dismutase gene has been developed (O'Conner and Coates, 2002). Biological reduction of perchlorate is promoted by different electron donors and these include fatty acids (eg., acetate, citrate, lactate), mixed and pure sugars (eg., molasses, glucose, protein rich substrates (whey, casamino acids), alcohols (eg., ethanol), vegetable oils and hydrogen gas (Borden *et al.,* 2004; Henry *et al.,* 2003; Logan, 1998; Hunter, 2002; Waller *et al.,* 2004; Zhang *et al.,* 2002; Hatzinger, 2002). However, the specific substrates utilized as energy sources are strain- and site- specific. Despite of the large numbers of perchlorate degrading microorganisms existing in nature, perchlorate continues to persist in the environment. Thus it is important to develop other treatment technologies and biological processes in this field. Biological processes consist of *ex-situ* and *in-situ* bioremediation. Ex-situ bioremediation involves the use of continuous-flow stirred tank reactors (CSTRs), packed-bed reactors (PBRs) and fluidized-bed reactors (FBRs). Perchlorate-reducing bacteria are indigenous to many soils, sediments, surface waters and groundwater. In in-situ bioremediation these organisms can often be stimulated to degrade perchlorate to below detection limit by adding a microbial growth substrate to these environments (Wu *et al.,* 2001; Hatzinger *et al.,* 2002; Waller *et al.,* 2004; Tan *et al.,* 2004; Perlmutter *et al.,* 2001; Zawtocki *et al.,* 2004; Hatzinger, 2005; Cramer *et al.,* 2004; Cox *et al.,* 2001).

Soil remediation

Remediation processes for perchlorate in soil have focused mainly on the application of bioremediation. Perchlorate-reducing bacteria are present in most surface soil and the perchlorate bioreduction can be stimulated through the addition of appropriate organic substrates to these soils (Wu *et al.,* 2001; Hatzinger, 2002). Field-scale treatment of perchlorate contaminated soils has been performed using in situ and ex situ techniques. Limiting factors in stimulating bacterial reduction of perchlorate in soils appears to be insufficient food and moisture.

In situ treatment has been tested at several sites with near-surface perchlorate contamination. A variety of different carbon sources, including various types of manure, ethanol, molasses and calcium magnesium acetate, have been tested as biological substrates. These amendments were either placed on the surface (followed by soil wetting) or dissolved directly into water prior to application. Horse manure, chicken manure, ethanol, cow manure and acetate were also used as carbon sources (O'Niell and Nzengung, 2003; ITRC, 2005).

Ex situ treatment methods have focused on treatment cells using anaerobic composting or lined treatment cells containing excavated soils. These methods have been evaluated in pilot- and/or full-scale applications. For composting applications, carbon sources, water and, in some cases, bulking agents are blended with the contaminated soil (Cox *et al.,* 2000; ITRC, 2005).

Thermal remediation is another process investigated for the remediation of perchlorate in soils. This process generally relies on volatilization or evaporation mechanisms as an integral part of the destruction process (ITRC, 2005). Thermal remediation systems can be applied to soil contaminated with perchlorate; however, because of cost, many of these should probably be considered only when perchlorate-impacted soils are mixed with other hazardous and toxic substances, such as explosives, radionuclides or various metals (Gangopadhyay *et al.,* 2005). Higher temperatures would be needed for concentrations >100mg/kg perchlorate (ITRC, 2005).

Traditional water treatment approaches like carbon adsorption, chemical oxidation, air-stripping etc. are ineffective in the removal of perchlorates as these are highly soluble in water, non-adsorptive, non-volatile and chemically stable (Logan, 2001;

Damian and Pontius, 1999). Emerging processes or developing technologies are expected to give more promising results than the traditional technologies. Some of the newly emerging processes for perchlorate treatment include vapor-phase electron donor injection (Rainwater *et al.,* 2001; Jackson *et al.,* 2003), phytoremediation (WWW.hqafcee.brooks.af.mil/products/techtrans/phytorem.arp), constructed wetlands (Best *et al.,* 1998), nano scale bimetallic particles (Zhang, 2003), Titanium chemical reduction, zero valent iron reduction under ultraviolet light (Gurol and Kim, 2000), electrochemical reduction, capacitive deionization (Farmer *et al.,* 1996), reverse osmosis, electro dialysis, monitored natural attenuation (Lieberman *et al.,* 2005), nanofiltration/ultra filtration (AWWA, 2001) and catalytic gas membrane. All these technologies are intended to remove perchlorate from soil and water in appreciable amounts so that the perchlorate level will be well below the reference dose published by USEPA (ITRC, 2005).

Two methods, currently used widely for the removal of perchlorate are physical removal through the use of ion-exchange resins and biological treatment with reactor systems. Another rapidly emerging technique to treat perchlorate is *in-situ* bioremediation (Cox *et al.,* 2001; Hatzinger *et al.,* 2002). The application of these techniques varies, depending on the factors like perchlorate concentration, plume characteristics, groundwater geochemistry, presence of co-contaminants, and economics.

1.8 BACKGROUND STUDY

Natural presence of perchlorates in Chilean saltpeter was reported by Beckurts (1886). However, reports on perchlorate contamination in drinking water came from US (Takata, 1985). 34 states in America reported about the perchlorate contamination (USEPA, 2004a). The contamination was also reported from Colorado River, which supplies drinking water to ~15 million people (Hogue, 2003a). Further studies showed the presence of perchlorate in groundwater beneath some military training ranges, concluding the source as the use of munitions in the area (Smith *et al.,* 2001; Smith *et al.,* 2005). Recently, the U.S. Geological survey reported the presence of perchlorate in some minerals in the South-Western United States (Orris*et al*., 2003). Apart from this, studies on perchlorate contamination in drinking water were carried out and

reported only from a few countries like China (Shi *et al.,* 2007), South Korea (Quinones *et al.,* 2007), Japan (Kosaka *et al.,* 2007) etc.

Based on the reports available, only four works on perchlorate contamination in drinking water were conducted in India. Kannan *et al.,* (2009) have reported the presence of perchlorate in water samples from six states (Tamil Nadu, West Bengal, Bihar, Maharashtra, Karnataka and Pondicherry). Perchlorate contamination was investigated in groundwater from Sivakasi and Madurai (Isobe *et al.,* 2012) and perchlorate was detected from most of the samples suggesting ubiquitous contamination of drinking water.

From Kerala, only two works has been published which is mainly linked with the coastal areas and rocket propellants usage in Kerala (Anupama *et al.,* 2012; Anupama *et al.,* 2015).

1.9 RELEVANCE OF THE WORK

Keralites conduct a variety of firework displays during festivals and other celebrations. Moreover, 800 tonnes of ammonium perchlorate is manufactured in APEP, Aluva and the same is being used by ISRO, Trivandrum. These sources could contaminate our environment with perchlorate. The oxidizer, perchlorate, is a persistent environmental pollutant and can result in thyroid disorders, once exceeded 24.5 ppb in drinking water (ITRC, 2005). It will pass onto placenta and mammary gland and would result in nervous disorders in fetuses and infants. Studies on perchlorate contamination in drinking water resources of Kerala were very less. The present study will help to reveal the role of sources especially fireworks in the perchlorate contamination of drinking water sources. The reasons for the increasing perchlorate contamination in Kerala need to be identified and should come up with a treatment option, as the treatment options are limited. No research is done to bring out the extent of perchlorate contamination and its relationship with the thyroid disorder in Kerala.

2.1 Perchlorate-Properties

Perchlorate is a good oxidizer. Organic perchlorates are self-contained explosives (Bretherick, 1981). Perchlorate commonly originates as a contaminant in the environment from the improper disposal of solid salts of ammonium, potassium or sodium perchlorate (Houge, 2003). Ammonium perchlorate is considered as a strategic chemical in US (Mendiratta *et al.,* 1999). Under ambient environmental conditions perchlorate is unreactive (Urbansky, 1998), has poor adsorption to minerals (Urbansky *et al.,* 2001), highly mobile, persistent (Urbansky and Brown, 2003) and stable (Stetson *et al.,* 2006). Perchlorate acts as an inorganic endocrine disruptor (Snyder *et al.,* 2003).

2.2 Sources of perchlorate

Perchlorate occurs both naturally and as a manufactured compound (Dasgupta *et al.,* 2005). Natural perchlorates can be differentiated from artificial perchlorates by using isotopic mass ratio differences (Dasgupta *et al.,* 2005). Its success lies in the fact that an isotope of oxygen has more mass in naturally occurring perchlorate, while an isotope of chlorine has more mass in man-made perchlorate (Bao and Gu, 2004).

Natural sources

Perchlorates are formed naturally due to natural atmospheric processes (Dasgupta *et al.,* 2005). Evaporation of sea water, lightening, caliche deposits, post volcanic activity etc. are found to be the processes resulting in natural formation of perchlorate (Dasgupta *et al.,* 2005; Walvoord *et al.,* 2003; Jackson *et al.,* 2003; Ericksen, 1983; Schumacher, 1960). Perchlorate has been detected in natural samples like seaweed, Kelp, Antarctica soil, saline deposits etc. (Orris *et al.,* 2003; Baas *et al.,* 1958; Greenhalgh and Riley, 1960; Loach, 1962; Kounaves *et al.,* 2010).

Anthropogenic sources

Man-made perchlorate includes ammonium perchlorate, sodium perchlorate, potassium perchlorate and perchloric acid (ITRC, 2005). Perchlorate contamination in ground and drinking water came into front when reports on perchlorate contamination came from US in 1997 (USEPA, 2004a). Later from Colorado River, which supplies drinking water to ~15 million people, the contamination was reported (Hogue, 2003a). Further studies showed the presence of perchlorate in groundwater beneath some military training ranges, concluding the source as the use of munitions in the area (Smith *et al.,* 2001; Smith *et al.,* 2005). Recently, the U.S. Geological survey reported the presence of perchlorate in some minerals in the South-Western United States (Orris*et al*., 2003).

Fireworks act as a major source of perchlorate contamination. Fireworks residue consists of fine particles of burnt black powder, paper debris and residue, where perchlorate in paper residue alone ranges from 302 to 34,200 µg/kg (DEP, 2006). Direct contamination of lake water from fireworks display was also reported (Backus *et al.,* 2005; Wilkin *et al.,* 2007). Concentration of perchlorate increased in total deposition after a fireworks display at six sites in Suffolk County, Long Island and New York, US (Munster *et al.,* 2009). Factors influencing perchlorate concentration from fireworks fallout are amount and type of fireworks ignited, efficiency of perchlorate oxidation, wind direction and velocity, volume of water, rainfall and evaporation (Wu *et al.,* 2011; Munster *et al.,* 2009; Wilkin *et al.,* 2007). Perchlorate contamination due to fireworks were also reported from Canada (Backus *et al.,* 2005), and New York (Munster *et al.,* 2009). Perchlorate contamination in groundwater around a firework manufacturing site at Sivakasi and Madurai in Tamil Nadu state, India was found to be significantly higher than the groundwater in the other locations (Isobe *et al.,* 2012). In China, the largest fireworks manufacturing country, the presence of perchlorate in groundwater, tap water, surface water and bottled water was accountable to the firework production and display (Shi *et al.,* 2007). The average daily intake of perchlorate in China by way of water is 0.08 µg/kg/day, assuming a daily water consumption rate of 2L and an average body weight of 60 kg of adults (Wu *et al.,* 2010). Perchlorate contamination in drinking water in South Korea was assumed to be from the industrial waste discharge from a

Liquid- Crystal Display (LCD) monitor manufacturing industry, where perchlorate is used as a cleaning agent (Her *et al.,* 2011). Salts of chlorate have been used as defoliants, leading to the speculation that these could be sources of perchlorate in groundwater (Jackson *et al.,* 2005). Waste water from perchlorate manufacturing companies, dispersed into water bodies also causes widespread perchlorate contamination (Hogue, 2003a). In aging bleach solutions also, there is a possibility of perchlorate formation (Greiner *et al.,* 2008).

2.3 Uses of perchlorate

Perchlorate salts serve as oxidizing agents in the manufacturing of solid rocket propellants, explosives, fireworks, signal flares, matches and automotive air bag inflators (ITRC, 2005; Trumpolt *et al.,* 2007). These are also used in electronic tubes, lubricating oils, leather tanning and finishing processes, electro-plating and aluminium refining, paint and enamel production, production of chlorate-based herbicides, bleaching agents etc. (Urbansky, 1998; Burns *et al.,* 1989).

In the case of munitions, perchlorate is used in training simulators, smokes or obscurants, pyrotechnics, grenades, signals and flares, and fuses. Some types of simulators contain relatively high perchlorate concentrations as do most of those with solid rocket motors (ITRC, 2005). In road safety flares and fireworks, potassium perchlorate is used as an important ingredient. Road safety flares contain about 6.5% by weight perchlorate, and in most of the fireworks, it is used up to 70% by weight and some contain little or no perchlorate (Conkling, 1985). In fireworks, potassium perchlorate is used along with fine aluminium or magnesium powder to get the "flash and sound" effect. Rock concerts, fire crackers, illumination for night photography etc. are some applications (Conkling, 1990). Firework displays are an important source of environmental contamination, although the impact depends on the amount of fireworks used (Wu *et al.,* 2011).

The perchlorate contamination prevailing in the US is related to Chilean nitrate based fertilizers, containing perchlorate in the concentration of 0.03% to 15%, which has been widely used as fertilizer (Grossling *et al.,* 1971; Caldwell *et al.,* 2005; Urbansky *et al.,* 2000).

2.4 Fate and transport in the environment

Perchlorates are readily water soluble salts. Once perchlorate combines with water or reaches aqueous systems, it readily dissociates into perchlorate anion and the corresponding cationic ligands (Urbansky, 1998). Perchlorate anion then remains stable for long periods under ambient environmental conditions. Perchlorate from soil may either leach into water bodies or may be absorbed by the plants through soil moisture and accumulate in plant tissues (Urbansky *et al.,* 2001; Ellington *et al.,* 2001) or may be held in solution in the vadose zone by capillary forces. The mobility of highly concentrated perchlorate brine solution buried near to rocket motor washout facilities was influenced by the density (Flowers and Hunt, 2000). The brine moves vertically with minimal influence by groundwater movement due to the density contrast. These brine pools may form on top of confining layers, and significant perchlorate mass may move into low-permeability confining layers by diffusion (ITRC, 2005). Through water perchlorate may reach vegetation, insects, mammals, fishes etc. (Smith *et al.,* 2005; Park *et al.,* 2007; Smith *et al.,* 2001; Calderon *et al*., 2017; Cheng *et al*., 2008).

The natural perchlorate may leach down from soil into aquifers. From aquifers, there is a probability for absorption of perchlorate by plants and thus entering food chain (Dasgupta *et al.,* 2006). However, evidences are there on the degradation of perchlorate on plants (Nzengung *et al.,* 1999; Susarla *et al.,* 2000; Van and Schnoor, 2002; Urbansky *et al.,* 2000; Yu *et al.,* 2004 and Tan *et al.,* 2004), by bacteria (Okeke *et al.,* 2002; Coates and Achenbach, 2004; Wolterink *et al.,* 2005; Shrout and Parkin, 2006 and Yu *et al.,* 2006), in soils and sediments (Tipton *et al.,* 2003; Nozawa *et al.,* 2005 and Simon and Weber, 2006) and in the digestive system of ruminant animals (Capuco *et al.,* 2005). Another study found that perchlorate was potentially bio available to both aquatic and terrestrial organisms (Smith *et al.,* 2001). Once this anion is found in irrigation water, soil or some natural fertilizers, it can result in perchlorate accumulation in food and forage crops (Dasgupta *et al.,* 2006; Sanchez *et al.,* 2009; Robles, 1999). In humans, this perchlorate can be actively transported across membrane barriers by NIS (Dohan *et al.,* 2007; Tran *et al.,* 2008). The most sensitive life stage, for perchlorate, is fetal stage (Rebecca, 2008).

2.5 Perchlorate contamination in the environment

Presence of perchlorate was detected in groundwater, surface water and drinking water, sea water, tea and soft drinks, milk, saliva and waste water effluent (Snyder *et al.,* 2005; Crawford-Brown *et al.,* 2006; Rajagopalan *et al.,* 2006; Stetson *et al.,* 2006; Kimbrough and Parekh, 2007; Kosaka *et al.,* 2007; Quinones *et al.,* 2007; Wagner *et al.,* 2007; Asami *et al.,* 2009; Kannan *et al.,* 2009; USEPA, 2008a; Her *et al.,* 2011; Martilengo *et al.,* 2006; Asami *et al.,* 2009; Dyke *et al.,* 2007; Oldi and Kannan, 2009; Kim *et al.,* 2009; Jackson *et al.,* 2003; CDHS, 2005; USEPA, 2004b).

Perchlorate contamination was reported from surface and groundwater sources in United States, Korea, Japan, India and China (Gullick *et al.,* 2001; Kosaka *et al.,* 2007; Quinones *et al.,* 2007; Kannan *et al.,* 2009; Wu *et al.,* 2010). Perchlorate has been detected in numerous wild plant and animal species including amphibians, fish and small mammals near perchlorate manufacturing and handling sites (Smith *et al.,* 2001; Anderson and Wu, 2002).

The first discovery of perchlorate in groundwater was in US where the samples were from wells in San Gabriel valley, CA, in early 1985. Later, reports came that the lower Colorado River is contaminated with 4-16 µg/L levels of perchlorate (Hogue, 2003a). Perchlorate accumulation was noticed in broad leaf vegetables such as lettuce, irrigated with Colorado River water (Hogue, 2003b). Bioaccumulation of perchlorate was found in natural products like cabbages and beets in the range of 6.5-8.5 µg/kg (Loach, 1962). Quinones *et al.,* (2007) conducted a preliminary assessment for perchlorate in surface water, drinking water and waste water treatment plant effluent samples obtained from the Nakdong and Yeongsan watersheds in the Republic of Korea using Ion Chromatography with suppressed conductivity detection and liquid chromatography with tandem mass spectrometry (LC-MS/MS). The highest concentrations of perchlorate were found in surface water (60 µg/L) whereas in drinking water it is 35 µg/L.

Perchlorate was found in soil, water, sediment and vegetation samples (Smith *et al.,* 2001). Water and soil analysis for perchlorates were also done in an agricultural company in Southern California (Robles, 1999). Analysis of groundwater samples showed that the perchlorate concentration (109.8± 14.4 µg/L) exceeded the California

Department of Health Services' Provisional Action Level of 18 μg/L, whereas the perchlorates in the soil and vegetable samples were found to be within the risk assessment levels. Bioconcentration factor of ~200 was reported for a staple crop like wheat, relative to the water to irrigate them (Jackson *et al.,* 2005). Bull rushes (Scirpus sp.), crab grass (Digitaria sp.), cup grass (Erichloa sp.) and goldenrod (Solidago sp.) were found to have high concentrations of perchlorate in blades and leaves (Smith *et al.,* 2001). Perchlorate concentrations were highest in goldenrod leaves compared to seeds, stems and roots, and these results were similar to the studies of Nzengung *et al.,* (1999) using willow trees (*Salix nigra*) where most of the perchlorate accumulated in leaves.

Perchlorate was also detected from dairy products and human breast milk (Kirk *et al.,* 2005), in dietary supplements and flavor enhancers (Snyder *et al.,* 2006), in plants (Sundberg *et al.,* 2003; Sanchez *et al.,* 2005a), fish (Dodds *et al.,* 2004), blood from exposed cattle (Cheng *et al.,* 2004), urine (Valentin-Blasini *et al.,* 2005), cow's milk, natural and bottled waters (Snyder *et al.,* 2005; Sijimol *et al.,* 2016) etc. Murphy and Thomson, (Murphy and Thomson, 2000) using single particle mass spectrometry reported the presence of small amounts of perchlorate in stratospheric sulfate aerosols.

2.6 Perchlorate exposure

Perchlorate exposure and health risk is linked with iodine uptake. Perchlorate exposure doses is found to be the highest in age group (6-11 years) surveyed by National Health and Nutrition Examination Survey, 2001-2002 (Blount *et al.,* 2007). Infants are more susceptible to perchlorate exposure than adults (Baier *et al.,* 2006; Ginsberg *et al.,* 2007; Kirk *et al.,* 2007; Dasgupta *et al.,* 2008). The greatest potential sensitive populations to perchlorate are pregnant women, fetuses and infants (NRC, 2005). Iodide is pumped into the thyroid by sodium-iodide symporter (NIS), which is a transmembrane protein. Human NIS has a 30 fold higher affinity for perchlorate compared to iodide (Tonachera *et al.,* 2004). NIS can also actively transport perchlorate across membrane barriers in other NIS-containing tissues like the lactating mammary gland (Tran *et al.,* 2008). This could competitively inhibit iodide secretion into milk and decrease iodide intake by the infant (Kirk *et al.,* 2007). Exposure to

perchlorate is also associated with increased urinary TSH and T4 in infants (Cao *et al.,* 2010).

Perchlorate exposure differs in various groups like humans, animals, ecosystem etc (Smith *et al.,* 2001). The difference lies in the routes of exposure. The major routes of perchlorate exposure may be ingestion, dermal (skin) absorption or inhalation (ITRC, 2005). Ingestion of perchlorate through contaminated water or food is considered as the primary exposure root for humans (Greer *et al.,* 2002; Blasini *et al.,* 2011). Once the perchlorate is ingested, it gets absorbed readily and completely from the gastro intestinal tract and excreted rapidly through urine (Eichler, 1929; Stanbury and Wyngaarden, 1952; Durand, 1938). Inorganic nature of perchlorate and its ionization capacity makes the exposure through skin absorption and inhalation negligible. However, individuals working at the perchlorate manufacturing industries are susceptible to inhalation of suspended particles in the air (Lamm *et al.,* 1999). Drinking water and food contaminated with perchlorate is the main source by which perchlorate can enter human body through ingestion. Irrigation using perchlorate contaminated water may lead to its accumulation in plant parts (Robles, 1999). Various studies also proved the accumulation of perchlorate in plant parts like lettuce leaves, stems and roots (Sanchez and Krieger, 2004; Susarla *et al.,* 1999) etc. The presence of perchlorate was also detected in some animal feed crops like alfalfa (Sanchez and Krieger, 2004). Raccoons (*Procyon lotor*) in a contaminated site were found to be having perchlorate (Smith *et al.,* 2005). Milk samples also showed the presence of perchlorate (USFDA, 2004a, 2004b; Kirk *et al.,* 2005). In Japan, perchlorate was detected in dairy milk three fold higher than that from USA (Dyke *et al.,* 2007).

Perchlorate can pass through the placenta and enter the fetal blood stream (Clewell *et al.,* 2003a). Another source of perchlorate for infantsis breast milk (Kirk *et al.,* 2005; Blasini *et al.,* 2011). During early development stage, infants depend on maternal iodide present in the breast milk. Hence the presence of perchlorate is of great concern, as it inhibits the active transport of iodide into the mammary gland (Tazebay *et al.,* 2000; Blount *et al.,* 2009). In the case of animal studies, high concentration of perchlorate was found in the milk than the serum (Clewell *et al.,* 2003b). This is a reflection in the case of humans too. As the newborn begins to consume breast milk or

formula, the perchlorate exposure pattern changes significantly (Kirk *et al.,* 2005; Pearce *et al.,* 2007; Schier *et al.,* 2009). During lactation, perchlorate will be concentrated in milk (Dohan *et al.,* 2007; Schier *et al.,* 2009), and so the infants consuming milk-based formula or breast milk may have elevated perchlorate exposure compared with other life stages (Kirk *et al.,* 2005; Baier *et al.,* 2006; Ginsberg and Rice, 2005). Perchlorate was found to be in the increasing order of breast-fed infants (95%)> cow milk based formula consuming infants (86%)> infants consuming soy formula (68%) (Blasini *et al.,* 2011, Kirk *et al.,* 2007; Dasgupta *et al.,* 2008; Pearce *et al.,* 2007; Schier *et al.,* 2009). Infants of age less than 2 months possessed the highest urinary perchlorate (Blasini *et al.,* 2011, Kirk *et al.,* 2007). Hence due to dietary habit infants have higher perchlorate intake doses than adults (Ginsberg *et al.,* 2007). The presence of perchlorate in cord blood serum provides relevant information about in utero exposure (Blount *et al.,* 2009). Perchlorate was present in food stuffs (Kirk *et al.,* 2005), especially leafy vegetables and bovine milk (Kirk *et al.,* 2003, 2005; Sanchez *et al.,*2007, 2008). For example, kelp used in many different food products showed perchlorate concentrations up to 8,85,000 ppb (Orris *et al.,* 2003). Shi *et al.,* (2007) observed the presence of perchlorate in rice, bottled water and milk in China.

It is found that ingestion of contaminated water, soil, sediment and vegetation may be a path of perchlorate exposure for wild life (Smith *et al.,* 2001; Smith *et al.,* 2005; Beyer *et al.,* 1994; Rainwater *et al*., 2008). Several species of fish, amphibians and aquatic insect larvae were also found to be having perchlorate in tissues and the likely route of exposure may be through respiratory surfaces (Smith *et al.,* 2001; Park *et al.,* 2007; Theodorakis et al., 2006a). Bioconcentration was not evident in fish and amphibian samples (Smith *et al.,* 2001) and it may be due to the high water solubility of perchlorate (Rand 1995).

2.7 Toxicity of perchlorate

Perchlorate is a potent thyroid disruptor. It will competitively inhibit the uptake of iodide by thyroid gland, and results in the decreased production of thyroid hormones-thyroxin and triiodothyronine (Tonachera *et al.,* 2004; Saito *et al.,* 1983), and thereby increasing the TSH levels in blood (Lawrence *et al.,* 2000; ITRC, 2005). Competitive inhibition of perchlorate and iodide ions is a consequence of the hydration energies of

the two ions. When 20% of iodine enters breast milk, about 50% perchlorate reaches the mammary glands, and this is fed to the new borns. The chances for thyroid disorders and abnormal growth of infants cannot be neglected (Renner, 2008). Thyroid hormones are essential for proper protein expression, neuronal differentiation, migration and myelination of fetus and are received from mother during the first trimester of gestation (Haddow *et al.,* 1999; Dowling *et al.,* 2000; Alvarez *et al.,* 2000; Tonachera *et al.,* 2004; Greer *et al.,* 2002). If TH deficiency occurs, it may result in characteristic functional deficits, especially difficulty in processing visual-spatial information, poor sensorimotor coordination, and memory/attention deficits (Rovet, 2002; Clewell *et al.,* 2003b). Earlier study showed that perchlorate can be selectively transferred to the mammary gland (Dasgupta *et al.,* 2008; Sijimol *et al*., 2015).

Normal thyroid functions can be maintained, even in the presence of iodide inhibitors, if there is sufficient iodide consumption (Delange and Ermans, 1996). 150 µg iodine daily would protect against goiter in a person whose perchlorate ingestion is 4mg/day (0.057 mg/kg/day in a 70 kg adult) (Greer *et al.,* 2002). It can be inferred that adequate iodine uptake is key to the resiliency of the thyroid-pituitary axis when challenged with perchlorate or any other inhibitor of thyroidal iodide uptake (Greer *et al.,* 2002).

During pregnancy, it causes extra stress on many maternal biological functions, including thyroid activity (Glinoer *et al.,* 1992). If the maternal thyroid is not able to maintain adequate levels of thyroid hormones, especially during the first trimester, irreversible alterations in fetal neurological development could occur. T4 is solely supplied by the mother till the fetal thyroid gland becomes functional (Tillotson *et al.,* 1994). Another study suggested that T4 supplied by mother throughout the pregnancy period has an overall protective effect from fetal neurological impairment (Morreale *et al.,* 2000). The recommended daily allowance (RDA) for iodine ranges from 110 µL (0-6 months), 130 µL (7-12 months), 150 µL (>14 year), 220 µL (pregnant woman) to 290 µL (lactating women) (FNB, 2001; Pearce *et al.,* 2004). In US population, iodine deficiency was reported, especially among women of child bearing age (Pearce *et al.,* 2004). Out of 100 healthy pregnant women, about 49% were found to have low levels of urinary iodide levels, than needed (Kirk *et al.,* 2005).

The perchlorate contamination of Colorado River caused for abnormal thyroid functions of newborns in Arizona (Brechner *et al.*, 2000) where as in California it was due to gestational exposure (Schwartz, 2001). Based on the background studies, USEPA (2002) released a draft toxicological review on perchlorate and suggested a reference dose of 0.03µg perchlorate/kg body weight/day (µg/kg/day), which equates to ~1 µg/L in drinking water (USEPA, 2002). But National Academy of Sciences (NAS, 2005) suggested 0.7 µg/kg/day as the reference dose for perchlorate in drinking water (NRC, 2005), corresponding to a drinking water equivalent (DWEL) of 24.5 µg/L. Perchlorate analysis was done in dairy milk and human milk (Kirk *et al.*,, 2005). Perchlorate was detected in all the samples and in human milk it ranged from 0.6 to 92.20 µg/L (Kirk *et al.*, 2005). In another study dairy milk samples from Texas City, were found to be contaminated (1-6 µg/L) (Kirk *et al.*, 2003).

Infant dosage of perchlorate from breast milk was calculated using data obtained from rat studies by Clewell *et al.*, (2003a). A physiologically based pharmacokinetic model for nursing rat pups predicted that at low levels of maternal exposure (~10 µg/kg/day), up to 50% of the maternal intake is transferred to the infant. From this, it was assumed that, transfer of 30µg/day to a newborn of 1 month age having an average 4.1 kg weight, will exceed the 6 µg/kg/d safe dose recommended for children (Strawson *et al.*, 2004).

2.7.1 Animal toxicity studies

A fairly extensive database of animal toxicity studies was built in keeping with risk assessment guidelines, to determine the health effects of perchlorate in humans (Cheng et al., 2008, 2007; McNabb *et al.*, 2004; York *et al.*, 2001). Immunological effects in mice (Keil *et al.*, 1999), developmental effects in rats and rabbits (York *et al.*, 2001, 2003), two-generation reproductive studies in rats (Bekkedal *et al.*, 2000; Bekkedal *et al.*, 2004; York *et al.*, 2004) etc. comes under the animal studies done to assess the risk of exposure to perchlorate. Siglin *et al.*, (2000) conducted a 90-day perchlorate mode of action study in rats and the entire animal study database collectively supported the mode of action for perchlorate and the competitive iodide uptake inhibition. Perchlorate has been shown to induce brain morphological changes in rats, at dosage down to 10 µg/kg/day (ARL, 2001). Peak blood levels of perchlorate

were reported after a 3 hour exposure, in rats and the half-life was approximately 8 hours (Wolf, 1998). Retention time of perchlorate is different for different mammalian tissues (Yu *et al.,* 2002). In Sprague-Dawley rats, T3 concentrations were significantly altered by low doses of perchlorate (0.01 mg/kg/day) (Siglin *et al.,* 2000). Even though low levels of perchlorate are not sufficient to affect hormone profiles, it may affect thyroid gland through production of hypertrophic cells and colloid tissue (Becker *et al.,* 1995). Perchlorate doses as low as 0.0085 mg/kg/day decreased the T4 and increased TSH, in maternal laboratory rats (York *et al.,* 2003). In rats, even short-term iodide deficiency during fetal development results in altered neuronal migration, along with aberrant response to acoustic stimuli, including seizures (Auso *et al.,* 2003). When perchlorate was given at around 100 µg/L, for 30 days, fish developed increased thyroid follicular hyperplasia, hypertrophy and colloid depletion (Bradford *et al.,* 2005; Theodorakis *et al.,* 2006b). In amphibians perchlorate has shown to alter the metamorphosis and sex ratios (Goleman *et al.,* 2002a; 2002b). They also showed sensitivity to high concentrations of perchlorate during metamorphosis (Dean *et al.,* 2004; Goleman *et al.,* 2002a; Miranda *et al.,* 1995). It was also noticed that infusion of perchlorate in large doses in goats, cause major reduction of iodide expression in milk (Mountford *et al.,* 1987). Perchlorate also inhibits larval development in amphibians (Miranda *et al.,* 1996; Brown 1997), disrupts iodide accumulation in lamprey (Manzon and Youson, 2002) and results in hermaphroditism in fish (Bernhardt *et al.,* 2006).

In another study, the maternal perchlorate exposure led to embryonic hypothyroidism in Japanese quail (Chen *et al.,* 2008). Fathead minnow (*Pimephales promelas*) embryos exhibited decreased scale of production, and altered thyroid histopathology, when they were reared in 1-100mg/L perchlorate for 28 days (Crane *et al.,* 2005). Thyroid hormone levels decreased in pups of exposed dams as well as dose-dependent deficits in hippocampal synaptic function were reported (Gilbert and Sui, 2008). Lack of bioconcentration of perchlorate were demonstrated in terrestrial mammals, birds, fish, amphibians, insects (Parsons, 2001), rodent tissue (Smith *et al.,* 2004) etc.

2.7.2 Epidemiological studies

Perchlorate dose-response studies have been conducted on rats as the rat thyroid is much more rapidly responsive to any perturbation of iodine metabolism leading to decreased thyroid hormone formation (Studer and Greer, 1968). However, the data may not be accurate in the case of humans. In situations of thyroid hormone synthesis prevention, rat thyroid will have stored hormone to last a few days only (Studer and Greer, 1968; Fukada *et al.,* 1975) whereas human thyroid hormone will last for several months (Dunn and Dunn, 2000; Brabant *et al.,* 1992).

Epidemiological studies so far have examined the associations of environmental exposure to perchlorate in drinking water at about 4-120 µg/L and abnormalities of thyroid hormone and TSH production in newborns and thyroid diseases in infants and adults (Lamm and Doemland, 1999; Brechner *et al.,* 2000; Crump *et al.,* 2000; Li FX *et al.,*, 2000; Li Z *et al.,* 2000; Schwartz, 2001; Morgan and Cassady, 2002; Kelsh *et al.,* 2003; Lamm, 2003; Buffler *et al.,* 2004). Occupational studies of respiratory exposures up to 0.5 mg/kg perchlorate per day and abnormalities of thyroid hormone and TSH production in adult workers have been observed (Gibbs *et al.,* 1998; Lamm *et al.,* 1999; Braverman *et al.,* 2004). A possible relation between perchlorate exposure and adverse neurodevelopmental outcomes in children (attention-deficit/hyper activity disorder and autism) has also been noticed (Chang *et al.,* 2003).

The presence of perchlorate was noticed in maternal urine, maternal blood, amniotic fluid and cord blood (Blount *et al.,* 2009). This proves the passage of perchlorate through placental membrane/barriers. Maternal serum perchlorate was higher than cord serum perchlorate and maternal urine perchlorate was higher than fetal amniotic fluid perchlorate levels (Blount *et al.,* 2009). Perchlorate at doses of 10 mg/day in drinking water, for 14 days, caused inhibition of thyroidal radioiodine uptake in 9 male volunteers (Lawrence *et al.,* 2000). The dose response in humans for perchlorate inhibition of thyroidal upake and short-term effects on thyroid hormones were determined by giving perchlorate in drinking water at 0.007, 0.02, 0.01 or 0.5 mg/kg/day to 37 male and female volunteers for 14 days (Greer *et al.,* 2002). They also reported that, 5.2-6.4 µg/kg/day perchlorates will enter adults, if drinking water contained perchlorate levels of approximately 180 and 220 µg/L, assuming the only

source of perchlorate exposure is drinking water (Greer *et al.,* 2002). A mean perchlorate dose of 0.12 mg/kg/day inhibited the radioiodine uptake (Lawrence *et al.,* 2000).

2.7.3 Pharmacological use and clinical studies

Potassium perchlorate was used in the treatment of hyperthyroidism and Graves disease in 1950s and 1960s (Von, 1995; Orgiassi and Mornex, 1990). The clinical studies measured inhibition of iodide uptake into the thyroid glands as well as TSH and thyroid hormones when exposed to potassium perchlorate (Lawrence *et al.,* 2000; Lawrence *et al.,* 2001; Greer *et al.,* 2002; Braverman *et al.,* 2004).. However a few studies showed no response too (Brabant *et al.,* 1992)

2.7.4 Ecological toxicity

Perchlorate shows its impacts not only on humans but also on various ecological features. Perchlorate effects were assessed in various aquatic and terrestrial species. Detectable levels of perchlorate were found in periphyton, tree leaves, aquatic plants, small birds and mammals, native fish etc. (Tan *et al.,* 2005). Some aquatic invertebrates like water flea (*Ceriodaphniadubia*) tolerated perchlorate up to 9.3 mg/L under chronic conditions and up to 20 mg/L under acute conditions (Dean *et al.,* 2004).

2.8 Human health risk assessment

An oral RfD is an estimate of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious noncancer health effects during a lifetime. A high-confidence RfD is based on data that address all potentially critical life stages (ITRC, 2005). Thyroid hormone imbalance occurs due to the inhibition of iodide uptake, alterations in thyroid hormone synthesis, or some other measurable end point (Blount *et al.,* 2009; Blasini *et al.,* 2011). Potential receptors of concern are developing fetus (Haddow *et al.,* 1999; Howdwshell 2002; Heindel and Zoeller 2003; Lavado-Autric *et al.,* 2003; Auso *et al.,* 2003), nursing infants (Clewell *et al.,* 2003b; Tazebay *et al.,* 2000), children (Giedd *et al.,* 1999; Sowell *et al.,* 1999; Thompson *et al.,* 2000; Webster *et al.,* 2003) and post menopausal women (Hollowell *et al.,* 2002; Surks et al. 2004).

Primary concerns regarding iodide deficiency in fetus are decreased IQ and alterations in psychomotor development. Allowable perchlorate concentrations derivation is complicated because of the uncertainties in the identification of the threshold for maternal and fetal thyroid effects (Morreale *et al.,* 2000). Adequate dietary iodine intake may reduce the susceptibility of individuals to the effects of perchlorate exposure (Kirk *et al.,* 2005).

2.9 Perchlorate uncertainties and data gaps

Even though data is available on the health effects (Hershman, 2005; Studer and Greer, 1968), accumulation (Robles, 1999; Smith *et al.,* 2001) etc. of perchlorate, uncertainties and data gaps exists in many areas like toxicity, exposure, risk assessment etc. Toxicity uncertainty arises due to the iodide uptake fluctuation every day as a result of diet and other factors and the body's natural adaptive processes compensate for these fluctuations (Park *et al.,* 2007). The relationship between reduced iodide uptake with compensatory changes in thyroid regulation and an irreversible developmental effect (hormone dysregulation) still need to be elucidated. Very high concentrations of perchlorate can cause cancer in the laboratory animals (Capen, 1997; York *et al.,* 2001), but has not been shown to cause cancer in humans. Even in highly contaminated industrial settings, the concentrations of perchlorate required to produce tumors are far greater than the amounts encountered by human populations (Gibbs *et al.,* 1998; Lamm *et al.,* 1999). Further research on exposure of perchlorate and its effects on various subpopulations need to be done. Data lack on dose-response extrapolation and exposure estimation. Additional research is required on the exposure sources of perchlorate, potential impacts to other species like plants, animals, fish etc., accumulation and transmittance to humans through food chain etc. (ITRC, 2005).

2.10 Risk management and regulatory status

The evaluation of strategies to eliminate or minimize risks due to contaminants at a site, is known as risk management (Quinones *et al.,* 2007; Hatzinger, 2005). It typically involves implementing remedial activities that reduce contaminant concentrations to acceptable risk-based levels (established during the risk-assessment), taking other measures to prevent completion of exposure pathways, or

combining these approaches (ITRC, 2005). Initial evaluation of the potential and actual occurrence of a perchlorate source is to be identified prior to risk management.

2.10.1Risk management strategies

Strategies for risk management include pollution prevention, recycling, risk reduction etc. The best risk management approach is to prevent a chemical release, before it occurs. Proper management and storage of perchlorate can also prevent perchlorate release to the environment (ITRC, 2005). Usually perchlorates are stored in "super-sacks" or bags, steel drums, in pallets in concrete floors etc., all of these can be corroded. If the storage vessels, piping and secondary containment are not corrosion resistant, leakage may occur resulting in environmental/groundwater contamination. Release of perchlorate in the form of dust may also occur during transfer processes. Some operation like capturing of wash water for further production, rinsing of affected containers before disposal, recycling of residual perchlorate into new product, incineration etc. can ensure zero discharge of perchlorate waste (Trumpolt *et al.*, 2007). Inorder to reduce the risk of perchlorate contamination in drinking water, alternate drinking water supply can be provided. Blending of water from different sources, pre-treatment of perchlorate before use and the treatment of plume (groundwater contaminants that have moved away from the source) are also possible for risk reduction.

2.10.2 Regulatory status

Perchlorate has been listed as a candidate for drinking water-monitoring programs since 1997 (USEPA, 1998). Then it was added to the USEPA Contaminant Candidate List and the Unregulated Contaminant Monitoring Rule in 1998 (Federal Register, 1998; USEPA, 1998).

In US, an Interim health advisory level of 15 µg/L of perchlorate in drinking water was established (USEPA, 2005a). Later, it was changed into an official RfD of 0.0007 mg/kg/day of perchlorate (NRC, 2005). But some states like Massachusetts, California etc. have promulgated advisory levels of perchlorate in drinking water as 1 ppb and 6 ppb respectively (CDHS, 1997; http://www.mass.gov/dep/water/dwstand.pdf). National Research Council concluded that the levels of perchlorate that have been found in groundwater are unlikely to affect a healthy adult (NRCHIPI, 2005) and suggested a

reference dose of 0.7 µg/kg of body weight. This is supposed to protect the health of even the most sensitive population. At present, there are no standards or maximum permissible limits for perchlorate. As perchlorate is a potent thyroid disrupter (Renner, 2008), it is essential to have a regulation. The plans to treat perchlorate in drinking water are also going on.

2.11 Sampling and analysis of perchlorate

Sampling for perchlorate analysis requires some knowledge on perchlorate usage at the site, quantity released at one time, number of occurrences, time period over which the release occurred, environment geology etc (Wu *et al.,* 2011; Munster *et al.,* 2008). In the case of groundwater, perchlorate tends to move with groundwater flow unless stagnant conditions exist. It may also be associated with other contaminants, such as nitrates, explosives, solvents or metals (Conkling, 1990). Requirement of soil testing depends on the release of perchlorate either continuous or intermittent at any point source. For a better result, both surface and at depth samples should be taken for soil analysis (Smith *et al.,* 2001). In unfiltered soil surface samples, perchlorate degrades with time, but concentrations in filtered samples and groundwater samples perchlorate remains stable well over 300 days (Stetson *et al.,* 2006).

Numerous techniques for the detection of perchlorate have been evolved since 1997. The detection limit was 4 ppb for the initial techniques whereas it is now at concentration of 1 ppb and lower (Smith *et al.,* 2001; Wendelken *et al.,* 2005). Analytical techniques for perchlorate must be given due considerations because of the potential interferences, laboratory contamination and potential false positives that may probably occur.

Important points to be noted during perchlorate detection are

a. Potential for false positives and false negatives.
b. Potential for bias in the analytical results due to field or laboratory activities.

To overcome these drawbacks, method blank should be routinely analyzed and evaluated (Wendelken *et al.,* 2006).

Commonly used laboratory methods for the analysis of perchlorate includes EPA 314.0 (Ion chromatography, IC), EPA 314.1 (IC), EPA 9058 (IC), EPA 6850

(LC/MS), EPA 331.0 (LC/MS or LC/MS/MS), EPA 332.0 (IC/MS or IC/MS/MS) and FDA Method (IC/MS/MS). Method 314.0, the only method for perchlorate promulgated by the USEPA to date, was developed for drinking water. Aqueous samples are introduced into an ion chromatograph. The perchlorate ion is separated from other ions in the sample based on its affinity for the material in the chromatographic column and is detected using a conductivity detector (USEPA, 1999a). Method 314.1 (USEPA, 2005a).This method is intended to add increased sensitivity, better tolerance of TDS, and better selectivity through use of a confirmation column and in-line concentration. Method 9058 is the USEPA's Office of Solid Waste (OSW) method using IC. The method is substantially the same as Method 314.0, although the Matrix Conductivity Threshold requirement is not included. The method is stated to perform adequately on water samples with conductivity up to 1000 µS/cm and is potentially applicable to surface water, mixed domestic water, and industrial waste waters. The LC/MS method uses a liquid chromatograph with a peptide-impregnated reverse-phase column to perform the separation followed by MS detection after a minimum sample pretreatment. Perchlorate parent ions (mass-to-charge [m/z] 99 and 101) are used for peak identification. This method has been evaluated with drinking water, soil, biota, synthetic groundwater (7700 µS/cm^2), and Great Salt Lake Water (10x dilution, 21,000 µS) (Di Rienzo *et al.,* 2005). The advantages of LC/MS are the increased sensitivity, increased specificity, the minimum sample pretreatment, and the lack of additional instrumentation. The reporting limit in water is reported to be 0.1 µg/L (Kannan *et al.,* 2009; Quinones *et al.,* 2007). Method 331.0 (Liquid Chromatography Electrospray Ionization Mass Spectrometry) published in 2005 (USEPA, 2005b) is a liquid chromatography/electrospray ionization/mass spectrometry (LC/ESI/MS) method for the determination of perchlorate in raw and finished drinking waters. This method can be used to acquire data using either selected ion monitoring or multiple reactions monitoring detection. The IC/MS method, Method 332.0 (Ion Chromatography with Suppressed Conductivity and Electrospray Ionization Mass Spectrometry) also published (USEPA, 2005c) is essentially the same as the IC method; however, an MS with an electrospray interface is added (Smith *et al.,* 2001). IC/MS methodology can be enhanced by coupling the IC with a conductivity detector

and a tandem MS, thereby increasing the sensitivity and specificity over that of IC/MS. The quantitation limit in water is reported to be 0.01 µg/L (Penfold, 2004). The method has been used on water, soil, milk, lettuce and other biota samples (Munster *et al.*, 2008). Capillary electrophoresis (CE) has been used to analyze perchlorate for certain applications (primarily forensics). CE is not currently viable for analysis of perchlorate in environmental media at low concentrations. The best limit of detection available with most widely available equipment and reagents for CE is 100 µg/L (Urbansky, 2000). Two methods are widely employed for the field analysis of perchlorate: Ion-selective electrode and colorimetry (ITRC, 2005). Ion-selective electrode can potentially detect perchlorate in the low-ppb range. This method is potential for in-situ sampling for groundwater monitoring wells. A reliable and inexpensive colorimetric method for perchlorate in water and soil extracts has also been developed and tested with surface water, well water, bioreactor effluent and soil extracts.

When groundwater samples are collected for analysis, it should be ultra filtered through a sterile 0.2-micron filter into a presterilized nalgene bottle (Isobe *et al.*, 2012; Her *et al.*, 2011), and the samples be collected with significant headspace (USEPA, 2005 a, b, c). The analysis are to be done within 28 days after sample collection, since the prescribed holding time for perchlorate by USEPA is 28 days (USEPA, 1999b), when the sample is held at 4° ± 2°C. A very little data do exist about the distribution of perchlorate on soil (Smith *et al.*, 2001). Even though perchlorate may be initially distributed in soil particles, because of its greater solubility; it may migrate to the lower levels (Smith *et al.*, 2001). If perchlorate is distributed in a dissolved source, it is expected to be very mobile in the soil and if in the solid phase, it could be expected to be distributed due to the physical transport of the detonation (ITRC, 2005). One issue regarding soil sample collection for perchlorate analysis is sample representativeness due to anticipation in composition of samples collected (Gerlach and Nocerino, 2003). If the anticipated source is a detonation, composite sampling is recommended (Walsh *et al.*, 1993; Jenkins *et al.*, 1996; Thiboutot *et al.*, 1997; Crockett *et al.*, 1996). The holding time for perchlorate in soil has not been established and it is appropriate to set the holding time similar to water holding time of 28 days, when the sample is held at 4° ± 2°C.

2.12 Forensic Techniques/Chemometrics

The systematic investigation of a contaminated site or event focused on defensibly allocating liability for the contamination is known as chemometrics or simply forensics techniques (ITRC, 2005). Forensic investigative approaches to identify the source(s) of perchlorate contamination in soil or groundwater include traditional source identification and concentration profiling, association with affiliated chemicals and isotopic analysis. Possible forensic techniques include chlorine isotopes for defining multiple or commingled perchlorate plumes (Motzer, 2001). Stable isotope ratio analysis of the perchlorate molecule is used for differentiating between naturally occurring and manmade perchlorate in the environment (Bao and Gu, 2004). From the isotope ratio analysis the distinction between natural perchlorate that forms by environmental processes and artificial perchlorate manufactured through industrial electrolytic process can be identified.

2.13 Remediation of perchlorate

Possible technologies for perchlorate reduction include physical separation (precipitation, anion exchange or membrane filtration, reverse osmosis and electro dialysis), chemical and electrochemical reduction, and biological or biochemical reduction (Srinivasan and Viraraghavan, 2009; Urbansky, 1998). But it is difficult to remove perchlorate using typical physical-chemical water treatment technologies (Logan, 1998).

Biological approaches are gaining attention for the treatment of perchlorate (Hatzinger, 2005). Biodegradation of perchlorate was identified as one of the most effective techniques from 1950's onwards, but its importance was noticed only when perchlorate contamination emerged as a threat. Perchlorate can be effectively attenuated by microaerophilic or anaerobic microorganisms (Coates and Achenbach, 2004; Logan, 1998; Rikken *et al.,* 1996; Wu *et al.,* 2001; Holdren *et al.,* 2008). Dechloromonas, Azospira and Dechlorospirillum genera showed reliable degradation of perchlorate (Achenbach *et al.,* 2001; Zhang *et al.,* 2002; Coates *et al.,* 1999 and Coates and Achenbach, 2004). Later about 40 phylogenetically and metabolically diverse microbial species including members of the Proteobacteria, Firmicutes, *Moorella perchloratireducens* and Sporomusa sp. were found to be capable of

perchlorate reduction (John and Laurie, 2004). Novel dissimilatory perchlorate-reducing bacteria *Dechloromonas hydrogenophilus* and *Propionivibrio militaris* were isolated from enrichments (Thrash *et al.*, 2010).

Perchlorate reduction produces chloride and oxygen as degradation products by the following pathway (Rikken *et al.,* 1996):

$ClO_4^- \Longrightarrow ClO_3^- \Longrightarrow ClO_2^- \Longrightarrow Cl^- + O_2$

This is a two-enzyme catalyzed reaction. Perchlorate is reduced to chlorate and chlorite by reductase enzyme (Kengen *et al.,* 1999) and chlorite dismutase disproportionate the chlorite into chloride and oxygen (Coates and Achenbach, 2004; vanGlinkel *et al.,* 1996).

Microbial respiration of perchlorate is influenced by environmental conditions, and reduction of perchlorate is directly dependent on bioavailable molybdenum and presence or absence of competing electron acceptors (Chaudhuri *et al.,* 2002; Kim and Logan, 2001; Logan, 2001; Rikken *et al.,* 1996; Coates *et al.,* 1999). In some strains molybdenum is essential and in some strains presence of oxygen and nitrate can inhibit the process (Coates and Achenbach, 2004; Song and Logan, 2004; Chauduri *et al.,* 2002; Rikken *et al.,* 1996; vanGlinkel *et al.,* 1996; Xu and Logan, 2003). Bacterial species found to reduce perchlorate (*Dechloromonas aromatica, Azospira suillum* and *Dechloromonas agitate*), are inhibited by oxygen (Sun *et al.,* 2009). Perchlorate ion acts as an electron acceptor aiding successful bacterial reduction of perchlorate (Sellers *et al.,* 2007).

Perchlorate reducer *Dechlorosoma suillum*, reduced perchlorate only under anaerobic conditions and was dependent on presence of molybdenum. Dissolved oxygen concentrations less than 2 mg/L too inhibited perchlorate reduction by D. *suillum*. Nitrate had inhibitory effects on perchlorate reduction with D. *suillum*, whereas nitrate had no inhibitory effects on perchlorate reduction with *Dechloromonas agitata* (Chaudhuri *et al.,* 2002). Lag time for microbial reduction of perchlorate is inversely proportional to nitrate reduction (Gal *et al.,* 2008). Information are available on the aerobic perchlorate reducers that are independent of molybdenum (Shete *et al.,* 2008) Three isolates of microbes- *Pseudomonas stulzeri* (Proteobacteria) and the other two belonging to *Arthrobacter* (Actinobacteria)) were found to be capable of perchlorate

reduction under aerobic condition, and independent of molybdenum (Shete *et al.*, 2008). But these showed some inhibition of perchlorate reduction at perchlorate concentrations higher than 17mM (Shete *et al.*, 2008). Most of the perchlorate-contaminated sites have perchlorate reducing bacteria and can be used in perchlorate degradation through the addition of different electron donors, such as acetate and lactate (Wu *et al.*, 2001).

Bioreactors are engineered systems that maintain high densities of pollutant-metabolizing organisms in contact with groundwater or waste water (Hatzinger, 2005; Rittman and McCarty, 2001). Bioreactors are used to treat perchlorate in high-strength waste water treatment, groundwater treatment and drinking water treatment. In the case of drinking water treatment various designs of hydrogen-based reactors have been tested in laboratory, to reduce perchlorate (Logan and LaPoint, 2002; Miller and Logan, 2000 and Nerenberg *et al.*, 2002; Chung *et al.*, 2007). The main drawback is that hydrogen is only sparingly soluble in water; this can result in an insufficient supply being available to completely bioreduce perchlorate, particularly in waters containing appreciable quantities of competing electron acceptors such as nitrate and oxygen (Logan and LaPoint, 2002; Miller and Logan, 2000). For drinking water treatment (Kim and Logan, 2001; Xu *et al.*, 2003) and in-situ groundwater remediation (Giblin *et al.*, 2000; Hunter, 2002; Logan and LaPoint, 2002 and Leeson *et al.*, 2006) biological processes are effective.

Microbial reduction is a cost-effective, in-situ bioremediation technique for perchlorate-contaminated water (Sturchio *et al.*, 2003). Salt tolerant bacterial isolates-*Haloferaxdenitrificans, Paracoccus halodenitrificans* and *Citrobacter* sp. were found to be very effective in the removal of perchlorate from the spent regenerant brine used in ion-exchange technology (Okeke *et al.*, 2002). Biological perchlorate reduction can be achieved using a hydrogen-oxidizing hollow-fiber membrane-biofilm reactor system. Here, the optimal pH is 8 and no specialized inoculation is required. Perchlorate reduction occurs simultaneously with nitrate reduction (Nerenberg *et al.*, 2002). Perchlorate-degrading fed-batch reactors were also tested (Anupama *et al.*, 2013) to study the kinetics of chlorite dismutase, the enzyme involved in perchlorate degradation and came up with the result that the compounds such as ammonia, nitrite and metal-chelating chemicals can retard the activity of the enzyme. Graphene,

prepared by a facile liquid-phase reactor exfoliation is an excellent perchlorate adsorbent, removes perchlorate from water, making it drinkable (Lakshmi and Vasudevan, 2013).

Phyto-remediation is another method for the removal of perchlorate from soil and groundwater (Seyfferth et al., 2008b). Trees such as ash, chinaberry, elm, willow, mulberry and hackberry are proved as perchlorate accumulators (Tan *et al.*, 2004). Wheat stem and head, alfalfa, smart weed, water cress etc. also accumulate perchlorate (Cope *et al.*, 1967). Phyto-remediation of perchlorate was observed inside poplar trees (*Populusdeltoid x nigra*) and the perchlorate undergone reduction to chlorate, chlorite and chloride (van Aken and Schnoor, 2002).

Perchlorate uptake by plants is largely affected by nitrate and pH. Increased nitrate concentration and pH reduces perchlorate uptake thereby rendering the phyto-remediation process bit herculious (Seyfferth *et al.*, 2008a).

2.18 OBJECTIVES OF THE STUDY

1. To assess the perchlorate content in drinking water in the selected regions of Kerala.
2. To study the seasonal variation of perchlorate.
3. To study the role of fireworks in perchlorate contamination.
4. To conduct a survey to study the relationship between perchlorate and the thyroid disorders in the selected regions.
5. To study the effectiveness of Advanced Reduction Processes as a treatment method for perchlorate in water.

The study area and general methodology for sample collection and analysis are discussed in this chapter. The detailed methodology wil be described in respective chapters.

3.1 Study area

The study area covers selected regions of the entire state of Kerala. Kerala is located in the southwest corner of India with 8º18’ and 12º48’ north latitudes and 74º52’ and 77º24’ east longitudes. It covers an area of 38,863 sq.km. There are a total of 14 districts in Kerala with a population density of 860 persons per sq.km. There are 44 rivers in Kerala (41 west-flowing and 3 east-flowing), numerous lakes, backwaters etc. It lies close to the equator when compared to other Indian states. It experiences a pleasant and equable climate because of the land’s nearness to sea and the presence of Western Ghats. It receives an average rainfall of about 3000mm per year and the temperature ranges from 28ºC to 32ºC on the plains and about 20ºC in the highlands. Major seasons in Kerala are monsoon (South-West and North-East), winter (post-monsoon) and summer (pre-monsoon) (www.prokerala.com>Kerala). Both literally and industrially, Kerala is a highly developed state. Numerous educational centers and a lot of industries like FACT, APEP, VSSC etc. add to the dignity of Kerala.

Perchlorate sources in Kerala

The major perchlorate source in Kerala is APEP (Ammonium Perchlorate Experiment Plant), Aluva. 800 tonnes of ammonium perchlorate is manufactured per year by APEP. The ammonium perchlorate manufactured is consumed at TERLS (Thumba Equatorial Rocket Launching Station), Trivandrum. At TERLS ammonium perchlorate is used as oxidizer in rocket propellants. Ground testing of rocket motors using ammonium perchlorate is a frequent process here. Apart from these major sources, a lot of firework manufacturing units also use perchlorate as a major content in fireworks. Fireworks displays that are an inevitable part of Kerala festivals also help perchlorate to reach environment.

3.2 Sample treatment and storage

Water samples

Grab samples were collected and filtered using 0.2µ nylon membrane filter paper to remove microbes. They were stored leaving the top one third of the bottle empty to reduce the potential of degradation by any remaining anaerobic organisms as there is a possibility of perchlorate to undergo microbiological degradation under anaerobic conditions. In the lab, samples were kept below 6˚C until analysis. Samples were analyzed within 28 days of collection (EPA Method 331.0) and calculated the final concentration with the following formula

Perchlorate in water samples (µg/L) = Concentration in extract from calibration curve (µg/L ClO_4^-) x Dilution factor

Soil samples

Soil samples were collected from the top layer (within 15cms) using a spade in polythene covers. They were weighed and diluted with water (1:2). The samples were then vortex mixed and sonicated for at least 10minutes. Sonicated samples were vortex mixed again and centrifuged. The samples were filtered using 0.2µ filter paper and stored in polypropylene bottles with head space to reduce potential anaerobic biodegradation, below 6˚C (Smith *et al.,* 2001).

Perchlorate in soil samples (µg/kg) = (Concentration in extract from calibration curve (µg/L ClO_4^-) x Final volume of sample extraction solution (L) x Dilution factor)/ Mass of initial sample extracted

3.3Parameters analyzed

Water samples

Parameters	Method of detection
• pH	pH meter
• EC	Conductivity meter
• TDS	Conductivity meter

- Salinity — Conductivity meter
- Chloride — Ion chromatography
- Nitrate — Ion chromatography
- Sulphate — Ion chromatography
- Ammonium — Ion chromatography
- Sodium — Ion chromatography
- Potassium — Ion chromatography
- Calcium — Ion chromatography
- Magnesium — Ion chromatography
- Chlorate — Liquid Chromatography Mass Spectrometry
- Perchlorate — Liquid Chromatography Mass Spectrometry

Soil samples

- pH — pH meter
- OC — Walkley and Black Method (1934)
- Chlorate — Liquid Chromatography Mass Spectrometry
- Perchlorate — Liquid Chromatography Mass Spectrometry

3.4Sample analysis/ Instrumentation

- **LC/MS**

LC/MS was used for perchlorate and chlorate analysis of both water and soil samples. LCMS instrument parameters are given in Table 3.1.

Table 3.1 LCMS Instrument parameters

Instrument	LCMS-2020 Shimadzu
LC degassing unit	DGU- 20A5R
Pump	LC-30 AD Nexera
Auto sampler	SIL-30 AC Nexera X2
Column Oven	CTO-20A
Communication Bus Mode	CBM-20A
MS	Single Quadrupole
Column Oven Temperature	Zero
Flow Rate	0.35 ml/min
Solvent system	Isocratic 100% methylamine (2%)
Injection volume	50 ml
Column	Dionex IonPac ™ AS21 2x 250 mm
Guard column	Dionex IonPac ™ AG21 2x 50 mm

Perchlorate analysis

Perchlorate has m/z99 and an isotopic mass m/z101. Usually drinking water has a sulfate ion at m/z99 ($H^{34}SO_4$) that can interfere with perchlorate analysis. In order to avoid the interference SIM 101 was used for identification of perchlorate. Perchlorate has a strong M+2 ion due to the presence of ^{37}Cl. For confirmation of a peak as perchlorate, the ratio of molecular ion to its M+2 ion (99/101) for the SIM technique (Ratio within ±25% of the theoretical value of 3.08 i.e. 2.31 to 3.85) was confirmed. As the SIM method is significantly more susceptible to interferences from hydrogen sulfate, the M+2 ion (SIM m/z101) was used for quantification of perchlorate (EPA Method 331.0).

Quantification of perchlorate

Sodium perchlorate, the salt of perchlorate was used to prepare standards. A series of standards in varying concentrations (from ppt to ppm) were prepared to obtain calibration curve. The Method Detection Limit (MDL) is 4 ppb and Limit of Quantification (LoQ) is 6 ppb. To every set of samples, a series of standards were run.

Chlorate analysis

Chlorate was quantified using the peak of SIM m/z83. Sodium chlorate was used as the standard. A series of standards (ppt to ppm) were prepared and run in LCMS to standardize the calibration curve. MDL for chlorate is 7 ppb and LoQ is 10 ppb. Standards were run with every set of samples.

- **Ion Chromatography (IC)**

Anions (chloride, nitrate and sulphate) and cations (ammonium, calcium, magnesium, sodium, and potassium) in water samples were detected using IC (Dionex ICS-1100) (Table 3.2). A series of standards of anions and cations were run in the system. Retention time was monitored for the analysis of different anions and cations and the peak area thus obtained was compared with that of the standards.

Table 3.2 Details of IC used

	Anions	**Cations**
Column	AS 12A	CS 12A
Suppressor type	ASRS_4mm	CSRS_4mm
Suppressor current	15mA	59mA
Retention time	Chloride- 5.45 minutes Nitrate- 12.553 minutes Sulphate- 18.700 minutes	Sodium- 4.030 minutes Potassium- 5.667 minutes Magnesium- 8.767 minutes Calcium- 10.903 minutes

- **Other instruments used**

Other instruments used for the study are given in Table 3.3.

Table 3.3 General instruments used for the study

Instrument used	Model No.	Parameters analyzed/Purpose of use
pH meter	Systronics µ pH system 362	pH
Conductivity meter	Mettler Toledo, Five Easy Conductivity Meter	EC, TDS and salinity
Ultra Sonicator	Ultra Sonic Processor, Cole Parmer	Sonication of soil samples
Centrifuge	KEMI C8C Centrifuge	Centrifugation of soil samples
Cyclo mixer	REMI Equipments, CM 101 cyclomixer	Mixing of soil samples with milli Q water
Magnetic stirrer	Rotek RMS 5H	Fentons reaction for degradation study
Sono reactor	L3 ELAC Nautik ultrasound generator, T & C power conversion, Model AG 1006	Sono chemical degradation study
UV Photolysis reactor	Scientific Aids & Instruments Corporation (SAIC, Chennai)	UV degradation study
Double distillation apparatus	Lab-Sil double distillation apparatus	Distillation study

3.5 Water quality standards

The water quality results of the samples were compared with standard values as given in Table 3.4.

Table 3.4 Drinking water quality standards used for the analysis.

Parameters	Values (Ref.)
pH	**6.5-8.5** BIS (2012)
EC	**300**USPHS (1969)
TDS	**500**BIS (2012)
NH_4^+	**0.5** BIS (2012)
Ca^{2+}	**75**BIS (2012)
Mg^{2+}	**30**BIS (2012)
Na^+	**200**WHO (2011)
K^+	**-**
Cl^-	**250**BIS (2012)
SO_4^{2-}	**150**BIS (2012)
NO_3^-	**45**BIS (2012)
PO_4^{3-}	**0.1**BIS (2012)

All parameters except EC (µS/cm) are expressed in mg/L.

4.1 Introduction

The contamination of drinking water is increasing in Kerala. It is almost unfit for human consumption and domestic use as the water is contaminated with various types of pollutants (Bijoy, 2006; Thomas *et al.,* 2011). One of the major contaminants is perchlorate. Various studies have reported perchlorate contamination of surface water, ground water, tea, soft drinks, beverages, baby formulas etc. (Snyder *et al.,* 2006; Kannan *et al.,* 2009; Anupama *et al.,* 2012). The permissible limit of perchlorate in drinking water is 24.5 ppb above which can result in thyroid disorders (Wolff, 1998; Anderson *et al.,* 2006).

The reduction of perchlorate can result in chlorate production (USEPA, 2008a,b). It is also widely used in matches, laboratories, herbicides, pulp, paper and textile industry etc. Sodium hypochlorite and chlorine dioxide is used in water treatment, disinfection of microorganisms etc.. About 10% of the applied chlorine dioxide is converted to chlorate. In hypochlorite solutions, chlorate is generated spontaneously. Like perchlorate, chlorate is also highly soluble (USEPA, 2008a,b; AWWA, 2014). It is included in the third Unregulated Contaminant Monitoring Rule (UCMR3) (AWWA, 2014). In drinking water, the chronic dietary assessment for chlorate is estimated to be 0.69 mg/L (USEPA, 2008a) whereas the estimated Health Reference Level (HRL) for chlorate is 210 µg/L (AWWA, 2014). Above this, chlorate acts as a thyroid disruptor, resulting in thyroid gland follicular cell hypertrophy but not as strong as perchlorate (USEPA, 2008a). It can also impair the oxygen carrying capacity of blood and thereby ruptures red blood cell membranes in infants and fetuses (NAS, 1987).

Bottled water is one of India's fastest-growing industries and the rate (40-50% annually) is also increasing on a more frequent basis. South India is the biggest consumer of bottled water, representing more than 50% of the total market in India (The Economic Times, 2012). Urban communities of Kerala depend mainly on bottled water for drinking purposes. Around 8 lakh liters of potable water is sold in

Kerala per day and is increasing every year (IWR, 2013). The bottled water and other drinking water resources are getting contaminated with perchlorate and chlorate.

The literature indicated that a very few researches based on the perchlorate contamination in drinking water have been carried out in India (Kannan *et al.,* 2009; Isobe *et al.,* 2012; Anupama *et al.,* 2012;Anupama *et al.,* 2015). Widespread occurrence of perchlorate in public drinking, open well and surface water sources was reported along the South-West coast of Kerala (Anupama *et al.,* 2012). Hence the present study aimed to understand the perchlorate and chlorate contamination of well water, bore well water, tap water, bottled water and rain water in Kerala.

4.2 Objectives

1. To assess the extent of perchlorate contamination of drinking water in different districts of Kerala.
2. To analyze perchlorate contamination in bottled water.
3. To assess the perchlorate content in rain water.

4. 3 Study area and sample collection

Kerala is situated along the southwest coast of India. Drinking water samples were collected from water supplies of selected towns from all the fourteen districts of Kerala (Table 4.1). The 14 districts were classified into 3 regions- Southern region (Trivandrum, Kollam, Pathanamthitta, Alappuzha), Central region (Kottayam, Idukki, Thrissur, Ernakulam, Palakkad) and Northern region (Kozhikode, Malappuram, Kannur, Kasaragod, Wayanad) (Fig. 4.1).

Drinking water samples (well, bore well and tap) were collected during April-May 2014 (pre-monsoon); August-September 2014 (monsoon) and December 2014-January 2015 (post-monsoon). Water samples were filtered using 0.2µ nylon membrane filter paper and stored below 4˚C until the analysis was performed.

Table 4.1 Latitude and longitude of sample points for well, borewell and tap water

Longitude	Latitude	Place	District
76.51722°	9.227622°	Chettikulangara	Alapuzha
76.339194°	9.497216°	Alapuzha Town	
76.453158°	9.281894°	Harippad	
76.33671°	9.68436°	Cherthala	
76.62543°	9.22437°	Edappon	
76.611041°	9.318349°	Chengannur	
76.539908°	9.250661°	Mavelikkara	
76.515242°	9.184153°	Kayamkulam	
76.472714°	9.175826°	Pullukulangara	
76.981053°	8.483303°	Poojappura	Trivandrum
77.0537°	8.560449°	Vellanadu	
77.167931°	8.680173°	Bonacaud	
77.085226°	8.578646°	Aryanad	
76.965746°	8.481931°	Karamana	
76.936638°	8.525334°	Trivandrum	
76.978708°	8.400697°	Kovalam	
76.866331°	8.57133°	Kazhakkuttam	
77.008427°	8.453824°	Nemom	
76.9825°	8.469871°	Pappanamcode	
76.904744°	8.53364°	Akkulam	
77.085226°	8.503553°	Kattakada	
76.771032°	8.683372°	Kadaikkavur	
77.08712°	8.401947°	Neyyattinkara	
77.174398°	8.331876°	Kaliakkavila	
76.785987°	9.386271°	Ranni	Pathanamthitta
76.716732°	9.21672°	Thumpamon	
76.849807°	9.226813°	Konni	
76.574316°	9.383665°	Thiruvalla	
75.753761°	11.654469°	Kuttiady	Kozhikode
75.781446°	11.2596°	Kozhikode town	

76.535537°	9.054657°	Karunagappally	Kollam
76.552854°	8.923123°	Sakthikulangara	
76.77215°	9.001023°	Kottarakkara	
76.922289°	8.829389°	Kadaikkal	
76.614399°	8.893425°	Kollam town	
76.594347°	9.862814°	Koothattukulam	Ernakulam
76.479259°	10.180775°	Cheranallur	
76.667519°	8.814402°	Paravur	
76.27162°	10.074551°	Varapuzha	
76.49208°	9.873178°	Piravom	
76.583258°	9.967212°	Moovattupuzha	
76.338328°	9.953532°	Thrippunnithura	
76.572044°	9.559816°	Puthuppally	Kottayam
76.506739°	9.578275°	Karapuzha	
76.586302°	9.596223°	Manarcad	
76.682755°	9.714136°	Pala	
76.532866°	9.668091°	Athirampuzha	
76.505379°	9.685526°	Neendoor	
76.54062°	9.446654°	Changanassery	
76.521808°	9.592333°	Kottayam Town	
76.541074°	9.613356°	Kumaranalloor	
76.644073°	9.565848°	Pampady	
76.633157°	9.500383°	Karukachal	
76.454827°	9.82955°	Velloor	
76.263041°	10.24089°	Mala	Thrissur
76.209199°	10.345049°	Irinjalakkuda	
76.19567°	10.20977°	Kodungalloor	
76.220305°	10.396234°	Karuvannoor	
76.333505°	10.308409°	Chalakkudy	
76.270275°	10.4178°	Pudukkad	
76.172491°	11.659742°	Meenangadi	Wayanad

76.065809°	11.584157°	Kalpetta	
76.262493°	11.665992°	Bathery	
75.492705°	11.754555°	Thalassery	Kannur
75.370323°	11.874794°	Kannur Town	
76.654448°	10.787493°	Palakkad Town	Palakkad
76.544879°	10.642183°	Alathur	
76.490098°	10.635036°	Thennilapuram	
76.464675°	10.696849°	Pazhambalacode	
77.059443°	10.089115°	Munnar	Idukki
76.783248°	10.050188°	Neriyamangalam	
75.090173°	12.301096°	Kanhangad	Kasargod
76.119795°	11.120679°	Manjeri	Malappuram
76.194208°	10.980361°	Angadipuram	
75.921748°	10.91539°	Thiroor	

- **Bottled water sampling**

Bottled water of different brands (local and international) (n=31) were collected from different districts of Kerala. A few bottled water samples (n=5) were randomly collected from other states also (Maharashtra, Andhra Pradesh, Tamil Nadu and Karnataka). The samples were filtered using 0.2µ filter paper and stored in sterile polypropylene bottles, under 4˚C for the analysis.

- **Rain water sampling**

Samples were collected from selected regions during April-May, 2015. Samples were filtered using 0.2µ nylon membrane filter paper and stored under 4ºC for further analysis.

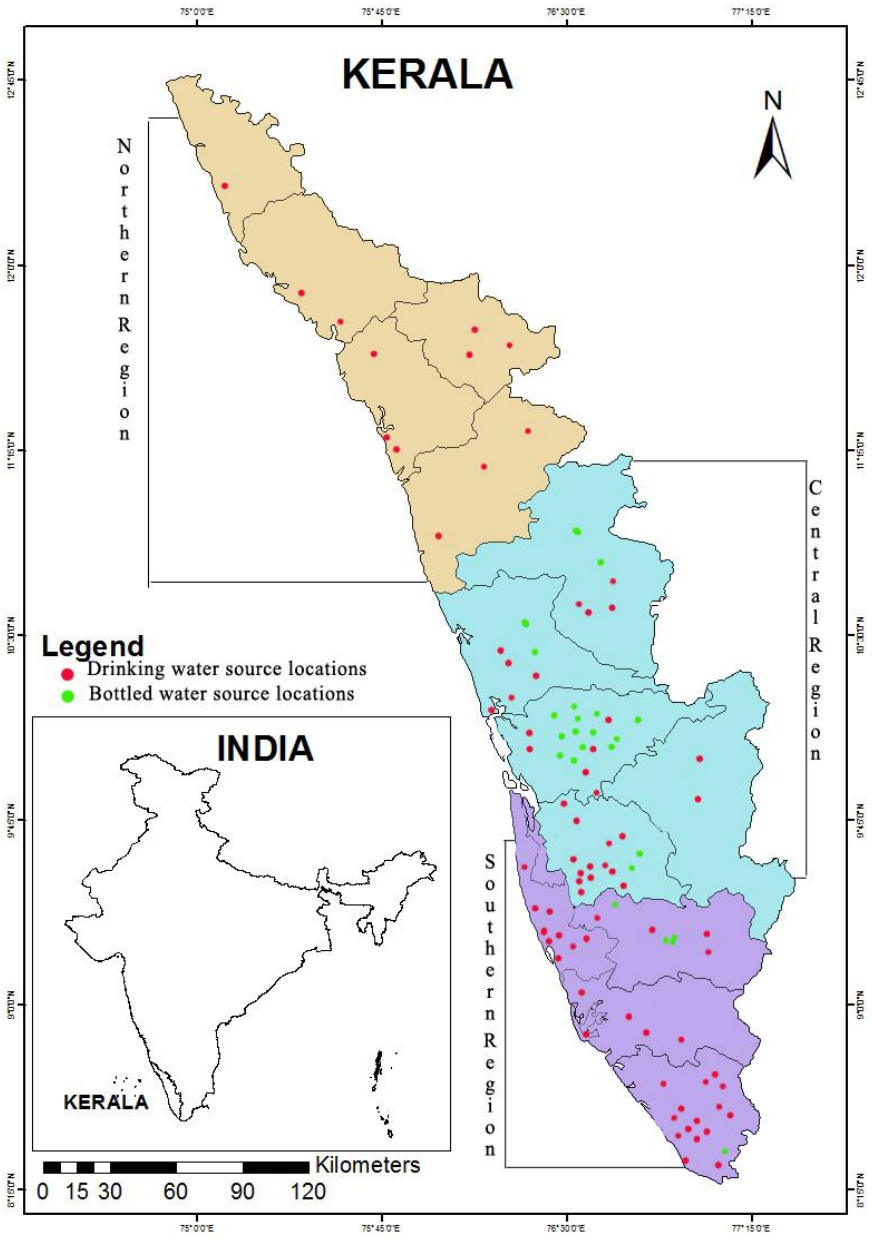


Fig. 4.1 Bottled water and other drinking water source locations

4.4 Results and discussion

Perchlorate contamination of drinking water from selected towns of Kerala

The perchlorate and chlorate levels in well, bore well and tap water during the different seasons collected were given in Table 4.2 to 4.12, as district wise data.

Set-I (Pre-monsoon)

Perchlorate was detected in well water samples collected from all districts during the pre-monsoon. Alapuzha district showed the maximum presence of perchlorate in well water. The concentration has exceeded the permissible limit of 24.5 ppb in all the districts except Kollam and Kannur (Table 4.2). However, the presence of perchlorate was noticed in the bore well samples of 3 districts only - Alapuzha, Ernakulam and Wayanad; in which Ernakulam (26.17 ppb) and Wayanad (156.31 ppb) exceeded the permissible limit (Table 4.3). Tap water samples from Thiruvananthapuram (38.32 ppb) and Ernakulam (91.18 ppb) showed the maximum perchlorate contamination (Table 4.4). Mean chlorate in well water samples during pre-monsoon was 111.96 ppb while in bore well and tap water it was 24.05 ppb and 309.96 ppb respectively. But the presence of chlorate in tap water exceeded the health reference level of 210 ppb (Table 4.2 to Table 4.4).

During pre-monsoon, the mean concentration of perchlorate in drinking water samples in Kerala was 78.45 ppb, where as chlorate was 247.19 ppb. Both the analytes exceeded the permissible limit (Table 4.5).

Table 4.2 Mean perchlorate in well water of different districts during pre-monsoon

Sl. No	District	No. of well water samples analyzed	No. of samples perchlorate detected	Mean (ppb) Perchlorate	No. of samples chlorate detected	Mean (ppb) Chlorate
1	Thiruvananthapuram	12	11	71.86*	7	365.05
2	Kollam	5	2	14.45	2	99.07
3	Pathanamthitta	5	3	178.93*	1	17.184
4	Alapuzha	8	6	1172.37*	5	289.95
5	Kottayam	12	8	30.69*	4	201.39
6	Idukki	2	2	102.19*	0	BDL
7	Ernakulam	8	6	40.48*	6	166.05
8	Thrissur	6	2	29.37*	1	15.07
9	Palakkad	4	3	60.09*	1	259.16
10	Malappuram	3	3	23.92	0	BDL
11	Kozhikode	2	2	39.09*	0	BDL
12	Wayanad	2	2	121.04*	0	BDL
13	Kannur	1	1	7.97	0	BDL
14	Kasaragod	1	1	254.14*	1	154.56

**Concentration exceeding maximum contaminant level of 24.5 ppb*

Table 4.3 Mean perchlorate in bore well water of different districts during pre-monsoon

Sl. No	District	No. of bore well water samples analyzed	No. of samples perchlorate detected	Mean (ppb) Perchlorate	No. of samples chlorate detected	Mean (ppb) Chlorate
1	Alapuzha	1	1	21.06	0	BDL
2	Ernakulam	1	1	26.17*	1	336.64
3	Malappuram	1	0	BDL	0	BDL
4	Wayanad	1	1	156.31*	0	BDL

Table 4.4 Mean perchlorate in tap water of different districts during pre-monsoon

Sl. No	District	No. of tap water samples analyzed	No. of samples perchlorate detected	Mean (ppb) Perchlorate	No. of samples chlorate detected	Mean (ppb) Chlorate
1	Thiruvananthapuram	3	3	38.32*	3	2772.99
2	Ernakulam	2	2	91.18*	1	1566.4

Table 4.5 Mean perchlorate in entire water of different districts during pre-monsoon

Sl. No	District	No. of water samples analyzed	No. of samples perchlorate detected	Mean (ppb) Perchlorate	No. of samples chlorate detected	Mean (ppb) Chlorate
1	Thiruvananthapuram	15	14	60.36*	7	1814.23
2	Kollam	5	2	5.78	2	99.07
3	Pathanamthitta	5	3	107.36*	1	17.184
4	Alapuzha	9	7	257.73*	5	463.92
5	Kottayam	12	8	20.46	4	201.39
6	Idukki	2	2	102.19*	0	BDL
7	Ernakulam	11	9	41.04*	6	436.17
8	Thrissur	6	2	9.79	1	15.07
9	Palakkad	4	3	45.07*	1	259.16
10	Malappuram	4	3	17.94	0	BDL
11	Kozhikode	2	2	31.71*	0	BDL
12	Wayanad	3	3	132.80*	0	BDL
13	Kannur	1	1	7.97	0	BDL
14	Kasaragod	1	1	258.14*	1	154.56

Set II (Monsoon)

Perchlorate in well water during monsoon was within the permissible limit. Moreover perchlorate was detected only from well water samples of Kottayam (0.47 ppb) and Idukki (5.82 ppb) (Table 4.6). Bore well sample from Thiruvananthapuram (49.72 ppb) and Alapuzha (7.9 ppb) showed the presence of perchlorate (Table 4.7). None of the tap water samples contained perchlorate (Table 4.8). Chlorate was noticed only in bore well samples from Thiruvananthapuram and Ernakulam (Table 4.7 and Table 4.8). The monsoon water samples were within the safe limit for both perchlorate and chlorate (Table 4.9).

Table 4.6 Mean perchlorate in well water of different districts during monsoon

Sl. No	District	No. of well water samples analyzed	No. of samples perchlorate detected	Mean (ppb) Perchlorate	No. of samples chlorate detected	Mean (ppb) Chlorate
1	Thiruvananthapuram	13	0	BDL	0	BDL
2	Kollam	5	0	BDL	0	BDL
3	Pathanamthitta	5	0	BDL	0	BDL
4	Alapuzha	9	0	BDL	0	BDL
5	Kottayam	13	1	0.47	0	BDL
6	Idukki	3	1	5.82	0	BDL
7	Ernakulam	8	0	BDL	0	BDL
8	Thrissur	6	0	BDL	0	BDL
9	Palakkad	4	0	BDL	0	BDL
10	Malappuram	4	0	BDL	0	BDL
11	Kozhikode	2	0	BDL	0	BDL
12	Wayanad	3	0	BDL	0	BDL
13	Kannur	1	0	BDL	0	BDL
14	Kasaragod	1	0	BDL	0	BDL

**Concentration exceeding maximum contaminant level of 24.5ppb*

Table 4.7 Mean perchlorate in bore well water of different districts during monsoon

Sl. No	District	No. of bore well water samples analyzed	No. of samples perchlorate detected	Mean (ppb) Perchlorate	No. of samples chlorate detected	Mean (ppb) Chlorate
1	Thiruvananthapuram	1	1	49.72*	1	894.48
2	Alapuzha	1	1	7.9	0	BDL
3	Ernakulam	1	0	BDL	0	BDL
4	Malappuram	1	0	BDL	0	BDL
5	Wayanad	1	0	BDL	0	BDL

Table 4.8 Mean perchlorate in tap water of different districts during monsoon

Sl. No	District	No. of tap water samples analyzed	No. of samples perchlorate detected	Mean (ppb) Perchlorate	No. of samples chlorate detected	Mean (ppb) Chlorate
1	Thiruvananthapuram	3	0	BDL	0	BDL
2	Ernakulam	2	0	BDL	1	63.76

Table 4.9 Mean perchlorate in entire water of different districts during monsoon

Sl. No	District	No. of water samples analyzed	No. of samples perchlorate detected	Mean (ppb) Perchlorate	No. of samples chlorate detected	Mean (ppb) Chlorate
1	Thiruvananthapuram	17	1	2.92	1	52.62
2	Kollam	5	0	BDL	0	BDL
3	Pathanamthitta	5	0	BDL	0	BDL
4	Alapuzha	10	1	0.79	0	BDL
5	Kottayam	13	1	0.47	0	BDL
6	Idukki	3	1	5.82	0	BDL
7	Ernakulam	11	0	BDL	1	11.59
8	Thrissur	6	0	BDL	0	BDL
9	Palakkad	0	0	0	0	0
10	Malappuram	4	0	BDL	0	BDL
11	Kozhikode	2	0	BDL	0	BDL
12	Wayanad	3	0	BDL	0	BDL
13	Kannur	1	0	BDL	0	BDL
14	Kasaragod	1	0	BDL	0	BDL

Set III (Post-monsoon)

The post-monsoon well water samples collected from Kollam, Alapuzha, Kozhikode and Kasaragod had perchlorate beyond the reference dose whereas samples from Pathanamthitta, Thrissur, Palakkad and Wayanad showed below detectable limits (BDL) values. The mean perchlorate in well water was 22.68 ppb (Table 4.10). None of the bore well samples were contaminated with perchlorate. The tap water from Ernakulam district showed the presence of perchlorate (19.18 ppb) whereas the other samples were at BDL level (Table 4.11). Chlorate was detected only from well water (16.19 ppb) and was within the limit (Table 4.10). The mean perchlorate content of drinking water samples were under safe limit except the samples taken from Kollam

(27.45 ppb), Kozhikode (61.68 ppb) and Kasaragod (95.72 ppb) (Table 4.12). Chlorate was traced out within the limits only.

Table 4.10 Mean perchlorate in well water of different districts during post-monsoon

Sl. No	District	No. of well water samples analyzed	No. of samples perchlorate detected	Mean (ppb) Perchlorate	No. of samples chlorate detected	Mean (ppb) chlorate
1	Thiruvananthapuram	13	1	1.98	0	BDL
2	Kollam	5	1	27.45*	1	33.71
3	Pathanamthitta	5	5	BDL	0	BDL
4	Alapuzha	8	1	27.34*	2	58.84
5	Kottayam	13	3	19.19	3	96.53
6	Idukki	2	1	19.3	0	BDL
7	Ernakulam	8	2	21.84	0	BDL
8	Thrissur	6	0	BDL	0	BDL
9	Palakkad	4	0	BDL	0	BDL
10	Malappuram	5	1	5.68	1	9.50
11	Kozhikode	3	2	64.68*	1	28.08
12	Wayanad	2	0	BDL	0	BDL
13	Kannur	2	1	34.34*	0	BDL
14	Kasaragod	1	1	95.72*	0	BDL

**Concentration exceeding maximum contaminant level of 24.5ppb*

Table 4.11 Mean perchlorate in tap water of different districts during post-monsoon

Sl. No	District	No. of tap water samples analyzed	No. of samples perchlorate detected	Mean (ppb) Perchlorate	No. of samples chlorate detected	Mean (ppb) chlorate
1	Thiruvananthapuram	3	0	BDL	0	BDL
2	Ernakulam	2	1	19.18	0	BDL
3	Malappuram	2	0	BDL	0	BDL
4	Kozhikode	1	0	BDL	0	BDL
5	Kannur	1	0	BDL	0	BDL

Table 4.12 Mean perchlorate in entire water samples of different districts during post-monsoon

Sl. No	District	No. of water samples analyzed	No. of samples perchlorate detected	Mean (ppb) Perchlorate	No. of samples chlorate detected	Mean (ppb) Chlorate
1	Thiruvananthapuram	17	1	1.52	0	BDL
2	Kollam	5	1	27.45*	1	33.71
3	Pathanamthitta	5	0	BDL	0	BDL
4	Alapuzha	9	8	24.30	2	52.30
5	Kottayam	13	3	19.19	3	96.53
6	Idukki	2	1	19.3	0	BDL
7	Ernakulam	11	3	19.37	0	BDL
8	Thrissur	6	0	BDL	0	BDL
9	Palakkad	4	0	BDL	0	BDL
10	Malappuram	8	1	3.55	1	5.94
11	Kozhikode	4	2	64.68*	1	21.06
12	Wayanad	3	0	BDL	0	BDL
13	Kannur	3	1	22.89	0	BDL
14	Kasaragod	1	1	95.72*	0	BDL

Region wise data classification

The results of drinking water samples taken from well, bore well and tap water were discussed based on north, south and central regions of Kerala and drinking water type. During pre-monsoon, well water samples showed far exceeding levels of perchlorate in all the regions. Bore well water of northern region had more perchlorate (31.26 ppb) and the tap water in all regions was under safe level. Chlorate was more in well water of south and central regions. In tap water, chlorate was BDL at northern region whereas in south and central region, the concentration was exceeding the limit. In case of monsoon, all the regions were having safe amount of perchlorate. Only chlorate exceeded in bore well water samples of southern region.

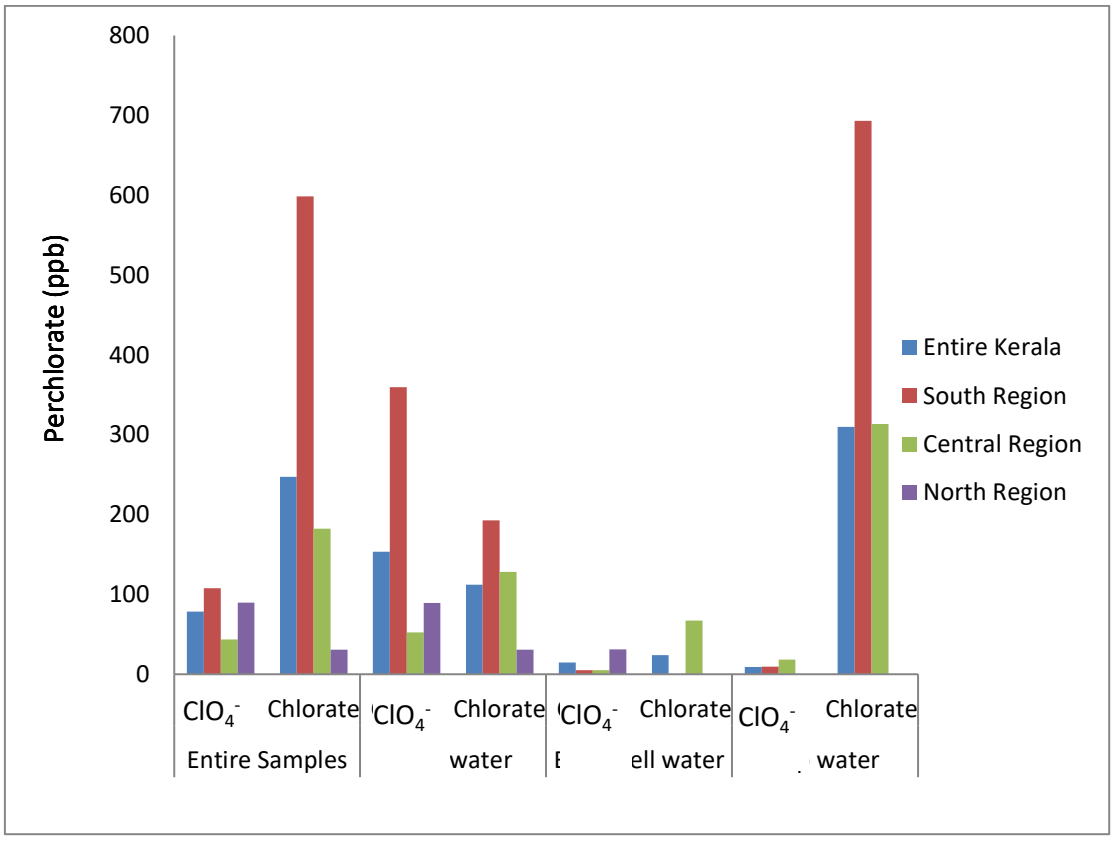


Fig. 4.2 Mean perchlorate and chlorate during pre-monsoon

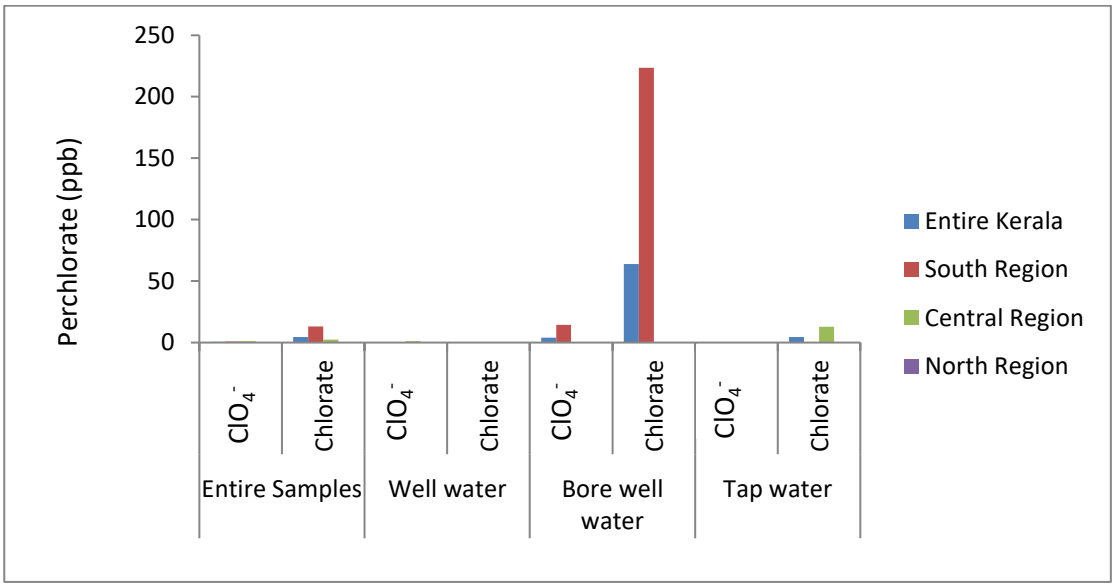


Fig. 4.3 Mean perchlorate and chlorate during monsoon

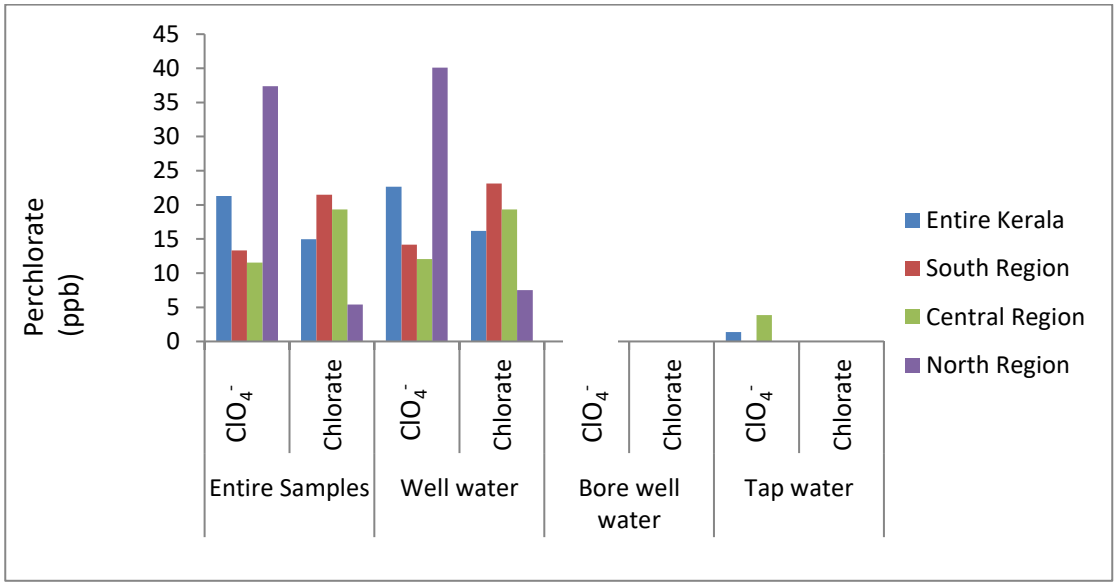


Fig. 4.4 Mean perchlorate and chlorate during post-monsoon

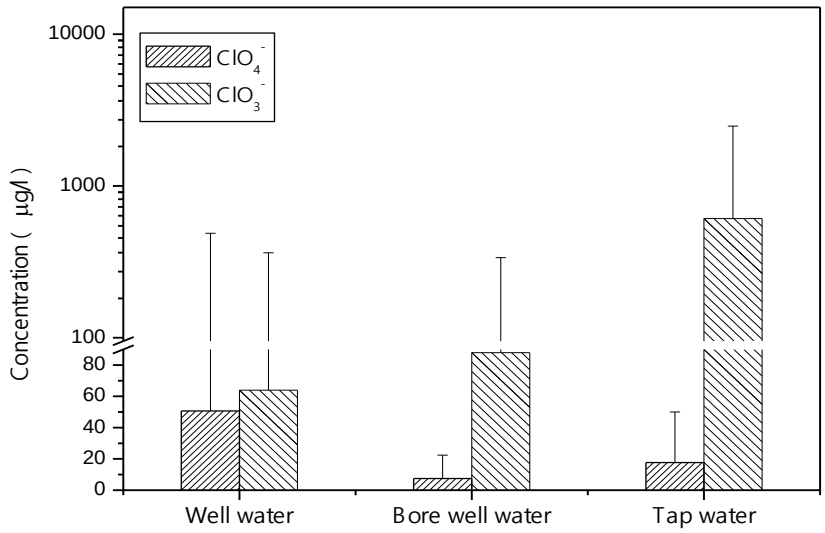
Results of water samples taken during post-monsoon showed more perchlorate content in Northern region (40.08 ppb). All the other water sources in all regions had perchlorate and chlorate content within the allowable limits.

Mean perchlorate content of the drinking water samples ranged from 0.71 ppb (monsoon) to 78.45 ppb (Pre-monsoon) with a mean value of 33.48 ppb. Maximum perchlorate was detected in pre-monsoon samples. Chlorate value ranged from 4.59 ppb (monsoon) to 247.19 ppb (pre-monsoon) with a mean of 58.04 ppb (Table 4.13).

Table 4.13 Mean perchlorate (ppb) and chlorate (ppb) (Set I, Set II and Set III) in drinking water

	Entire Drinking water Samples		**Water type**					
			Well water		**Bore well water**		**Tap water**	
	ClO_4^-	**ClO_3^-**	**ClO_4^-**	**ClO_3^-**	**ClO_4^-**	**ClO_3^-**	**ClO_4^-**	**ClO_3^-**
Kerala	33.48	58.04	58.82	42.72	6.22	29.30	3.54	104.84
South Region	40.69	211.07	124.53	71.98	6.56	74.54	3.19	231.08
Central Region	18.85	67.99	21.96	49.21	1.74	22.44	7.36	108.68
North Region	42.36	12.10	43.10	12.81	10.42	BDL	BDL	BDL

Perchlorate and chlorate concentrations in drinking water samples collected from the regions of entire Kerala were depicted using an error graph (Fig. 4.5). Perchlorate followed the order well water>tap water>bore well water and chlorate followed the order of tap water>bore well water and well water.



The data after the break are given in log10 scale

Fig. 4.5 Perchlorate and chlorate in different water samples

Region wise data of Kerala (Table 4.13) indicated high mean perchlorate content was from northern region (42.36 ppb) where as a minimum was traced at central regions (18.50 ppb). Southern part showed a mean perchlorate and chlorate content of 40.69

ppb and 211.07 ppb respectively. Chlorate was found to be maximum at the south and minimum at the northern parts (12.10 ppb).

The results were also compared based on the types of drinking water such as well, bore well and tap water (Table 4.13). The mean perchlorate and chlorate content in well water samples from the entire Kerala was 58.82 ppb and 42.72 ppb respectively and it varied from Southern (124.53 ppb and 71.98 ppb) to Central (21.96 ppb and 49.21 ppb) and Northern regions (43.10 ppb and 12.81 ppb) (Table 4.13).

In the case of bore well water, mean perchlorate and chlorate was 6.22 ppb and 29.30 ppb. Perchlorate content was maximum at northern region (10.44 ppb) where as with chlorate in the southern region. Minimum mean perchlorate content was noticed at central region (1.74 ppb) where as the chlorate content was BDL at northern region. Tap water was also found to be contaminated with perchlorate and chlorate (Table 4.13). The mean concentration of perchlorate and chlorate in tap water in Kerala was 3.54 ppb and 104.84 ppb respectively. Central region had a high mean perchlorate content (7.36 ppb) when compared with the other regions where as chlorate was high at southern region (231.08 ppb). Perchlorate and chlorate in tap water from northern region was found to be less than the detectable limit.

Not only the perchlorate and chlorate varied with respect to regions and types of drinking water but also with changes in season. The minimum perchlorate content during monsooncould be owed to dilution during rainfall. High concentration was seen in pre-monsoon. This may be due to the lack of rainfall and slow flow of ground water. Variation of perchlorate in different regions owed to the quantity used as well. Fireworks display might also be a reason for more perchlorate during pre-monsoon because April-May is the festival season in Kerala when huge firework displays are conducted. The amount of production of fireworks is uncertain but it may also result in the perchlorate contamination in drinking water. Uncertainty is also there regarding other sources relating perchlorate. Chlorate contamination may either be from perchlorate disintegration or from water treatment processes where sodium hypochlorate disinfection is practiced (The Hindu, 2008). The role of natural formation as a source of perchlorate in the study areas are also to be studied (Rajagopalan *et al.,* 2006; Anupama *et al.,* 2012).

Risk assessment

The recommended health protective dose of perchlorate is 0.0007 mg/kg body weight/day (0.7 µg/kg body weight/day) (USEPA, 2008b; Groef *et al.,* 2006) which is equivalent to 24.5 ppb in drinking water. Mean daily perchlorate intake was calculated with respect to both region wise and sample type. The calculation considered the intake of drinking water as 2L and the mean body weight of a healthy adult in Kerala as 60 kg (Shome *et al.,* 2014). The results were given in the Table 4.14. The whole water samples showed a higher risk value (1.12 µg/kg body weight/day) than the safe limit of 0.7 µg/kg body weight/day. High risk was observed for northern region followed by southern region where as central region was under safe limit. Its concentration in tap water and bore well water was also within the safe limit but in the well water (0.73 ppb to 4.15 ppb) it was higher than the safe limit.

Table 4.14 Mean perchlorate intakes from different sources in different regions

Category	Set 1		Set 2		Set 3		Entire Set (1+2+3)	
	ClO_4^- (ppb)	Intake/kg/day	ClO_4^- (ppb)	Intake/kg/day	ClO_4^- (ppb)	Intake/kg/day	ClO_4^- (ppb)	Intake/kg/day
Entire Kerala (Full samples)	78.45	**2.615***	0.71	0.02	21.28	**0.71***	33.48	**1.12***
South Region (Full samples)	107.81	**3.59***	0.93	0.03	13.32	0.44	40.69	**1.36***
Central Region (Full samples)	43.71	**1.457***	1.26	0.04	11.57	0.39	18.85	0.63
North Region (Full samples)	89.71	**2.99***	BDL	0	37.37	**1.25***	42.36	**1.41***
Entire Kerala well	153.33	**5.111***	0.45	0.01	22.68	**0.76***	58.82	**1.96***
South Region well	359.4	**11.98***	BDL	0	14.19	0.47	124.53	**4.15***
Central Region well	52.56	**1.752***	1.26	0.04	12.07	0.40	21.96	**0.73***
North Region well	89.23	**2.97***	BDL	0	40.08	**1.34***	43.1	**1.44***
Entire Kerala tap	9.25	0.31	BDL	0	1.37	0.05	3.54	0.12
South Region tap	9.58	0.32	BDL	0	BDL	0	3.19	0.11
Central Region tap	18.24	0.608	BDL	0	3.84	0.13	7.36	0.25
North Region tap	BDL	0	BDL	0	BDL	0	BDL	0
Entire Kerala borewell	14.54	0.48	4.12	**0.14***	BDL	0	6.22	0.21
South Region borewell	5.265	0.18	14.41	**0.48***	BDL	0	6.56	0.22
Central Region borewell	5.23	0.17	BDL	0	BDL	0	1.74	0.06
North Region borewell	31.26	**1.04***	BDL	0	BDL	0	10.42	0.35

**- Mean perchlorate intake higher than the recommended dose of 0.7 ppb*

Perchlorate contamination of bottled water

Among the 36 brands of bottled water analyzed, 20 samples were traced with perchlorate (Fig. 4.6) and 32 samples with chlorate contamination (Table 4.15). Mean perchlorate content in bottled water was 51.77±178.28 ppb where as the content of chlorate was 3281.84±7546.82 ppb. The observed perchlorate content in 9 samples was higher than the health reference for drinking water given by USEPA (24.5 ppb). 21 samples exceeded the health reference level for chlorate. More than 70% of the samples from Ernakulam district showed perchlorate contamination. Samples taken from Kottayam district where there is no major industrial sources had perchlorate within below detectable limit (<6ppb).

Table 4.15 Mean value of perchlorate and chlorate in different bottled water samples

Sample No.	No. of samples analyzed	No. of samples perchlorate identified	Perchlorate Mean (ppb)	No. of samples chlorate identified	Chlorate Mean(ppb)
BW1	8	5	1067.89*	8	7328.89
BW2	6	4	162.74*	6	1821.96
BW3	5	2	19.77	2	101.2
BW4	1	0	BDL	1	1304.64
BW5	6	0	BDL	1	399.68
BW6	1	1	90.34*	1	3014.24
BW7	1	1	42.65*	1	488.32
BW8	1	1	94.02*	1	40705.84
BW9	1	1	126.17*	1	20500.16
BW10	1	0	BDL	1	388.64
BW11	1	0	BDL	1	1942.56
BW12	1	0	BDL	1	75.92
BW13	2	0	BDL	1	120.8
BW14	1	0	BDL	1	10912.24

BW15	1	0	BDL	1	149.28
BW16	2	2	17.14	1	487.36
BW17	2	1	10.26	1	1007.76
BW18	3	3	44.63*	2	427.92
BW19	2	0	BDL	2	5644.4
BW20	2	1	15.97	2	1090.08
BW21	1	0	BDL	0	BDL
BW22	1	0	BDL	1	345.04
BW23	1	0	BDL	0	BDL
BW24	1	1	40.38*	1	462.96
BW25	1	1	24.12	1	108.48
BW26	1	0	BDL	1	1435.12
BW27	1	1	19.05	1	3651.68
BW28	2	1	16.05	2	2051.6
BW29	2	2	13.12	2	7129.84
BW30	1	1	9.51	1	521.92
BW31	1	1	9.78	0	BDL
BW32	1	0	BDL	1	434.4
BW33	1	1	32.2*	0	BDL
BW34	2	0	BDL	2	1711.48
BW35	1	1	7.91	1	430.88
BW36	2	0	BDL	2	1950.88
		Total Mean	**51.77±178.28**		**3281.84±7546.82**

**Concentration exceeding maximum contaminant level of 24.5ppb*

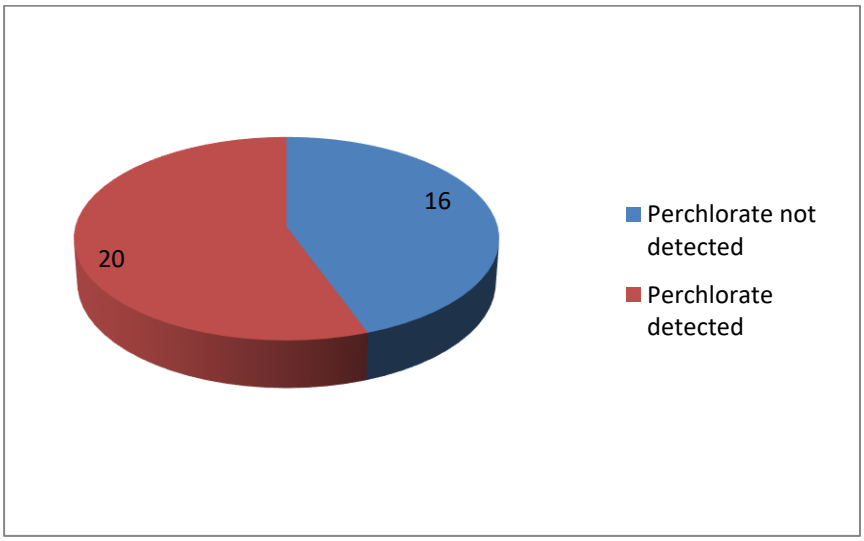


Fig. 4.6 Perchlorate detected and undetected bottled water samples

Perchlorate contamination was reported from ground water and surface water collected from Ernakulam district, near to APEP (Anupama *et al.,* 2012). The source of surface water for manufacturing bottled water in Ernakulam district was the Periyar River, and was the main reason behind the widespread perchlorate contamination of bottled water from the region. The sample contaminated with perchlorate obtained from Trivandrum district was manufactured from Thumba nearby TERLS. Veli Lake was the water source for manufacturing, which was reported to be contaminated with perchlorate (Anupama *et al.,* 2012). The contamination at other districts could be owed to the fire work manufacturing units as most of the districts in Kerala have licensed and unlicensed small-scale and large-scale such units. It was interesting to note that out of 5 outside state samples analyzed, only one (from Mumbai) had perchlorate (12.06 ppb) but within the safe limit whereas the other 4 samples did not showed even the presence of perchlorate (Fig. 4.7). This showed that there is either uncontrolled use and mishandling of the chemical or lacking of advanced systems for perchlorate removal in the study area. Thus the perchlorate contamination of bottled water was found to be dependent on the source of contamination.

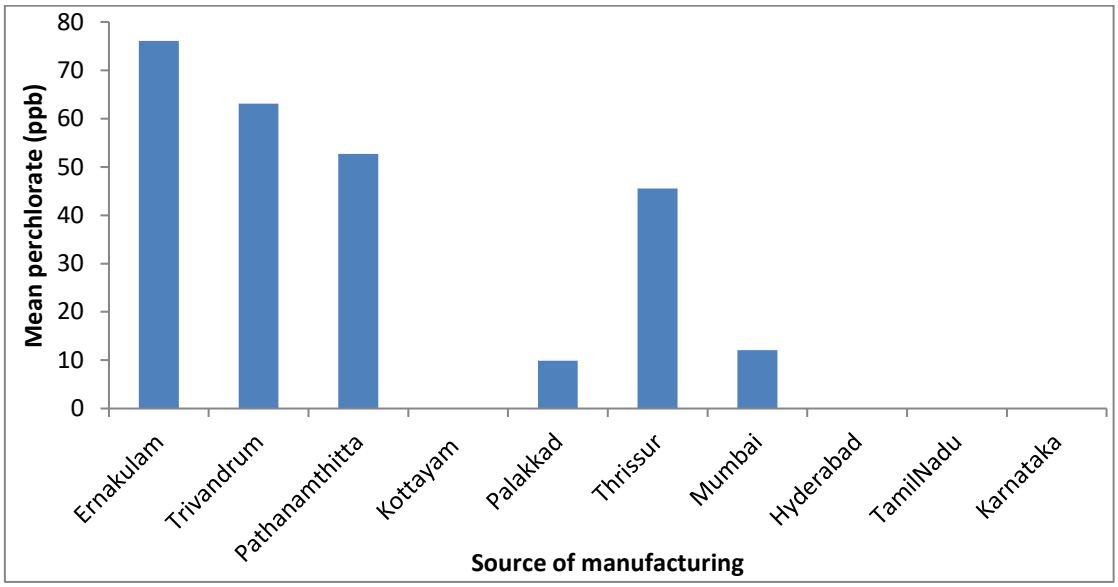


Fig. 4.7 Mean perchlorate in different bottled water sources

Chlorate contamination was noticed in almost all samples, irrespective of their source of manufacturing. Both within and outside state samples were contaminated with chlorate and was found to be source independent. This might be owed to the disinfection processes using hypochlorites. In Kerala, sodium hypochlorate as such was used in treating large quantities of drinking water supplies (The Hindu, 2008).

Almost all the samples underwent treatment processes like reverse osmosis, microfiltration, UV irradiation etc. before packaging and the results suggest that these processes are inefficient in removing perchlorate and chlorate (Table 4.16). Various studies reported the possibilities of applying technologies like physical separation (precipitation, anion exchange or membrane filtration, reverse osmosis and electro dialysis), chemical and electrochemical reduction, and biological or biochemical reduction (Urbansky, 1998; Srinivasan and Viraraghavan, 2009) for removal of perchlorate. However it is noticed that typical water treatment technologies cannot remove perchlorate (Logan, 1998).

Table 4.16 Bottled water source and the water treatment processes

Sample No.	No. of samples analysed	Source	Water treatments underwent
BW1	8	Kolenchery, Cochin, Kerala	UV and Ozone treatment
BW2	6	Thiruvalla, Pathanamthitta	Microfiltration, sand filtration, UV treatment, reverse osmosis, ozonisation
BW3	5	Palakkad, Kerala	Sand filtration, activated carbon filtration, UV treatment, reverse osmosis, ozonation
BW4	1	Kothamangalam, Kerala	Reverse osmosis, ozonation
BW5	6	Bangalore, Karnataka	UV treatment, reverse osmosis, microfiltration
BW6	1	Thiruvalla,Pathanamthitta	UV treatment, ozonation
BW7	1	Mala, Thrissur	UV treatment, ozonation
BW8	1	Chalakudy, Thrissur	UV treatment, microfiltration, ozonation
BW9	1	Thumba, Thiruvananthapuram	UV treatment, reverse osmosis, ozonation
BW10	1	Kothamangalam, Ernakulam	UV treatment, reverse osmosis, ozonation
BW11	1	Erumathala, Ernakulam	UV treatment, ozonation
BW12	1	Kanchipuram, Tamilnadu	UV treatment, reverse osmosis, ozonation, ultra filtration
BW13	2	Mallapally, Pathanamthitta	UV treatment, reverse osmosis, ozonation, micro filtration
BW14	1	Thiruvalla, Kerala	UV treatment, reverse osmosis, ozonation
BW15	1	Kavuri hills, Hyderabad	UV treatment, reverse osmosis, ozonation
BW16	2	Chowara, Ernakulam	UV treatment, microfiltration
BW17	2	Thiruvalla, Pathanamthitta	UV treatment, ozonation
BW18	2	Ernakulam	UV treatment, reverse osmosis, ozonation
BW19	2	Thrissur	UV treatment, reverse osmosis, ozonation
BW20	2	Marampilly, Ernakulam	Pressure sand, activated carbon and lead lag activated carbon filter, UV treatment, reverse osmosis, ozonation
BW21	1	Thiruvananthapuram	UV treatment, reverse osmosis, ozonation
BW22	1	Kinassery, Palakkad	UV treatment, reverse osmosis, ozonation
BW23	1	Mumbai	UV treatment, reverse osmosis, ozonation
BW24	1	Mullackal, Aluva	Sand, carbon and microfiltration, UV treatment, reverse osmosis, ozonation
BW25	1	Andheri, Mumbai	Micro filtration, ozonation
BW26	1	Angamaly, Kochi	UV treatment, reverse osmosis, ozonation, microfiltration
BW27	1	Perumbavoor, Ernakulam	UV treatment, reverse osmosis, ozonation
BW28	2	Perumbavoor, Ernakulam	UV treatment, reverse osmosis, ozonation,

			microfiltration
BW29	2	Erumathala, Aluva	UV treatment, ozonation
BW30	1	Nedumbassery, Ernakulam	UV treatment, reverse osmosis, ozonation, microfiltration
BW31	1	Perumbavoor, Ernakulam	UV treatment, reverse osmosis, ozonation
BW32	1	Thalayolaparambu, Kottayam	UV treatment, reverse osmosis, ozonation
BW33	1	Aluva, Ernakulam	UV treatment, reverse osmosis, ozonation, microfiltration
BW34	2	Villoonni, Kottayam	UV treatment, silver ozonation
BW35	1	Mullackal, Aluva	Chlorination, sand carbon and micro filtration, UV treatment, reverse osmosis, ozonation
BW36	2	Kuruppampady, Ernakulam	UV treatment, reverse osmosis, ozonation

Various studies in different countries reported the contamination of bottled water with perchlorate and chlorate (Table 4.17). Global perchlorate values ranged from <0.02 to 2.01 ppb and chlorate values ranged from 5.80 to 343.0 ppb, China being the topmost in both perchlorate and chlorate contamination. Perchlorate detected from bottled water in Kerala was much higher than the values reported from other countries. But the measured perchlorate from bottled water in the present study was comparable to the tap water (38.40 ppb), groundwater (34.10 ppb) and surface water (17.0 ppb) with the reported values in Kerala (Anupama *et al.,* 2012).

Table 4.17 Comparison of perchlorate in bottled water with reported studies

Sl. No	Country	Perchlorate (ppb)	Chlorate (ppb)	Reference
1	US	0.41	5.80	Snyder *et al.,*, 2005
2	Japan	0.53	14.0	Asami *et al.,*, 2009
3	China	2.01	343.0	Wu *et al.,*, 2010
4	South Korea	0.07	-	Her *et al.,*, 2011
5	Italy	0.07	-	Iannece *et al.,*, 2013
6	India (7 states excluding Kerala)	<0.02 (Quantitation limit)	-	Kannan *et al.,*, 2009
7	Canada	-	6.90	Dabeka *et al.,*, 2002

Perchlorate contamination of rain water

Out of the 15 rain water samples analyzed, two samples showed the presence of perchlorate with the values 6.90 ppb and 12.80 ppb (Table 4.18). Chlorate was not present in any of the samples. This might be the effect of firework residuals in the air, as the samples were collected during summer, the festival time of Kerala when lots of fireworks are displayed. Earlier studies also showed the presence of perchlorate in rain water samples from other parts of India (<0.02 ppb) but it was very low when compared with the mean perchlorate in rain water samples of the present study (9.85 ppb) (Kannan *et al.*, 2009).

Table 4.18 Perchlorate in rain water samples

Sl. No	Site name	Perchlorate (ppb)
1	MGU-1	BDL
2	MGU-2	BDL
3	MGU-3	BDL
4	Kakkanad-1	BDL
5	Kakkanad-2	6.90
6	Piravom-1	12.80
7	Piravom-2	BDL
8	Thumpamon-1	BDL
9	Thumpamon-2	BDL
10	Thumpamon-3	BDL
11	Eloor	BDL
12	Kanjikode	BDL
13	Erumeli	BDL
14	Marad	BDL
15	Adimali	BDL

4.5 Conclusion

A high perchlorate contamination of the drinking water sources was noticed which urges the need for an immediate action in this regard. All the drinking water sources (well, bore-well and tap) of South, Central and North regions of Kerala which were found to be contaminated with perchlorate and chlorate showed values above the reference levels. Perchlorate contamination of bottled water showed that water was neither treated properly nor the treatment was effective before they were packed and sold. The results clearly indicated the role of perchlorate production, its usage in industries and also in fireworks manufacturing and displaying processes leading to the contamination of water resources. Even rain water was found to be contaminated with perchlorate. The perchlorate and chlorate in exceeding amounts than the health reference levels points to a probability of increasing thyroid disorders in future, if chronic exposure to such levels occurred.

5.1 Introduction

Perchlorate is a colorless, odorless chemical and its salts are highly soluble and mobile in water (Motzer, 2001; ITRC, 2005; ATSDR, 2008; Sanchez *et al.*, 2005a,b). The perchlorate anion (ClO_4^-) in water remains highly stable, unreactive and may take decades to degrade (Siglin *et al.*, 2000; Srinivasan and Viraraghavan, 2009; Motzer, 2001). Perchlorate contamination was noticed in rain water, raw and treated drinking water, groundwater, bottled water, open well and surface water resources from different parts of the world (Srinivasan and Viraraghavan, 2009; Tikkanen, 2006; Stetson *et al.*, 2006; Kannan *et al.*, 2009; McLaughlin *et al.*, 2011; Anupama *et al.*, 2012, Snyder *et al.*, 2005; Crawford-Brown *et al.*, 2006; Rajagopalan *et al.*, 2006; Stetson *et al.*, 2006; Kimbrough and Parekh, 2007; Kosaka *et al.*, 2007; Quinones *et al.*, 2007; Wagner *et al.*, 2007; Sijimol *et al.*, 2017). The present study assessed the temporal variation of perchlorate around rocket propellant manufacturing and testing facilities and selected firework manufacturing sites in Kerala.

5.2 Objectives

1. To assess the seasonal variation of perchlorate around perchlorate manufacturing and handling industries and firework manufacturing units.
2. To find the correlation of perchlorate with other water quality parameters.

5.3 Materials and methods

Five regions were selected for studying the seasonal variation of perchlorate contamination in drinking water (Fig. 5.1). The geographical locations of samples were given in Table 5.1 to 5.5. Drinking water samples were collected before the monsoon (pre-monsoon), monsoon and after the monsoon (post-monsoon), 2014. Samples were collected from different directions within an area of 500 sq. mtrs. Water samples collected were filtered using 0.2µ nylon membrane filter paper and stored under 4ºC for further analysis.

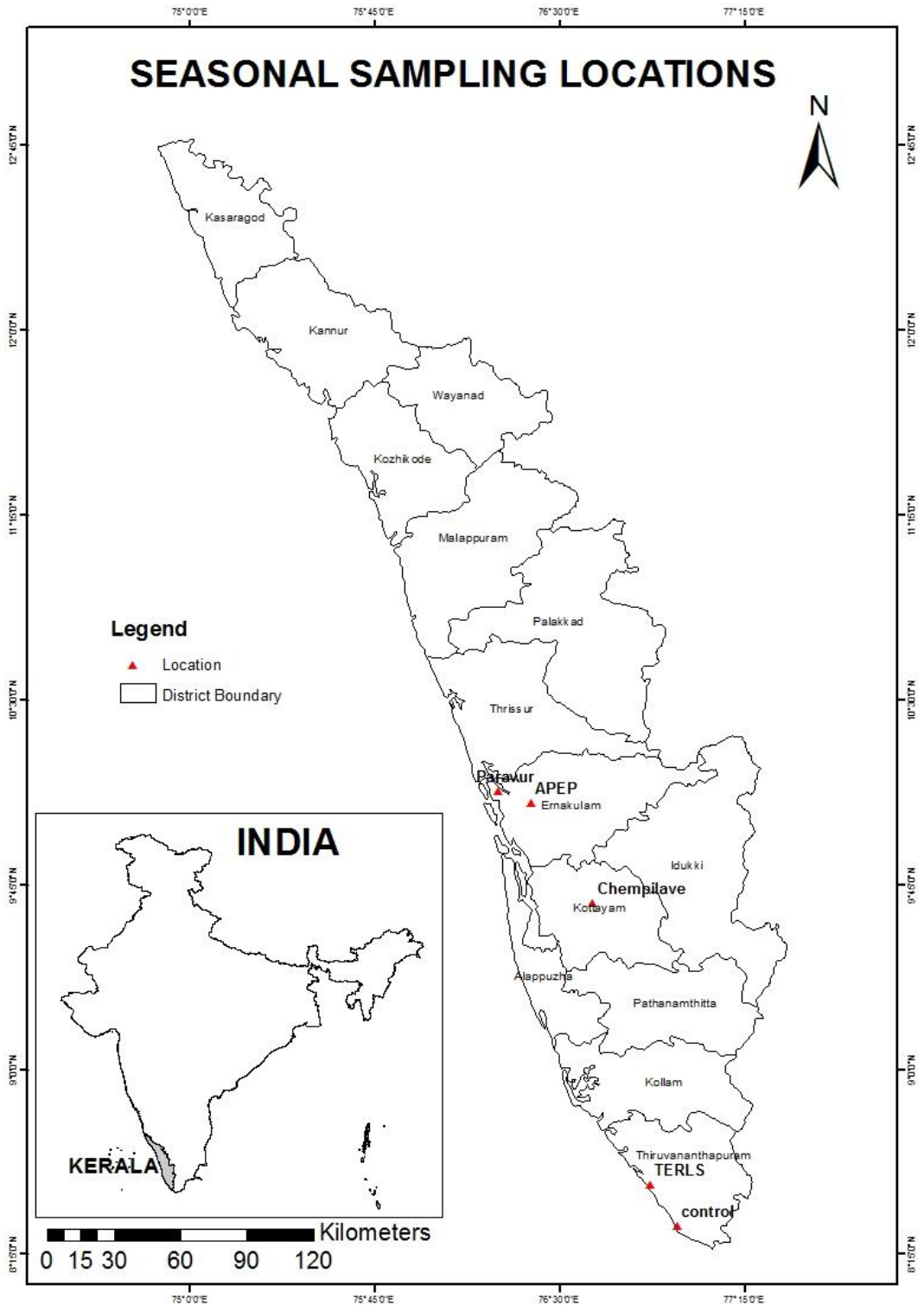


Fig. 5.1 Seasonal sample source locations

a. Site-1Ammonium Perchlorate Experimental Plant (APEP), Aluva, Ernakulam

Table 5.1 Latitude and longitude of sample locations in Site-1

Sl.No	Latitude	Longitude	Type of water sample
1	10.083447	76.383494	Well
2	10.083437	76.383497	Well
3	10.083474	76.383565	Well
4	10.083461	76.383541	Well
5	10.083484	76.383516	Well
6	10.083434	76.383481	Well
7	-	-	Tap

b. Site-2 Thumba Equatorial Rocket Launching Station (TERLS), Thumba, Trivandrum

Table 5.2 Latitude and longitude of sample locations in Site-2

Sl.No	Latitude	Longitude	Type of water sample
1	8.533502	76.866771	Well
2	8.516785	76.866825	Well
3	8.516742	76.866855	Well
4	-	-	Tap
5	8.51682	76.866922	Well
6	8.516809	76.866931	Well
7	8.516793	76.866811	Well

c. Site- 3 Fireworks manufacturing site, Paravur, Ernakulam

Table 5.3 Latitude and longitude of sample locations in Site-3

Sl.No	Latitude	Longitude	Type of water sample
1	10.133508	76.250208	Well
2	10.13351	76.250211	Well
3	10.133512	76.250216	Bore Well
4	10.133498	76.250219	Well
5	10.133491	76.250218	Well
6	10.133481	76.250216	Well

d. Site-4 Fireworks manufacturing site, Chempilavu, Kottayam

Table 5.4 Latitude and longitude of sample locations in Site-4

Sl.No	Latitude	Longitude	Type of water sample
1	9.676958	76.634808	Well water
2	9.679747	76.635381	Well water
3	9.680514	76.635183	Well water
4	-	-	Tap water
5	9.679278	76.633717	Well water
6	9.682189	76.631719	Well water
7	9.681683	76.632244	Well water

e. Site- 5 Seasonal control site

Table 5.5 Latitude and longitude of sample locations in Site-5

Sl.No	Latitude	Longitude	Type of water sample
1	8.433414	76.033416	Well
2	8.400424	77.033405	Well
3	8.433425	77.033411	Well
4	8.433424	77.033411	Well
5	8.433417	77.033401	Well

5.4 Results and discussion

Temporal variation of perchlorate

Perchlorate in drinking water samples of selected sites in Kerala such as -APEP; TERLS; fireworks site at Kottayam; fireworks site at Paravur and control site was analyzed. Perchlorate was detected in the drinking water samples collected during all the seasons except post-monsoon sample at Paravur fireworks manufacturing site (site 3). Mean values of perchlorate and other water quality parameters were given in Table 5.6 and Table 5.7 respectively. APEP (site-1) showed highest mean perchlorate during pre-monsoon and lowest during monsoon. However at TERLS (site- 2), maximum mean perchlorate was during post-monsoon and minimum in monsoon. The same trend was followed at Paravur fireworks manufacturing site (site-3) where as at Kottayam fireworks manufacturing site (site-4), monsoon season had the highest mean perchlorate and the lowest during pre-monsoon season. In control site perchlorate was below the detectable limits in all seasons (Table 5.6).

The results of water quality parameters (pH, EC, TDS, salinity, chloride, nitrate, sulphate, calcium, magnesium, sodium, potassium and chlorate) were given in the Table 5.7. All the parameters except a very few from APEP (site 1) and TERLS (site 2) were within the permissible limit (WHO, 2011; BIS, 2012). During PRM, the high concentration was observed for chlorate (APEP-site 1), nitrate and calcium (TERLS-site 2) where as in POM and MON, sulfate, chlorate (TERLS-site 2) and nitrate

showed high concentrations. Chlorate was high during the non-monsoon seasons for both industrial sites.

Mean pH was maximum during monsoon in all sites (Table 5.7) and minimum during pre-monsoon in TERLS (site 2) and control site (site 5). EC also varied with seasons. EC showed highest values for APEP (site 1), Kottayam fireworks manufacturing site (site 4) and control site (site 5) during post-monsoon and in TERLS (site 2) it was maximum during pre-monsoon and was highest during monsoon season at Paravur fireworks manufacturing site (site 3). But lowest EC values were shown during pre-monsoon at APEP (site 1), Paravur fireworks manufacturing site (site 3), Kottayam fireworks manufacturing site (site 4) and control site (site 5) and during monsoon in TERLS (site 2). TDS followed the same trend of EC in all sites during all seasons. Seasonal variation of salinity was less. At the same time chloride values showed much variation seasonally. At APEP (site 1), mean chloride was highest during post-monsoon and lowest during monsoon; but at TERLS (site 2) it was during pre-monsoon and post-monsoon respectively. Maximum chloride concentration was noticed at Kottayam fireworks manufacturing site (site 4) in post-monsoon and minimum during pre-monsoon; and in control site (site 5) it was maximum during monsoon and minimum during post-monsoon. Monsoon season had maximum mean nitrate in APEP (site 1), Kottayam fireworks manufacturing site (site 4) and control site (site 5) whereas in TERLS (site 2) and Paravur fireworks manufacturing site (site 3), it was maximum during pre-monsoon but post-monsoon had minimum mean nitrate in APEP (site 1), TERLS (site 2), Paravur fireworks manufacturing site (site 3) and control site (site 5); only Kottayam fireworks manufacturing site (site 4) had minimum nitrate during pre-monsoon. Sulfate showed almost same trend of seasonal variation in different sites, maximum during post-monsoon and minimum during monsoon, with slight changes. At APEP (site 1) sodium, potassium, calcium and magnesium was maximum during post-monsoon (except during pre-monsoon for calcium) and was minimum during monsoon. TERLS (site 2) samples had maximum sodium, potassium and calcium content during pre-monsoon. Ammonium was higher than the permissible limits at TERLS (site 2) and Paravur fireworks manufacturing site (site 3) in all the seasons. Chlorate was maximum during pre-monsoon and minimum during monsoon at APEP (site 1) and was same for control site (site 5).

Chlorate was highest during post-monsoon and minimum during monsoon at TERLS (site 2).However, Paravur fireworks manufacturing site (site 3) had maximum chlorate in monsoon and was BDL during post-monsoon.

Table 5.6 Mean perchlorate values in different season

Site	Season	Mean perchlorate ± SD (in ppb)
Site-I	POM	3760.16 ± 9007.53
	PRM	5094.87 ± 12159.55
	MON	601.28 ± 1360.64
Site-II	POM	640.40 ± 1727.04
	PRM	468.57 ± 1174.97
	MON	80.61 ± 146.04
Site-III	POM	61.56 ± 150.80
	PRM	25.42 ± 13.44
	MON	13.99 ± 16.90
Site-IV	POM	1.03 ± 2.72
	PRM	BDL
	MON	17.76 ± 14.25
Site-V	POM	BDL
	PRM	BDL
	MON	BDL

Table 5. 7 Mean± SD values of water quality parameters in different seasons

	Sl.No	pH	EC (µS/cm)	TDS(ppb)	SAL(psu)	Cl^-(mg/L)	NO_3^-(mg/L)	SO_4^{2-}(mg/L)	Na^+(mg/L)	K^+(mg/L)	Ca^{2+}(mg/L)	Mg^{2+}(mg/L)	NH_4^+(mg/L)	ClO_3^- (µg/L)
Site-I	POM	5.9± 0.55	66.8± 24.57	33.4± 12.28	0.03±0.01	14.8± 3.71	7.05± 10.03	3.31±1.38	17.08±4.12	4.40±1.92	9.66± 3 .29	3.02±0.89	BDL	664.59±1724.27
	PRM	5.8± 0.16	60.58±35.13	30.3± 17.56	0.03±0.02	9.48± 6.76	7.06± 10.19	1.38±0.67	11.6± 6.80	2.68±0.39	15.1± 14.58	2.7± 1.54	BDL	1362± 3371.03
	MON	7.68±0.34	62.72±43.83	31.17±22.05	0.03±0.02	9.17± 6.20	10.82± 9.02	1.18±0.70	10.35±5.43	1.89±0.92	5.17± 1.85	1.35±0.73	BDL	168.69±478.69
Site-II	POM	5.97±0.63	445.8±181.84	186.0±101.31	0.18±0.10	61.01±30.42	61.6± 54.68	58.7±18.27	105.9±49.16	34.6±19.10	27.5± 22.02	20.4±7.49	112.6±9.24	894.0± 1315.8
	PRM	6.32±0.27	476.9±242.53	238.4±121.16	0.23±0.12	146.2±79.21	151.5± 106.79	67.4±41.20	125.1±61.25	35.3±16.90	102.4±52.38	17.0±6.76	4.05±6.39	479.73±838.76
	MON	7.56±0.13	367± 181.73	183.6±90.87	0.17±0.08	56.8± 26.97	64.5± 33.35	25.4±16.23	74.6± 40.82	20.3±12.00	64.9± 42.81	9.92±5.75	5.07±5.34	BDL
Site-III	POM	6.7± 0.37	257.4±260.92	128.6±130.28	0.12±0.13	4.3± 55.89	4.51± 4.61	51.0±23.52	81.5± 75.54	18.9±12.70	56.5± 35.58	1.9± 17.77	104.8±1.14	BDL
	PRM	6.26±0.19	255.3±203.41	127.7±101.88	0.12±0.09	199.5±276.39	8.85± 8.36	70.1±93.43	69.1± 70.53	14.6±4.90	61.9± 44.73	23.7±26.87	11.3±25.83	35.2± 64.36
	MON	7.15±0.11	288.8±301.34	144.4±150.88	0.14±0.15	71.17±102.77	8.26± 11.96	36.9±55.74	87.2± 126.26	9.62±8.47	47.0± 44.71	13.9±24.99	1.72±3.73	32.98± 80.80
Site-IV	POM	5.2± 0.46	44.8± 15.28	22.40±7.64	0.02±0.01	7.29± 2.61	4.7± 3.72	3.58±3.49	8.90± 2.90	4.38±1.94	4.43± 2.14	2.33±0.47	0.46±9.27	BDL
	PRM	4.7± 0.24	33.3± 9.43	16.8± 4.63	0.02±0.01	6.34± 3.30	2.12± 1.42	1.28±0.60	7.57± 3.18	2.63±1.30	4.33± 2.14	2.51±0.86	BDL	46.09± 54.46
	MON	8.13±0.02	39.4± 11.74	19.7± 5.86	0.02±0.01	6.61± 1.85	5.37± 2.71	1.25±0.71	6.44± 1.99	2.48±0.45	4.80± 1.76	1.78±0.53	0.09±0.07	13.49± 35.71
Site-V	POM	5.4± 0.27	141.8±69.72	70.8± 34.85	0.07±0.03	34.4± 21.74	13.1± 8.09	2.92±1.62	34.7± 15.78	12.7±5.92	6.7± 6.67	3.52±2.02	BDL	23.9± 63.44
	PRM	5.9± 0.08	131.4±32.04	65.7± 16.04	0.06±0.02	41.7± 17.93	14.0± 7.59	1.55±0.43	40.9± 10.89	15.3±3.26	8.30± 3.93	5.17±2.13	BDL	97.10± 133.76
	MON	7.5± 0.05	136.3±45.27	68.1± 22.62	0.06±0.02	42.7± 15.89	15.19± 9.17	1.74±0.29	35.8± 8.28	14.2±2.53	6.5± 2.85	3.65±1.74	0.10±0.23	BDL

(A-APEP; T-TERLS; K-Kottayam fireworks site; P-Paravur fireworks site; SC-Seasonal control; POM- Post-monsoon; PRM- Pre-monsoon; MON- Monsoon; BDL-Below Detectable Limit)

At APEP (site 1) and TERLS (site 2), mean perchlorate levels in all seasons were more than 24.5 ppb. At APEP (site 1), perchlorate in drinking water ranged from <6 ppb to 24132.71 ppb during post-monsoon, 19.20 ppb to 32602.60 ppb during pre-monsoon and 30.18 ppb to 4171.78 ppb during monsoon . The range of perchlorate in water samples from TERLS (site 2) ranged from 8.09 ppb to 4913.77 ppb during post-monsoon, 14.68 ppb to 3133.05 ppb during pre-monsoon and 8.06 ppb to 410.86 ppb during monsoon season. Firework manufacturing sites also showed perchlorate variation in different seasons. The values ranged from <6 ppb to 369.38 ppb during post-monsoon, 16.22 ppb to 51.74 ppb during pre-monsoon and <6 ppb to 35.08 ppb during monsoon at Kottayam fireworks manufacturing site (site 4) where as in Paravur fireworks manufacturing site (site 3) the maximum variation was observed during monsoon (<6 ppb to 40.66 ppb). Perchlorate was not present in any of the samples collected from the control site during different seasons. The mean values of perchlorate in different sites during seasons were given in Fig. 5.2 to Fig. 5.5.

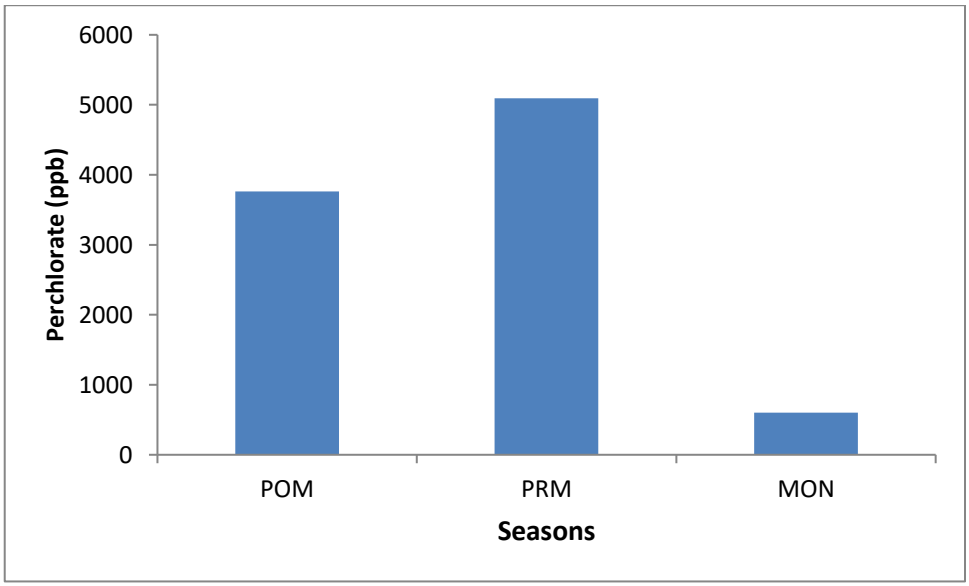


Fig. 5.2 Mean perchlorate at Site-1 in different seasons

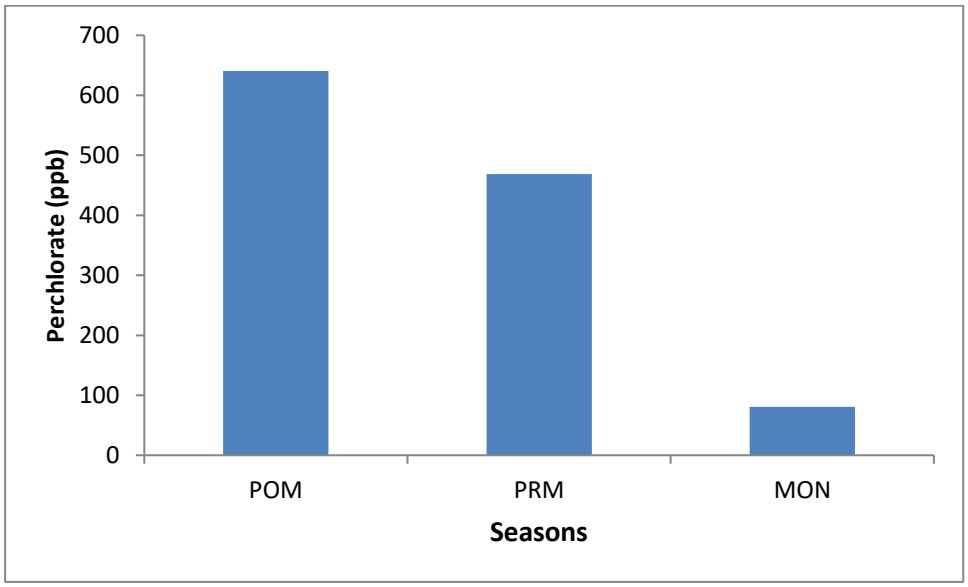


Fig. 5.3 Mean perchlorate at Site-2 in different seasons

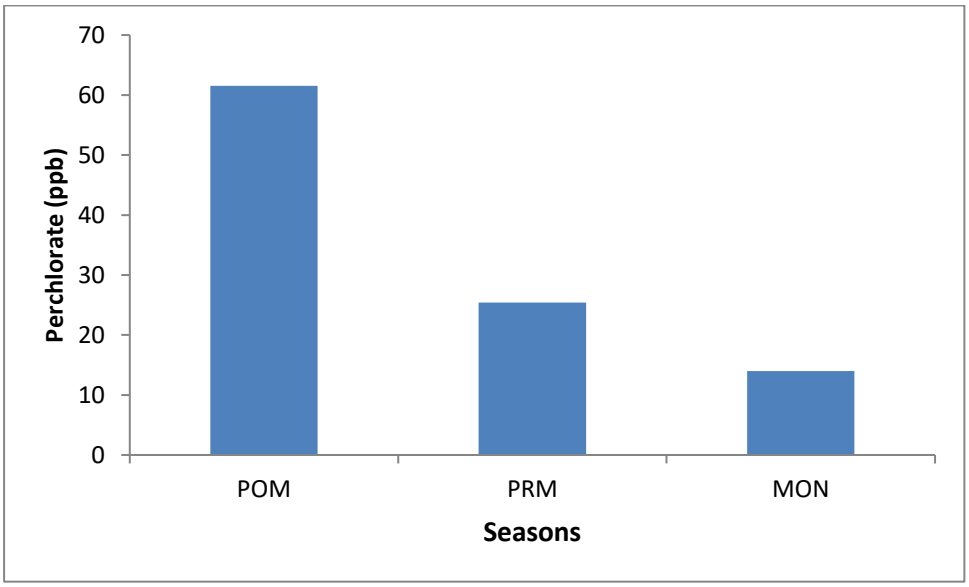


Fig. 5.4 Mean perchlorate at Site-3 in different seasons

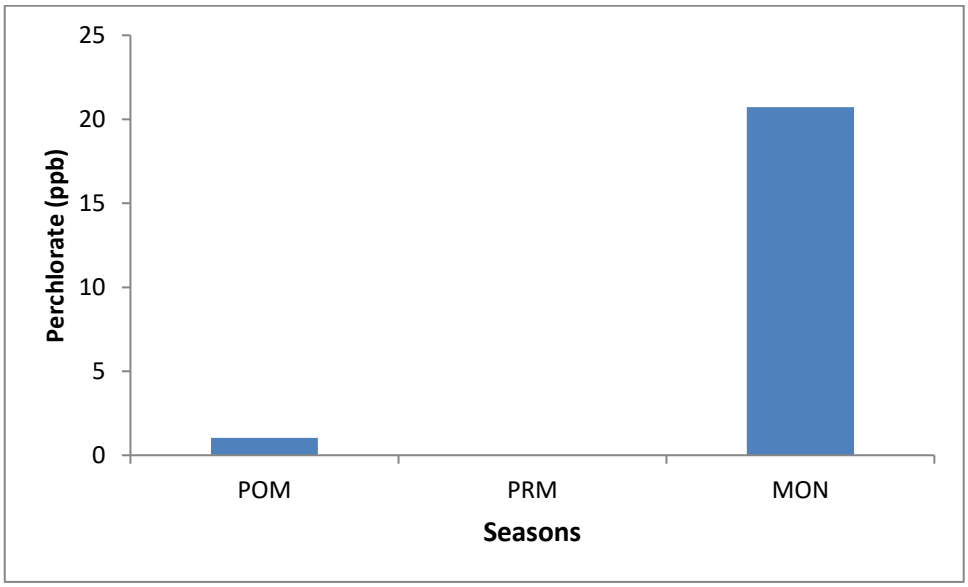


Fig. 5.5 Mean perchlorate at Site-4 in different seasons

All the sites showed the presence of perchlorate during the non-monsoon seasons (PRM and POM) except Kottayam fireworks manufacturing site (site 4), where high content was observed during MON. The mean values showed that at APEP (site 1), the maximum concentration was noted during PRM followed by POM. The results clearly indicated the high contamination at industrial sites (sites 1 & 2) than the firework manufacturing sites (Paravur and Kottayam fireworks manufacturing sites-site 3 and 4). In the case of tap water, perchlorate value at APEP (site 1) ranged from 19.20 ppb during PRM to 39.37 ppb during MON and Below Detectable Limits (BDL) during POM. At Kottayam fireworks manufacturing site (site 4), only the MON sample had the presence of perchlorate (10.92 ppb). Tap water from TERLS (site 2) was found to be contaminated with perchlorate during all seasons, ranging from 8.09 ppb to 25.08 ppb. Values of water quality parameters of individual sites in different seasons were given in Table 5.8 to Table 5.22.

Site- I Ammonium Perchlorate Experimental Plant (APEP), Aluva

The monsoon season samples collected from this region were found to be contaminated with perchlorate (Table 5.8). Perchlorate in all the samples exceeded the permissible limit. S1 (4171.78 ppb) and S2 (790.5 ppb) showed the highest perchlorate. Chlorate contamination was also seen in S1 and S2 where the value exceeded the health reference limit only in S1 (1443.52 ppb). The tap water sample was also contaminated

with perchlorate. This might be due to the leaching of perchlorate into the water bodies during rainfall. All other parameters were within the permissible limits only. During pre-monsoon, both S1 (32602.60 ppb) and S2 (2399.23 ppb) showed maximum perchlorate. Only tap water showed values within the limit (19.20 ppb) and all other samples had more than 24.5 ppb perchlorate. Apart from perchlorate, chlorate also showed widespread contamination during pre-monsoon (Table 5.9). Other analyzed parameters were within the limit only. Perchlorate values during post-monsoon varied from 28.32 ppb (S6) to 24132.71 ppb (S1) in well water where as in tap water it was BDL. Chlorate was again seen in S1 and S2 (Table 5.10). During POM no other parameters exceeded the permissible limits.

Perchlorate variation between the seasons was not significant ($p>0.1$). This showed that irrespective of seasons perchlorate was entering into the water bodies from various sources. But when compared to the control site, perchlorate contamination at APEP (site 1) was found to be significant ($p<0.1$). Certain water quality parameters like pH, chloride, sulfate, sodium, potassium, calcium, magnesium etc. had significant variation between the seasons.

Table 5.8 Perchlorate content and water quality in site 1, monsoon season

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
AMON S1	8.40	173.10	86.50	0.09	22.54	28.67	0.69	18.42	1.62	7.09	2.94	BDL	1443.52	4171.78
AMON S2	8.13	82.0	41.0	0.04	10.34	21.71	1.54	12.84	3.25	5.52	1.97	BDL	74.72	790.52
AMON S3	7.64	45.70	22.80	0.03	8.27	7.32	2.07	9.44	1.91	4.50	1.63	BDL	BDL	64.34
AMON S4	7.50	52.10	26.10	0.03	6.56	6.27	1.84	10.20	1.49	6.28	0.66	BDL	BDL	37.57
AMON S5	7.49	58.10	29.10	0.03	15.62	13.74	0.77	19.13	3.62	3.19	0.67	BDL	BDL	126.15
AMON S6	7.53	35.40	17.68	0.02	5.33	9.68	0.36	7.11	1.19	4.64	1.02	BDL	BDL	91.37
AMON S7	7.47	37.60	18.81	0.03	4.81	2.01	2.11	4.79	1.73	8.09	1.29	BDL	BDL	39.37
AMON S8	7.42	41.20	16.42	0.03	3.47	4.69	0.79	5.11	0.82	5.09	1.18	BDL	BDL	60.25
AMON S9	7.61	39.30	22.12	0.03	5.60	3.32	0.42	6.13	1.47	2.13	0.81	BDL	BDL	30.18

Table 5.9 Perchlorate content and water quality in site 1, Pre-monsoon season

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
APRM S1	6.02	117.50	58.80	0.06	21.93	29.62	0.69	26.21	3.01	18.50	5.51	BDL	9005.12	32602.60
APRM S2	5.93	46.50	23.30	0.03	6.93	5.28	1.42	10.06	2.86	6.51	1.69	BDL	116.96	2399.23
APRM S3	5.73	44.50	22.30	0.03	8.07	7.17	2.55	12.19	2.63	3.69	4.19	BDL	122.24	75.85
APRM S4	5.62	104.80	52.40	0.05	15.54	2.47	1.92	10.99	2.86	46.28	1.99	BDL	198.48	125.63
APRM S5	6.07	32.50	16.27	0.02	5.99	2.32	1.26	8.13	2.02	6.92	1.36	BDL	BDL	106.31
APRM S6	5.94	43.90	22.0	0.03	3.33	2.09	1.14	8.14	3.09	12.81	2.45	BDL	91.20	335.28
APRM S7	5.90	34.40	17.22	0.02	4.61	0.55	0.65	5.53	2.30	11.26	1.83	BDL	BDL	19.20

Table 5.10 Perchlorate content and water quality in site 1, Post-monsoon

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
APOM S1	5.86	112.20	56.10	0.06	20.56	25.85	2.77	24.64	3.68	15.31	4.72	BDL	4574.32	24132.71
APOM S2	5.77	52.80	26.40	0.03	8.43	4.99	4.31	10.99	4.17	6.54	1.72	BDL	77.84	1820.54
APOM S3	5.34	66.50	33.30	0.04	14.05	16.04	3.26	17.45	4.05	5.94	3.11	BDL	BDL	32.29
APOM S4	6.59	73.40	36.70	0.04	17.23	0.94	3.97	18.28	2.92	9.77	3.07	BDL	BDL	284.06
APOM S5	6.51	61.60	30.80	0.04	13.59	0.74	4.60	16.15	3.45	8.61	2.73	BDL	BDL	23.17
APOM S6	5.30	31.0	15.51	0.02	15.62	0.83	0.52	17.33	3.92	8.99	3.10	BDL	BDL	28.32
APOM S7	6.48	70.20	35.10	0.04	14.22	0.002	3.79	14.77	8.66	12.48	2.71	BDL	BDL	BDL

Pre-monsoon showed maximum perchlorate contamination followed by post-monsoon and monsoon seasons. During pre-monsoon perchlorate got concentrated and the same got diluted during post-monsoon and monsoon, the maximum dilution during monsoon. Samples S1 and S2 had maximum perchlorate in all seasons because these two sampling locations were in close proximity with the site and were comparatively low lying to the site. The wells were also shallow.

Site II Thumba Equatorial Rocket Launching Station (TERLS), Trivandrum

In TERLS, maximum perchlorate was reported from sample 2 (S2- 410.86 ppb) during monsoon (Table 5.11). All the samples except S5 and S6 showed more than 24.5 ppb perchlorate. Tap water (S4) also exceeded the permissible limit (25.08 ppb). EC was higher for S2, S3, S5, S6 and S7 than the limit. Nitrate was found to be higher in S1, S2, S3, S6 and S7. Only 3 samples (S3, S5 and S7) had calcium above the permissible limit. Ammonium in S1, S3, S5, S6 and S7 samples were also higher. But no chlorate was identified. During post-monsoon also S2 showed highest perchlorate (4913.77 ppb) (Table 5.12). S2, S7 and S8 had perchlorate outside the permissible limit ranging from 41.31 ppb (S8) to 4913.77 ppb (S2). The perchlorate content in tap water (S4) was only 8.09 ppb. Chlorate was found in S2, S4, S7 and S8. EC, nitrate, calcium and ammonium in some samples have also exceeded the permissible limit. Ammonium in the water samples was far higher than the permissible limits. S1 (39.40 ppb), S2 (3133.05 ppb) and S7 (36.05 ppb) had perchlorate higher than the health reference level during pre-monsoon (Table 5.13). In TERLS, chlorate values were also very high during PRM and POM. Other parameters that crossed the permissible limits during pre-monsoon were EC (S1, S2, S3, S5 and S7), chloride (S1), nitrate (S1, S2, S3, S5, S6 and S7), sodium (S2), calcium (S1, S2, S3, S5 and S7) and ammonium (S3 and S5). In the case of TERLS (site 2) also, perchlorate variation between the seasons was not significant however it varied significantly with control site ($p<0.1$). Here also the role of industry in causing perchlorate contamination in the nearby drinking water systems was depicted. pH, chloride, nitrate, sulfate, potassium, calcium, magnesium and ammonium had significant variation between the seasons.

Table 5.11 Perchlorate content and water quality in site 2, Monsoon

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
TMON S1	7.56	258.0	129.10	0.12	55.15	97.42	8.02	51.15	20.95	11.25	3.13	0.69	BDL	25.45
TMON S2	7.59	421.0	211.0	0.20	67.39	65.51	29.86	82.35	16.76	52.67	9.59	1.91	BDL	410.86
TMON S3	7.63	604.0	302.0	0.29	89.93	85.79	52.49	123.67	23.48	129.81	16.39	4.06	BDL	41.54
TMON S4	7.64	63.0	31.50	0.04	13.01	3.94	3.89	13.16	5.03	15.38	1.53	0.10	BDL	25.08
TMON S5	7.63	548.0	274.0	0.26	86.04	35.67	23.17	128.14	42.98	93.16	15.72	15.61	BDL	17.57
TMON S6	7.60	326.0	163.20	0.16	40.90	86.65	28.95	58.81	10.83	64.95	12.22	5.93	BDL	8.06
TMON S7	7.27	349.0	174.70	0.17	45.52	76.60	32.01	65.29	22.30	87.33	10.90	7.19	BDL	35.72

Table 5.12 Perchlorate content and water quality in site 2, post-monsoon

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
TPOM S1	4.78	493.0	247.0	0.24	62.15	166.57	64.57	110.35	39.94	78.78	22.04	119.68	BDL	BDL
TPOM S2	5.74	346.0	173.20	0.17	71.04	29.04	48.35	89.84	19.25	14.02	14.02	120.12	2344.16	4913.77
TPOM S3	6.23	590.0	295.0	0.29	99.43	40.10	88.58	165.99	27.18	20.90	20.90	99.45	BDL	17.40
TPOM S4	6.45	658.0	32.90	0.04	13.11	3.10	35.11	29.94	12.71	11.02	11.02	114.87	256.72	8.09
TPOM S5	5.98	598.0	299.0	0.29	91.66	84.94	64.31	136.45	56.51	27.91	27.91	126.32	BDL	15.78
TPOM S6	5.43	264.0	132.0	0.13	56.18	63.68	72.15	115.03	44.27	24.94	24.94	107.89	BDL	18.78
TPOM S7	6.45	482.0	241.0	0.23	88.47	98.84	61.45	155.38	62.65	30.82	30.82	110.37	1136.56	108.06
TPOM S8	6.7	136.10	68.0	0.07	30.05	6.54	35.76	44.31	14.71	11.72	11.72	102.71	3414.80	41.32

Table 5.13 Perchlorate content and water quality in site 2, pre-monsoon

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
TPRM S1	5.83	672.0	336.0	0.33	266.03	190.34	50.09	127.72	42.92	86.84	19.27	BDL	170.56	39.40
TPRM S2	6.26	668.0	334.0	0.32	206.23	250.89	84.38	201.92	37.19	145.75	19.36	0.91	323.76	3133.05
TPRM S3	6.37	779.0	389.0	0.38	190.88	314.19	84.13	191.60	53.21	192.09	27.69	12.43	BDL	16.74
TPRM S4	6.67	130.60	65.3.0	0.07	31.92	5.29	18.79	31.82	7.041	34.65	5.34	BDL	2358.48	23.49
TPRM S5	6.56	492.0	246.0	0.24	129.08	78.87	46.63	135.25	50.79	110.18	18.37	14.29	BDL	16.58
TPRM S6	6.27	258.0	129.10	0.12	96.02	127.15	144.61	67.18	37.99	71.41	14.89	0.79	316.40	14.68
TPRM S7	6.33	339.0	169.40	0.16	103.59	93.81	43.75	120.87	18.39	76.26	14.36	BDL	188.96	36.05

Site- III Paravur fireworks manufacturing site

Perchlorate content was higher than the permissible limit in samples S1 and S5 at Paravur firework manufacturing site during monsoon (Table 5.14). But chlorate was higher in S2 (197.92 ppb) only. Only S2 exceeded the permissible limit for EC, chloride, sodium, calcium, magnesium and ammonium. During post-monsoon, only S3 showed perchlorate contamination but the value was very high (369.38 ppb) (Table 5.15). Chlorate content was not observed during POM in the area. EC in S4, sodium in S3, calcium in S2 and S3, magnesium in S3 also exceeded during post-monsoon. Ammonium in all the samples exceeded the permissible limit during the time. Wide spread perchlorate contamination ranging from 16.22 ppb (S3) to 51.74 ppb (S4) was seen during pre-monsoon (Table 5. 16). Chlorate was detected from two samples only S6 (159.6 ppb) and S5 (52.0 ppb). The water quality parameters like EC, chloride, sulfate, sodium, calcium, magnesium and ammonium in a few samples were out of the limit during pre-monsoon. No significant variation in perchlorate was noted between the seasons where as significant variation was observed with the control site.

Table 5.14 Perchlorate content and water quality in site 3, Monsoon

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
PMON S1	7.04	244.0	121.70	0.12	50.35	0.29	18.42	51.29	10.39	48.07	7.29	0.17	BDL	35.08
PMON S2	7.11	897.0	449.0	0.44	278.47	29.29	150.33	343.72	25.39	135.56	64.84	9.30	197.92	BDL
PMON S3	7.27	173.20	86.60	0.09	16.75	2.08	17.24	34.65	2.65	13.74	0.88	0.90	BDL	15.03
PMON S4	7.20	170.40	85.20	0.08	47.59	0.24	11.65	47.96	5.37	27.05	3.27	BDL	BDL	BDL
PMON S5	7.28	107.60	53.80	0.06	16.41	1.55	6.81	20.22	3.18	29.92	3.08	BDL	BDL	33.88
PMON S6	7.05	140.80	70.40	0.07	17.46	16.14	16.98	25.36	10.78	28.21	4.58	BDL	BDL	BDL

Table 5.15 Perchlorate content and water quality in site 3, Post-monsoon

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
PPOM S1	6.81	53.0	26.50	0.03	16.19	4.05	34.56	39.61	12.06	23.98	9.90	108.81	BDL	BDL
PPOM S2	7.42	245.0	122.40	0.12	18.89	2.16	62.17	56.87	16.49	101.16	14.25	104.13	BDL	BDL
PPOM S3	6.57	741.0	370.0	0.36	151.58	4.69	88.12	216.31	19.20	101.23	55.67	93.10	BDL	369.38
PPOM S4	6.67	330.0	165.0	0.16	78.28	13.48	60.98	124.20	43.96	43.27	18.46	98.04	BDL	BDL
PPOM S5	6.36	118.10	59.0	0.06	15.87	1.56	34.52	31.46	12.53	43.54	11.59	105.28	BDL	BDL
PPOM S6	6.96	57.60	28.80	0.03	14.99	1.15	26.06	20.94	9.64	25.95	10.06	119.98	BDL	BDL

Table 5.16 Perchlorate content and water quality in site 3, Pre-monsoon

Sl.No	pH	EC (µS/cm)	TDS(ppb)	SAL(psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+(mg/L)	K^+(mg/L)	Ca^{2+}(mg/L)	Mg^{2+}(mg/L)	NH_4^+(mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
PPRM S1	6.01	380.0	190.10	0.18	598.13	12.98	20.81	71.18	19.59	49.73	55.40	63.99	BDL	16.54
PPRM S2	6.48	603.0	302.0	0.29	511.07	19.30	89.94	208.71	20.58	129.99	61.22	1.43	BDL	26.68
PPRM S3	6.41	225.0	112.50	0.11	21.35	0.97	19.79	42.19	10.92	103.79	8.26	BDL	BDL	16.22
PPRM S4	6.40	68.90	34.50	0.04	21.71	0.35	251.35	24.34	11.16	15.45	4.15	2.41	BDL	51.74
PPRM S5	6.14	95.0	47.50	0.05	19.51	3.18	7.26	24.04	9.06	36.31	5.29	BDL	52.0	20.86
PPRM S6	6.12	160.0	80.0	0.08	25.61	16.37	31.53	44.22	16.46	36.34	8.31	BDL	159.6	20.45

Site- IV Kottayam fireworks manufacturing site

Wide spread perchlorate contamination was noticed in water samples at Kottayam fireworks manufacturing site during monsoon season (Table 5.17). Perchlorate values ranged from BDL (S7) to 40.66 ppb (S1). Only S1 (40.66 ppb) and S5 (32.89 ppb) had exceeding levels of perchlorate than the reference limit. Chlorate was found in S5 (94.48 ppb) only. All other parameters were within the limit. During post-monsoon, the sample S7 (7.20 ppb) showed perchlorate contamination (Table 5.18). Chlorate was BDL in all the samples. None of the samples exceeded the permissible limit of water quality parameters during post-monsoon except ammonium in S7. Perchlorate was found to be BDL in all the samples during pre-monsoon. But chlorate was detected in S2 (146.08 ppb), S3 (37.92 ppb), S5 (57.44 ppb) and S7 (81.2 ppb) (Table 5.19). All other parameters of all the samples were within the limit during pre-monsoon.

Perchlorate showed highly significant variation between seasons ($p=0.01$) and with control ($p<0.05$). This indicated that seasonal factors like rainfall largely aided in bringing the perchlorate from the industrial area to the water table, as the site is located in an elevated location. Variation of other water quality parameters like nitrate, sulfate, potassium, magnesium and chlorate were also significant between seasons.

Table 5.17 Perchlorate content and water quality in site 4, Monsoon

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
KMON S1	8.16	59.10	29.50	0.03	8.92	6.49	2.04	6.46	2.73	7.21	1.17	BDL	BDL	40.66
KMON S2	8.14	32.90	16.44	0.02	4.59	2.64	0.57	5.38	1.95	3.14	1.95	0.11	BDL	16.14
KMON S3	8.13	40.80	20.40	0.03	5.79	0.74	2.17	6.08	2.78	5.37	2.15	0.11	BDL	7.97
KMON S4	8.11	51.80	25.90	0.03	8.86	6.54	1.81	10.77	3.03	7.09	2.66	BDL	BDL	10.92
KMON S5	8.13	31.60	15.80	0.02	5.94	7.42	0.83	6.14	2.49	3.72	1.60	0.11	94.48	32.89
KMON S6	8.13	28.40	14.21	0.02	7.57	5.52	0.66	5.53	1.79	3.23	1.19	0.17	BDL	15.71
KMON S7	8.11	31.70	15.84	0.02	4.59	8.28	0.74	4.78	2.65	3.85	1.81	0.13	BDL	BDL

Table 5.18 Perchlorate content and water quality in site 4, Post-monsoon

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
KPOM S1	6.05	67.60	33.80	0.02	10.82	4.31	2.56	12.92	5.17	7.76	2.66	BDL	BDL	BDL
KPOM S2	5.41	37.20	18.61	0.03	6.93	1.27	1.01	8.28	8.05	3.02	2.30	BDL	BDL	BDL
KPOM S3	5.10	33.50	16.76	0.02	5.58	0.34	3.64	6.32	3.56	4.27	1.88	BDL	BDL	BDL
KPOM S4	5.29	65.80	32.90	0.03	11.25	3.67	2.42	12.75	5.28	7.11	2.65	BDL	BDL	BDL
KPOM S5	4.95	33.50	16.77	0.02	5.53	5.93	0.95	6.33	2.71	2.45	1.60	0.12	BDL	BDL
KPOM S6	4.56	42.20	21.10	0.03	5.64	11.68	3.35	9.19	2.63	2.79	2.34	0.07	BDL	BDL
KPOM S7	5.27	33.80	16.89	0.02	5.32	5.70	11.14	6.52	3.32	3.64	2.93	3.04	BDL	7.20

Table 5.19 Perchlorate content and water quality in site 4, Pre-monsoon

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
KPRM S1	5.12	47.90	24.0	0.03	11.46	1.77	1.89	12.55	4.83	7.52	2.55	BDL	BDL	BDL
KPRM S2	4.96	28.40	15.66	0.02	4.60	1.42	0.45	5.42	1.6	2.73	1.90	BDL	146.08	BDL
KPRM S3	4.51	32.50	16.25	0.02	5.53	0.67	1.98	6.42	2.74	4.82	2.15	BDL	37.92	BDL
KPRM S4	4.72	44.10	22.0	0.03	10.69	0.98	1.78	11.79	3.98	6.81	2.48	BDL	BDL	BDL
KPRM S5	4.60	23.30	11.63	0.02	3.69	1.92	0.78	5.01	2.02	2.24	1.46	BDL	57.44	BDL
KPRM S6	4.62	33.0	16.52	0.02	4.71	4.59	0.97	6.25	1.86	3.79	4.15	BDL	BDL	BDL
KPRM S7	5.02	24.40	12.19	0.02	3.75	3.53	1.19	5.61	1.43	2.43	2.93	BDL	81.20	BDL

Site V Control site

Perchlorate was not observed in any of the samples collected in different seasons, from the control site (Table 5.20 to Table 5.22). Chlorate was detected in S1 (167.84 ppb) during post-monsoon (Table 5.20) and S3 (263.36 ppb) and S5 (222.16 ppb) during pre-monsoon (Table 5.21). All other water quality parameters were in safe limits. Chlorate and sulfate showed a significant variation ($p<0.1$) between the seasons.

Table 5.20 Perchlorate content and water quality in site 5, Monsoon

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
SCPOM S1	5.66	199.60	99.70	0.10	35.97	15.15	4.65	37.97	20.88	5.03	3.36	BDL	167.84	BDL
SCPOM S2	5.56	161.20	80.6	0.08	63.82	7.30	2.52	49.57	15.73	5.06	5.16	BDL	BDL	BDL
SCPOM S3	5.45	203.0	101.40	0.10	32.12	12.30	1.99	33.65	13.22	6.89	3.74	BDL	BDL	BDL
SCPOM S4	5.65	149.90	74.90	0.07	30.87	13.27	5.69	35.71	13.57	20.24	3.25	BDL	BDL	BDL
SCPOM S5	5.54	191.10	95.60	0.09	60.06	29.93	2.58	56.33	15.68	8.82	6.80	BDL	BDL	BDL
SCPOM S6	5.16	51.10	25.50	0.03	10.37	6.33	1.63	16.07	6.59	0.61	1.39	BDL	BDL	BDL
SCPOM S7	4.95	37.0	18.48	0.02	7.66	8.11	1.39	13.62	3.36	0.68	1.0	BDL	BDL	BDL

Table 5.21 Perchlorate content and water quality in site 5, Post- monsoon

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
SCPRM S1	6.0	99.80	49.90	0.05	25.59	11.48	1.73	32.67	12.18	4.49	3.07	BDL	BDL	BDL
SCPRM S2	5.82	148.30	74.10	0.07	62.43	7.28	1.25	50.97	16.36	5.59	5.36	BDL	BDL	BDL
SCPRM S3	5.84	153.30	76.70	0.08	50.33	20.89	1.33	46.20	17.88	8.25	7.09	BDL	263.36	BDL
SCPRM S4	5.98	93.90	46.90	0.05	49.94	23.34	1.21	48.61	18.64	8.56	7.42	BDL	BDL	BDL
SCPRM S5	5.86	162.0	81.0	0.08	20.37	7.35	2.23	26.15	11.58	14.63	2.94	BDL	222.16	BDL

Table 5.22 Perchlorate content and water quality in site 5, Pre-monsoon

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
SCMON S1	7.63	191.80	95.90	0.09	52.62	25.89	1.58	36.38	15.49	4.94	2.58	0.51	BDL	BDL
SCMON S2	7.50	97.10	48.50	0.05	30.25	12.62	1.92	32.88	12.56	4.17	3.12	BDL	BDL	BDL
SCMON S3	7.51	138.30	69.10	0.07	54.90	6.49	1.41	41.35	14.58	5.82	4.11	BDL	BDL	BDL
SCMON S4	7.53	168.50	84.20	0.08	54.89	23.84	1.66	44.97	17.55	11.41	6.44	BDL	BDL	BDL
SCMON S5	7.55	85.90	43.0	0.05	21.26	7.16	2.15	23.54	11.05	6.42	2.02	BDL	BDL	BDL

In all the sites, the maximum range of perchlorate was observed during POM where as widespread contamination was noticed during MON season besides the low perchlorate values compared to other seasons. Runoff during MON season might have resulted in widespread contamination and dilution of the chemical. Well water samples showed more perchlorate than tap water as perchlorate remained BDL in most of the tap water samples and thus proved the source of contamination was from the sites itself. Perchlorate contamination was found to be site dependent. At TERLS, perchlorate was detected from tap water samples also. When city water supply fails to provide water in the area, water is supplied from the TERLS water supply, which uses a large well within the rocket ground testing site, which might be the reason for the presence of perchlorate in tap water samples. No perchlorate was detected in the water samples collected from the control site in any of the seasons and confirmed the role of the selected sources in perchlorate contamination.

The perchlorate concentration at various sites was presented in the Box plot (Fig. 5.6 to 5.8). Very high values were observed at sample 1 of APEP (site 1) irrespective of seasons (24132.71 ppb, 32602.60 ppb, 4171.78 ppb) and sample 2 of TERLS (site 2) during post-monsoon (4913.77ppb). These extreme values were not considered during the preparation of box plot. Box plot compared the results during various seasons. High perchlorate concentration was observed for APEP (site 1) and TERLS (site 2) during pre-monsoon and monsoon compared with other sites whereas during post-monsoon it was APEP (site 1) and Paravur fireworks manufacturing site (site 3). During pre-monsoon and monsoon high variability was observed for TERLS (site 2) and APEP (site 1) respectively. However, Paravur fireworks manufacturing site (site 3) showed high variability in post-monsoon only.

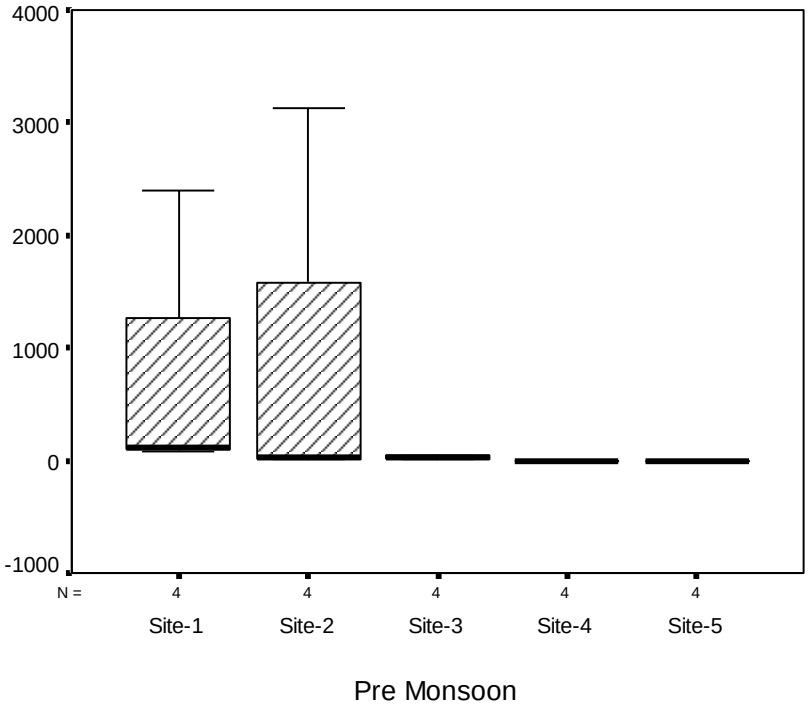


Fig. 5.6 Variations in perchlorate content (ppb) at different sites during pre-monsoon

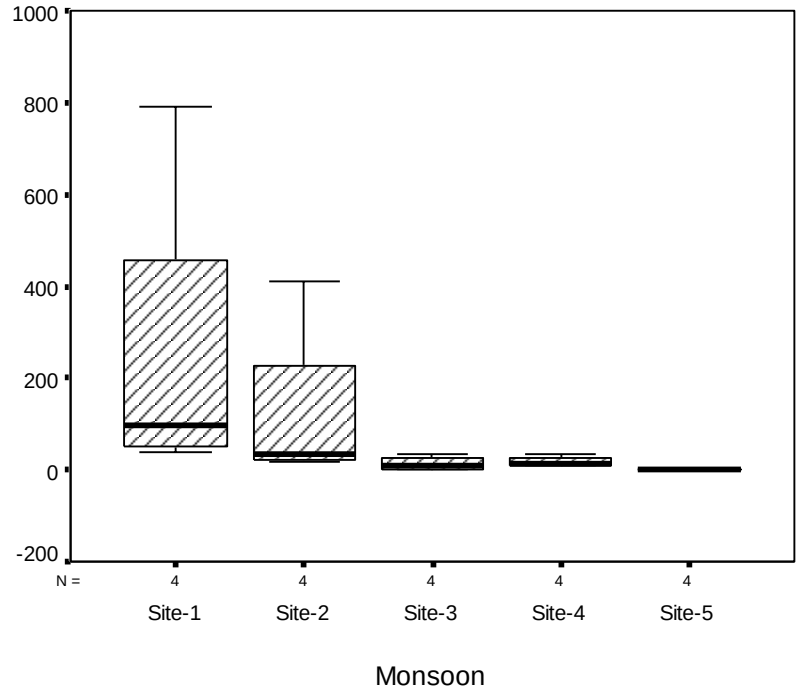


Fig. 5.7 Variations in perchlorate content (ppb) at different sites during monsoon

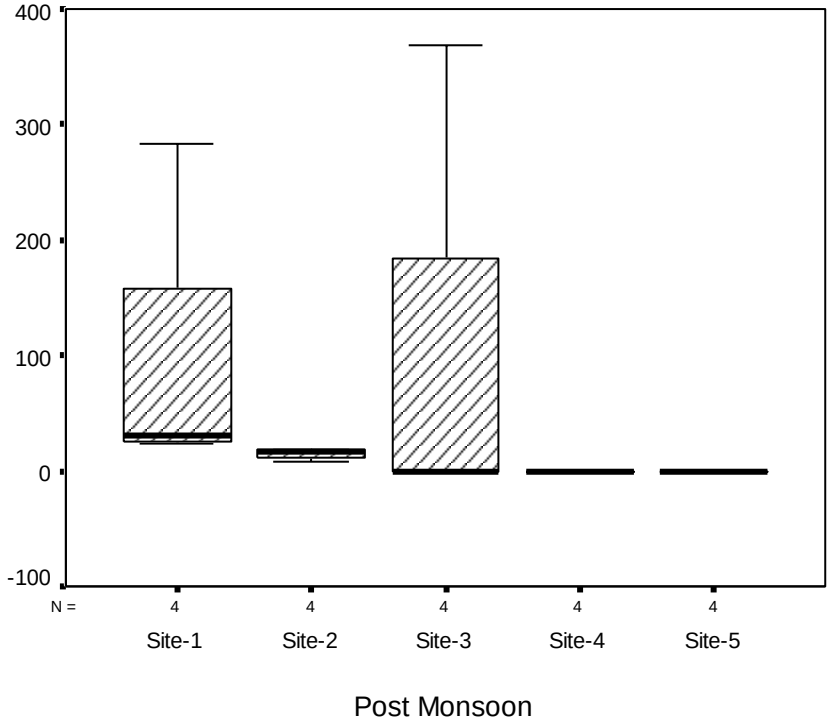


Fig. 5.8 Variations in perchlorate content (ppb) at different sites during post-monsoon

Use of perchlorate in rocket installations was found to be the major reason for perchlorate contamination of drinking water (ITRC, 2005). The present study also confirmed the fact that the major reason for drinking water contamination by perchlorate in Kerala was rocket propellant manufacturing (APEP) and rocket testing facilities (TERLS) as observed by the earlier studies (Anupama *et al.,* 2012). They observed 1.33 ppb to 91.40 ppb of perchlorate in drinking water during POM (during the year 2009) which was lower than the concentration detected in the present study (Table 5.23). In another study by Anupama *et al.,* (2015), perchlorate content varied from 2.76 ppb to 7270.0 ppb values during PRM (in the year 2012) and is also lower than the concentrations observed in this study (BDL to 32,602.60 ppb). But the mean value in the present study was lower than the earlier study because of the variation in the number of samples, sampling locations etc. and samples were collected from both high and low lying areas around APEP in present study. The same trend was also observed at TERLS, i.e. High concentration in the present study (mean- 468.57 ppb) when compared to the earlier one (mean – 300 ppb) (Table 5.23). This clearly showed

the increase in the concentration of perchlorate in the surrounding environment of the industries. This might be due to slow rate of degradation along with industrial output.

Table 5.23 Comparison of perchlorate in present study with earlier study

	APEP (PRM)			**TERLS (PRM)**		
	No: of samples	**Maximum value (ppb)**	**Mean value (ppb)**	**No: of samples**	**Maximum value (ppb)**	**Mean value (ppb)**
Anupama *et al.*,2015	2	7270.0	7230.0	2	300.0	300.0
Present study	7	32602.60	5094.87	7	3133.05	468.57

The present study also established the role of firework manufacturing units in the perchlorate contamination of water bodies. Ground water contamination of perchlorate due to firework manufacturing had been reported from other parts of the country (Isobe *et al.,* 2012). The present study also showed perchlorate contamination of drinking water sources nearby firework manufacturing units. At Kottayam fireworks manufacturing site (site 4), the higher concentration was observed during MON where as at Paravur fireworks manufacturing site (site 3), it was during POM. Kottayam fireworks manufacturing site (site 4) is located at an elevated region and rainfall could bring down the perchlorate from the soils to aquatic systems of lower lands, where as Paravur fireworks manufacturing site (site 3) is located in a plain land and is surrounded by wetlands. Hence the seasonal variation could be owed to the geography and local climatic conditions of the region. Seasonal variation could not be said of as the single reason behind difference in perchlorate around firework manufacturing sites. It also depends on the time of firework manufacturing, amount of perchlorate usage, waste disposal etc. Perchlorate concentration in drinking water also depends on the depth to water, saturated thickness and land use patterns (Rajagopalan *et al.,* 2006).

The health safe reference dose of perchlorate in drinking water is 24.5 ppb. Above this can result in thyroid disorders. But at APEP and TERLS, perchlorate dosage in drinking water is far above 24.5 ppb in all the seasons. The results showed a probability of thyroid disorders in some areas.

Correlation of perchlorate with other physico-chemical parameters

The interrelationship between perchlorate and other water quality parameters were tested with Pearsons correlation analysis. Water samples analyzed from APEP in all seasons showed significant positive correlation between perchlorate and chlorate (p=0.01). Correlation analysis of samples from APEP further showed positive significant correlation between perchlorate and sodium, nitrate and sulphate during POM and with pH, EC, TDS, SAL, chloride, nitrate and magnesium during MON (p=0.01) (Table 5.24 to Table 5.26). Samples from TERLS showed highly significant correlation between perchlorate and chloride during POM (P=0.01) and no other parameters showed correlation with perchlorate in any of the seasons (Table 5.27 to 5.29). At Paravur fireworks manufacturing site, perchlorate in water samples showed significant positive correlation with magnesium during POM and with sulphate during PRM (p=0.01) (Table 5.30 to 5.32). Perchlorate was significantly correlated (p=0.01) to sulphate and ammonium during POM at fireworks manufacturing site (site 4) (Table 5.33 to 5.35). Variation of correlation in different sites might be due to the change in general flushing of salts from the land surface or unsaturated zone to water table by means of precipitation-irrigation-evaporation cycles (Rajagopalan *et al.*, 2006). The possibility of atmospheric deposition also needs to be considered (Rajagopalan *et al.,* 2006). However, in the general correlation table (considering mean of parameters in all sites), perchlorate showed highly significant correlation with chlorate only. It was not correlated with any other parameters.

Table 5.24 Correlation between water quality parameters at APEP, Post-monsoon

		POM pH	POM EC	POM TDS	POM SAL	POM Cl^-	POM NO_3^-	POM SO_4^{2-}	POM Na^+	POM K^+	POM Ca^{2+}	POM Mg^{2+}	POM NH_4^+	POM ClO_3^-	POM ClO_4^-
POM pH		1	.307	.306	.330	.091	-.419	.680	-.070	.221	.342	-.109		-.098	-.104
POM EC			1	1.000**	.985**	.625	.724	.298	.698	-.009	.703	.709		.813*	.806*
POM TDS				1	.985**	.625	.725	.298	.698	-.009	.702	.709		.812*	.806*
POM SAL					1	.601	.712	.349	.689	-.017	.657	.698		.775*	.764*
POM Cl^-						1	.476	-.390	.954**	-.181	.744	.942**		.671	.636
POM NO_3^-							1	-.131	.690	-.244	.350	.720		.827*	.826*
POM SO_4^{2-}								1	-.364	.085	-.149	-.398		-.170	-.151
POM Na^+									1	-.316	.672	.990**		.799*	.769*
POM K^+										1	.293	-.205		-.168	-.178
POM Ca^{2+}											1	.721		.751	.733
POM Mg^{2+}												1		.830*	.800*
POM NH_4^+															
POM ClO_3^-														1	.998**
POM ClO_4^-															1
Aluva-post-monsoon															

a. Cannot be computed because at least one of the variables is constant.

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 5. 25 Correlation between water quality parameters at Aluva- Pre-monsoon

	PRM pH	PRM EC	PRM TDS	PRM SAL	PRM Cl^-	PRM NO_3^-	PRM SO_4^{2-}	PRM Na^+	PRM K^+	PRM Ca^{2+}	PRM Mg^{2+}	PRM NH_4^+	PRM ClO_3^-	PRM ClO_4^-
PRM pH	1	-.259	-.258	-.230	-.136	.300	.368	.162	-.244	-.584	.011		.352	.381
PRM EC		1	1.000**	.984**	.957**	.694	.714	.789*	.560	.731	.564		.726	.709
PRM TDS			1	.984**	.957**	.695	.715	.790*	.561	.730	.565		.727	.710
PRM SAL				1	.943**	.754	.750	.845*	.666	.639	.655		.763*	.749
PRM Cl^-					1	.814*	.812*	.886**	.399	.560	.665		.821*	.807*
PRM NO_3^-						1	.976**	.983**	.404	.026	.869*		.978**	.979**
PRM SO_4^{2-}							1	.947**	.364	.102	.799*		1.000**	.998**
PRM Na^+								1	.467	.163	.870*		.952**	.949**
PRM K^+									1	.341	.449		.378	.387
PRM Ca^{2+}										1	-.045		.115	.085
PRM Mg^{2+}											1		.803*	.786*
PRM NH_4^+													.	.
PRM ClO_3^-													1	.998**
PRM ClO_4^-														1

a. Cannot be computed because at least one of the variables is constant.

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 5.26 Correlation between water quality parameters at APEP- Monsoon

	MON pH	MON EC	MON TDS	MON SAL	MON Cl^-	MON NO_3^-	MON SO_4^{2-}	MON Na^+	MON K^+	MON Ca^{2+}	MON Mg^{2+}	MON NH_4^+	MON ClO_3^-	MON ClO_4^-
MON pH	1	.905**	.914**	.867**	.748*	.906**	-.094	.583	.239	.286	.898**		.813**	.874**
MON EC		1	.997**	.981**	.888**	.896**	-.168	.712*	.147	.372	.849**		.958**	.981**
MON TDS			1	.977**	.895**	.894**	-.169	.719*	.168	.348	.838**		.954**	.978**
MON SAL				1	.832**	.800**	-.147	.604	.024	.406	.860**		.978**	.986**
MON Cl^-					1	.870**	-.206	.928**	.457	.127	.643		.815**	.834**
MON NO_3^-						1	-.219	.809**	.427	.208	.775*		.769*	.835**
MON SO_4^{2-}							1	-.157	.156	.535	.050		-.247	-.231
MON Na^+								1	.667*	-.023	.399		.569	.604
MON K^+									1	-.192	.032		-.086	-.006
MON Ca^{2+}										1	.486		.395	.397
MON Mg^{2+}											1		.827**	.866**
MON NH_4^+														
MON ClO_3^-													1	.992**
MON ClO_4^-														1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 5.27 Correlation between water quality parameters at TERLS, Post-monsoon

	POM pH	POM EC	POM TDS	POM SAL	POM Cl^-	POM NO_3^-	POM SO_4^{2-}	POM Na^+	POM K^+	POM Ca^{2+}	POM Mg^{2+}	POM NH_4^+	POM ClO_3^-	POM ClO_4^-
POM pH	1	-.004	-.320	-.318	-.147	-.717*	-.379	-.221	-.251	-.778*	-.257	-.440	.448	-.137
POM EC		1	.411	.423	-.222	.205	.268	.291	.198	.173	.229	.348	-.714*	-.226
POM TDS			1	1.000**	-.050	.632	.781*	.907**	.658	.470	.729*	.214	-.439	-.049
POM SAL				1	-.051	.621	.786*	.903**	.642	.464	.716*	.210	-.448	-.051
POM Cl^-					1	-.240	-.230	-.131	-.325	-.247	-.344	.325	.445	1.000**
POM NO_3^-						1	.460	.537	.707*	.940**	.687	.401	-.471	-.240
POM SO_4^{2-}							1	.894**	.520	.345	.671	-.210	-.631	-.232
POM Na^+								1	.739*	.320	.843**	-.056	-.467	-.126
POM K^+									1	.435	.980**	.291	-.443	-.317
POM Ca^{2+}										1	.420	.335	-.424	-.251
POM Mg^{2+}											1	.165	-.512	-.338
POM NH_4^+												1	-.219	.321
POM ClO_3^-													1	.453
POM ClO_4^-														1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 5.28 Correlation between water quality parameters at TERLS, Pre-monsoon

	PRM pH	PRM EC	PRM TDS	PRM SAL	PRM Cl^-	PRM NO_3^-	PRM SO_4^{2-}	PRM Na^+	PRM K^+	PRM Ca^{2+}	PRM Mg^{2+}	PRM NH_4^+	PRM ClO_3^-	PRM ClO_4^-
PRM pH	1	-.514	-.515	-.507	-.804*	-.495	-.269	-.305	-.348	-.132	-.405	.367	.509	-.116
PRM EC		1	1.000**	.999**	.907**	.891**	.130	.909**	.773*	.870*	.916**	.427	-.669	.348
PRM TDS			1	.999**	.907**	.891**	.130	.909**	.773*	.870*	.915**	.427	-.670	.349
PRM SAL				1	.906**	.882**	.104	.897**	.768*	.863*	.908**	.434	-.648	.332
PRM Cl^-					1	.779*	.140	.738	.669	.604	.753	.107	-.637	.337
PRM NO_3^-						1	.448	.844*	.675	.891**	.894**	.258	-.604	.410
PRM SO_4^{2-}							1	.153	.445	.298	.369	-.010	-.446	.177
PRM Na^+								1	.654	.912**	.859*	.423	-.695	.553
PRM K^+									1	.746	.879**	.689	-.791*	.045
PRM Ca^{2+}										1	.923**	.617	-.620	.362
PRM Mg^{2+}											1	.586	-.813*	.150
PRM NH_4^+												1	-.407	-.223
PRM ClO_3^-													1	-.082
PRM ClO_4^-														1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 5.29 Correlation between water quality parameters at TERLS, Monsoon

	MON pH	MON EC	MON TDS	MON SAL	MON Cl^-	MON NO_3^-	MON SO_4^{2-}	MON Na^+	MON K^+	MON Ca^{2+}	MON Mg^{2+}	MON NH_4^+	MON ClO_3^-	MON ClO_4^-
MON pH	1	.071	.071	.073	.180	-.304	-.127	.143	-.051	-.128	-.003	-.097		.074
MON EC		1	1.000**	.999**	.954**	.373	.815*	.984**	.733	.864*	.916**	.586		.150
MON TDS			1	.999**	.954**	.374	.816*	.984**	.732	.864*	.916**	.586		.151
MON SAL				1	.943**	.356	.831*	.982**	.719	.882**	.928**	.589		.139
MON Cl^-					1	.367	.655	.963**	.786*	.700	.765*	.496		.192
MON NO_3^-						1	.473	.244	.071	.240	.276	-.119		.024
MON SO_4^{2-}							1	.719	.271	.909**	.847*	.260		.151
MON Na^+								1	.815*	.829*	.891**	.661		.099
MON K^+									1	.537	.621	.822*		-.125
MON Ca^{2+}										1	.941**	.583		-.098
MON Mg^{2+}											1	.711		-.020
MON NH_4^+												1		-.279
MON ClO_3^-														.[a]
MON ClO_4^-														1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 5.30 Correlation between water quality parameters at Paravur, Post-monsoon

	POM pH	POM EC	POM TDS	POM SAL	POM Cl^-	POM NO_3^-	POM SO_4^{2-}	POM Na^+	POM K^+	POM Ca^{2+}	POM Mg^{2+}	POM NH_4^+	POM ClO_3^-	POM ClO_4^-
POM pH	1	-.211	-.211	-.214	-.363	-.226	.004	-.288	-.153	.300	-.293	.318		-.305
POM EC		1	1.000**	1.000**	.963**	.323	.951**	.977**	.370	.747	.967**	-.832*		.908*
POM TDS			1	1.000**	.963**	.324	.951**	.977**	.370	.747	.967**	-.832*		.908*
POM SAL				1	.963**	.319	.950**	.977**	.364	.746	.969**	-.832*		.911*
POM Cl^-					1	.450	.867*	.991**	.447	.542	.953**	-.788		.897*
POM NO_3^-						1	.387	.480	.969**	-.073	.168	-.540		.019
POM SO_4^{2-}							1	.921**	.457	.845*	.860*	-.882*		.772
POM Na^+								1	.487	.612	.943**	-.846*		.874*
POM K^+									1	.072	.178	-.581		.008
POM Ca^{2+}										1	.664	-.645		.616
POM Mg^{2+}											1	-.726		.984**
POM NH_4^+												1		-.623
POM ClO_3^-														
POM ClO_4^-														1
Paravur-post-monsoon														

a. Cannot be computed because at least one of the variables is constant.

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 5.31 Correlation between water quality parameters at Paravur, pre-monsoon

	PRM pH	PRM EC	PRM TDS	PRM SAL	PRM Cl^-	PRM NO_3^-	PRM SO_4^{2-}	PRM Na^+	PRM K^+	PRM Ca^{2+}	PRM Mg^{2+}	PRM NH_4^+	PRM ClO_3^-	PRM ClO_4^-
PRM pH	1	.240	.241	.257	-.138	-.183	.525	.422	-.118	.565	-.014	-.614	-.459	.465
PRM EC		1	1.000**	1.000**	.861*	.725	-.187	.942**	.835*	.793	.934**	.306	-.360	-.299
PRM TDS			1	1.000**	.861*	.725	-.186	.942**	.835*	.793	.934**	.305	-.360	-.299
PRM SAL				1	.854*	.723	-.172	.949**	.831*	.796	.930**	.289	-.362	-.283
PRM Cl^-					1	.652	-.145	.713	.855*	.424	.984**	.715	-.417	-.242
PRM NO_3^-						1	-.275	.722	.911*	.363	.712	.239	.336	-.331
PRM SO_4^{2-}							1	-.009	-.126	-.286	-.146	-.223	-.314	.983**
PRM Na^+								1	.753	.775	.824*	.025	-.278	-.094
PRM K^+									1	.407	.881*	.502	.002	-.235
PRM Ca^{2+}										1	.548	-.138	-.376	-.389
PRM Mg^{2+}											1	.585	-.397	-.247
PRM NH_4^+												1	-.288	-.290
PRM ClO_3^-													1	-.238
PRM ClO_4^-														1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 5.32 Correlation between water quality parameters at Paravur, Monsoon

	MON pH	MON EC	MON TDS	MON SAL	MON Cl^-	MON NO_3^-	MON SO_4^{2-}	MON Na^+	MON K^+	MON Ca^{2+}	MON Mg^{2+}	MON NH_4^+	MON ClO_3^-	MON ClO_4^-
MON pH	1	-.298	-.297	-.285	-.282	-.433	-.270	-.254	-.601	-.377	-.291	-.185	-.222	.183
MON EC		1	1.000**	1.000**	.994**	.825*	.994**	.997**	.929**	.978**	.992**	.988**	.989**	-.371
MON TDS			1	1.000**	.994**	.825*	.994**	.997**	.929**	.978**	.992**	.988**	.989**	-.372
MON SAL				1	.993**	.825*	.995**	.997**	.925**	.978**	.993**	.990**	.990**	-.358
MON Cl^-					1	.813*	.987**	.997**	.924**	.982**	.993**	.979**	.988**	-.392
MON NO_3^-						1	.870*	.832*	.898*	.818*	.862*	.846*	.861*	-.593
MON SO_4^{2-}							1	.996**	.928**	.969**	.995**	.996**	.997**	-.417
MON Na^+								1	.918**	.975**	.995**	.992**	.995**	-.405
MON K^+									1	.952**	.938**	.890*	.912*	-.414
MON Ca^{2+}										1	.986**	.952**	.969**	-.278
MON Mg^{2+}											1	.988**	.996**	-.379
MON NH_4^+												1	.996**	-.399
MON ClO_3^-													1	-.406
MON ClO_4^-														1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 5.33 Correlation between water quality parameters at Kottayam, Post-monsoon

	POM pH	POM EC	POM TDS	POM SAL	POM Cl^-	POM NO_3^-	POM SO_4^{2-}	POM Na^+	POM K^+	POM Ca^{2+}	POM Mg^{2+}	POM NH_4^+	POM ClO_3^-	POM ClO_4^-
POM pH	1	.585	.585	-.299	.671	-.530	-.019	.526	.577	.729	.441	.010		.036
POM EC		1	1.000**	.220	.967**	.005	-.255	.982**	.300	.917**	.495	-.335		-.317
POM TDS			1	.220	.967**	.005	-.256	.982**	.300	.917**	.494	-.336		-.318
POM SAL				1	.231	.211	-.354	.378	.449	-.056	.186	-.359		-.354
POM Cl^-					1	-.213	-.316	.943**	.472	.921**	.451	-.355		-.334
POM NO_3^-						1	.165	.067	-.590	-.276	.132	.145		.118
POM SO_4^{2-}							1	-.304	-.358	-.073	.593	.951**		.955**
POM Na^+								1	.379	.846*	.516	-.380		-.362
POM K^+									1	.282	.253	-.270		-.243
POM Ca^{2+}										1	.504	-.189		-.164
POM Mg^{2+}											1	.539		.560
POM NH_4^+												1		.999**
POM ClO_3^-														
POM ClO_4^-														1

a. Cannot be computed because at least one of the variables is constant.

**. Correlation is significant at the 0.01 level (2-tailed).

Table 5.34 Correlation between water quality parameters at Kottayam, Pre-monsoon

	PRM pH	PRM EC	PRM TDS	PRM SAL	PRM Cl^-	PRM NO_3^-	PRM SO_4^{2-}	PRM Na^+	PRM K^+	PRM Ca^{2+}	PRM Mg^{2+}	PRM NH_4^+	PRM ClO_3^-	PRM ClO_4^-
PRM pH	1	.249	.294	.365	.319	.094	-.054	.344	.214	.171	.024		.271	
PRM EC		1	.993**	.915**	.970**	-.300	.698	.962**	.933**	.982**	.201		-.670	
PRM TDS			1	.902**	.962**	-.330	.638	.946**	.911**	.963**	.170		-.588	
PRM SAL				1	.980**	-.362	.617	.986**	.929**	.905**	-.002		-.578	
PRM Cl^-					1	-.410	.693	.994**	.965**	.966**	.026		-.602	
PRM NO_3^-						1	-.394	-.329	-.471	-.392	.790*		-.121	
PRM SO_4^{2-}							1	.697	.769*	.811*	.077		-.685	
PRM Na^+								1	.954**	.957**	.091		-.642	
PRM K^+									1	.962**	-.073		-.662	
PRM Ca^{2+}										1	.123		-.703	
PRM Mg^{2+}											1		-.465	
PRM NH_4^+													.[a]	
PRM ClO_3^-													1	
PRM ClO_4^-														

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 5.35 Correlation between water quality parameters at Kottayam, Monsoon

	MON pH	MON EC	MON TDS	MON SAL	MON Cl^-	MON NO_3^-	MON SO_4^{2-}	MON Na^+	MON K^+	MON Ca^{2+}	MON Mg^{2+}	MON NH_4^+	MON ClO_3^-	MON ClO_4^-
MON pH	1	.354	.353	.180	.230	-.268	.216	-.306	-.261	.158	-.632	-.210	.000	.785*
MON EC			1.000**	.884**	.732	.040	.837*	.612	.678	.970**	.157	-.944**	-.296	.403
MON TDS			1	.885**	.733	.040	.838*	.614	.679	.970**	.159	-.944**	-.296	.402
MON SAL				1	.630	-.271	.983**	.623	.734	.931**	.355	-.765*	-.354	.137
MON Cl^-					1	.245	.563	.676	.323	.753	-.102	-.660	-.159	.458
MON NO_3^-						1	-.284	.126	.195	.071	-.251	-.186	.331	.198
MON SO_4^{2-}							1	.511	.749	.891**	.280	-.695	-.269	.169
MON Na^+								1	.587	.707	.632	-.725	-.068	.018
MON K^+									1	.792*	.524	-.716	.005	-.040
MON Ca^{2+}										1	.276	-.916**	-.270	.269
MON Mg^{2+}											1	-.307	-.156	-.572
MON NH_4^+												1	.127	-.397
MON ClO_3^-													1	.468
MON ClO_4^-														1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Table 5.36 General correlation between mean values of all water quality parameters

	pH	**EC**	**TDS**	**SAL**	**Cl^-**	**NO_3^-**	**SO_4^{2-}**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**NH_4^+**	**ClO_3^-**	**ClO_4^-**
pH	1	.168	.196	.186	.028	.068	.042	.142	.025	.193	-.006	-.047	-.307	-.253
EC		1	.993**	.994**	.634*	.773**	.864**	.978**	.952**	.842**	.782**	.471	.056	-.315
TDS			1	.999**	.661*	.783**	.864**	.978**	.928**	.896**	.764**	.403	.004	-.326
SAL				1	.662*	.790**	.865**	.981**	.931**	.891**	.769**	.403	.014	-.327
Cl^-					1	.502	.800**	.646*	.556	.741**	.895**	-.044	-.076	-.257
NO_3^-						1	.549	.709**	.818**	.727**	.509	.085	.186	-.140
SO_4^{2-}							1	.912**	.843**	.828**	.849**	.520	-.044	-.362
Na^+								1	.922**	.867**	.770**	.502	.013	-.331
K^+									1	.763**	.712**	.582*	.148	-.275
Ca^{2+}										1	.645*	.167	-.118	-.281
Mg^{2+}											1	.237	.068	-.270
NH_4^+												1	.142	-.174
ClO_3^-													1	.840**
ClO_4^-														1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

5.5 Conclusion

Perchlorate contamination was noticed in all the sites in all seasons. But it varied with season and source. The contamination of perchlorate was found to be site dependant. More the usage more was the contamination. Natural processes like rainfall, temperature etc. also aided in bringing perchlorate to drinking water sources. Rocket propellant manufacturing and consumption and firework manufacturing were found to be the major sources of perchlorate in Kerala. Firework manufacturing sites were located in almost all districts of Kerala and show a chance of widespread contamination of perchlorate in drinking water. Correlation of perchlorate with other water quality parameters showed that it was significantly correlated to chlorate and almost nil with other parameters except a few. Research in this area is needed.

6.1 Introduction

Fireworks are used worldwide to celebrate festivals (Vecchi *et al.,* 2008). Chemicals such as potassium nitrates, potassium chlorate, potassium perchlorate, charcoal, sulfur, manganese, sodium oxalate, aluminum and iron dust powder, strontium nitrate, barium nitrate, etc. are mainly used in fireworks (Ravindra *et al.*, 2003). Hence the fireworks release pollutants, such as sulfur dioxide, carbon dioxide, carbon monoxide, suspended particles, perchlorate and several metals. Fireworks can cause perchlorate contamination in the environment and was reported elsewhere (Sijimol *et al.,* 2014a,b; SERDP, 2005; Backus *et al.,* 2005; Munster *et al.,* 2009; Isobe *et al.,* 2012 ; Shi *et al.*, 2007). Fireworks vary greatly in perchlorate content with respect to the loudness of explosions, colored flames and bright light (SERDP, 2005; Thomson and Potter, 2000). Potassium perchlorate and ammonium perchlorate are commonly used for manufacturing fireworks (Wu *et al.*, 2011; Motzer, 2001). However there are crackers which have no perchlorate or very little perchlorate (Conkling, 1985; Zhang, 2010).

Kerala is having a variety of firework displays during the festivals and other celebrations. However, very less number of data is available on perchlorate contamination of water bodies in Kerala (Anupama *et al.*, 2012) and still more to be studied on the real role of fireworks behind the contamination.Hence the present study assessed the role of fireworks in perchlorate contamination of water resources.

6.2 Objective

To assess the role of fireworks in environmental perchlorate contamination

6.3 Methodology

Study area and sample collection

Kerala is a host of firework displays. Festivals and celebrations are always enjoyed with huge firework displays. Major five firework display sites (Site 1 to Site 5) were selected for the study which includes mainly temple and church festivals (Fig. 6.1).

Geographical locations of sites were given in Table 6.1. The samples (n=5) were collected from the vicinity of firework display ground (around 500 meters surrounding). A control site (Site 6) was also selected near the site 2 (5kms away, opposite to wind direction). Water and soil samples were collected before and after fireworks and analyzed for perchlorate and chlorate. In order to study the transport of perchlorate near the firework display areas, a continuous sampling was done at a selected site (site 5-Athirampuzha). At Athirampuzha fireworks display site (site 5), sampling was done on alternate days for first week, intermittently during the next week and then weekly (Days 1, 3, 5, 7, 10, 15, 20, 30 and 60), till the perchlorate values reached the baseline as before fireworks. Each time nine soil samples (2 from the firework displaying ground) and seven water samples were collected from the surrounding areas. A total of 90 soil samples and 70 water samples were collected.

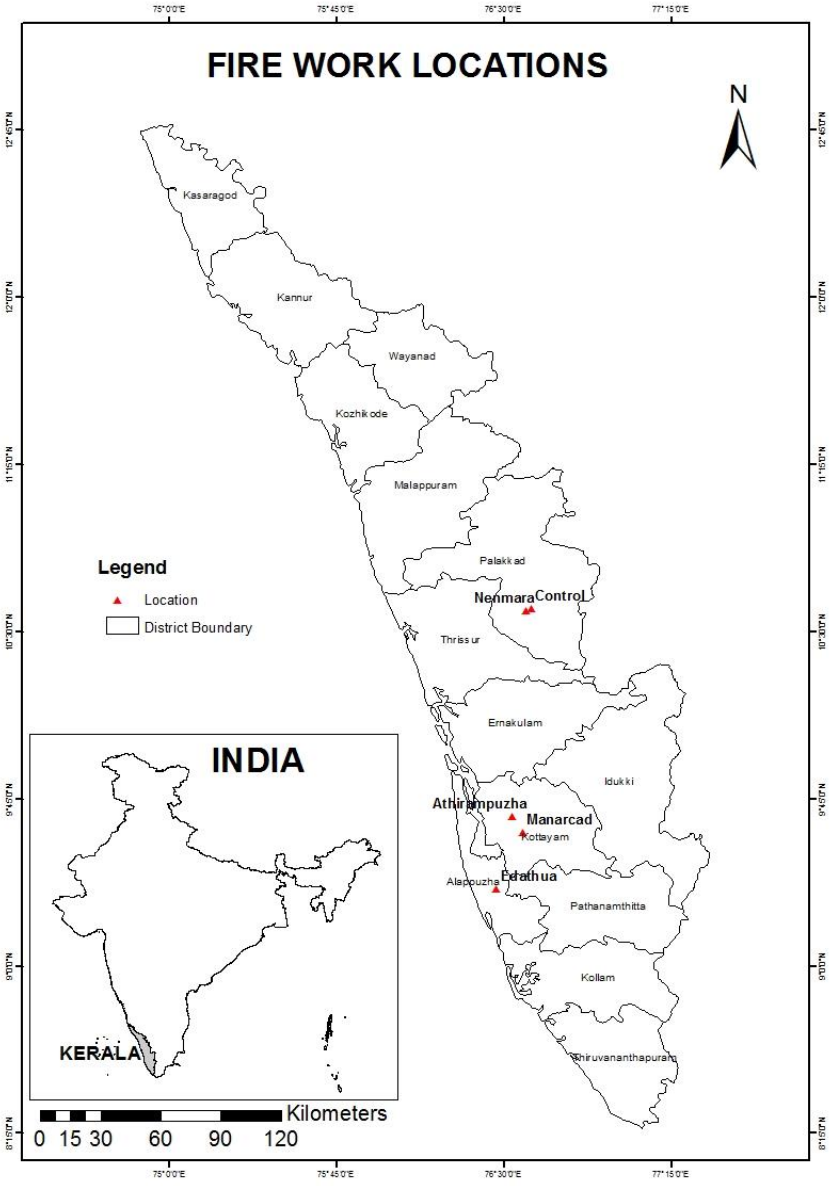


Fig. 6.1 Firework display sampling locations

Table 6.1 Latitude and longitude of firework display and control sites

Sl.No	Latitude	Longitude	Type of water sample
a. Site-1 Thrissur Pooram			
1	10.516769	76.200191	Well
2	10.516776	76.200199	Well
3	10.516823	76.216709	Well
Ground	10.516774	76.200232	Soil
b. Site 2 Nenmara vallangi vela, Palakkad			
1	10.593222	76.599378	Well
2	10.600478	76.611481	Well
3	10.594392	76.605444	Well
4	10.585294	76.604278	Well
c. Site-3 Edathua fireworks display, Alappuzha			
1	9.350266	76.466796	Well
2	9.366687	76.466783	Well
3	9.350268	76.466779	Well
4	9.350264	76.466774	Well
R	9.350275	76.466817	River
Ground	9.350276	76.466794	Soil
d. Site-4 Manarcad fireworks display, Kottayam			
1	9.602	76.583806	Well
2	9.601028	76.583806	Well
3	9.600306	76.584278	Well
4	9.600139	76.583861	Well

5	9.601056	76.585778	Well
6	9.599889	76.586444	Well
7	9.601333	76.586528	Well
8	9.601444	76.586639	Well
e. Site-5 Athirampuzha fireworks display, Kottayam			
1	9.671947	76.5364	Well water
2	9.669369	76.536317	Well water
3	9.663808	76.542303	Well water
4	9.605992	76.546060	Well water
5	9.7678	76.5455	Well water
6	9.668847	76.5394	Well water
7	9.666687	76.538103	Well water
Ground	9.665233	76.546333	Soil
f. Site-6 Fireworks control site			
1	10.60335	76.622867	Well
2	10.603742	76.623550	Well
3	10.603655	76.623286	Well
4	10.603925	76.623011	Well

Sample pre-treatment

Water samples (well and stream) were collected within 500 meters of the firework display site. Samples were immediately filtered using 0.2µ nylon membrane filter paper and stored in sterile bottles below 4˚C, for further analysis. Water quality parameters like pH, EC, TDS, salinity, anions like chloride, nitrate, sulfate, chlorate and perchlorate; and cations like sodium, potassium, calcium, magnesium and ammonium were measured (Described in detail in Chapter-3).

Soil samples were collected from the display ground, from the windward side and from different directions within an area of 500 meter sq. Perchlorate, chlorate, pH and organic carbon (OC) of soil samples were analyzed (Described in detail in Chapter-3).

6.4 Results and discussion

Firework display was found to be one of the reasons for environmental perchlorate contamination. None of the samples, both soil and water, before fireworks were found to be contaminated with perchlorate. However, after the fireworks display soil samples from all the sites were found to be heavily contaminated with perchlorate. The mean perchlorate before and after fireworks display of different sites were given in the Table 6.2.

Perchlorate content in soil samples varied with respect to site (Table 6.2). Mean perchlorate in soil after fireworks ranged from 16.62 ppb (Manarcad- site 4) to 20451.14 ppb (Palakkad- site 2). The perchlorate content in soil showed variation because of the variation in amount of fireworks cracked, distance from the site, partial combustion of fireworks etc. In the control site, perchlorate and chlorate in soil was below detectable limit. Perchlorate was detected from well water samples, after fireworks display at Palakkad (site 2) and Manarcad (site 4) (Table 6.2). Apart from perchlorate, soil samples were found to be heavily contaminated with chlorate, while the same was in BDL before fireworks display (Table 6.3). Chlorate ranged from 1035.32 ppb (Manarcad- site 4) to 298780.40 ppb (Palakkad- site 2). Site 2 (Palakkad) had highest mean perchlorate and chlorate and Site 4 (Manarcad) had lowest mean perchlorate and chlorate.

pH and OC of soil samples were also measured. Mean pH before fireworks ranged from 4.96 (Palakkad- site 2) to 6.81 (Edathua- site 3) and after fireworks it was 5.10 (Palakkad- site 2) to 6.90 (Edathua- site 3). In the case of OC, the values ranged from 1.27 % (Edathua- site 3) to 3.71 % (Manarcad- site 4) before fireworks and from 1.38 % (Edathua- site 3) to 3.81 % (Manarcad- site 4) after fireworks (Table 6.3).

Table 6.2 Mean perchlorate in water and soil before and after fireworks at different sites

Site name	Perchlorate (n=5)			
	Before		After	
	Water (ppb)	Soil (µg/kg)	Water (ppb)	Soil (µg/kg)
Site – 1 Thrissur	BDL	BDL	BDL	3230.62±1783.89
Site – 2 Palakkad	BDL	BDL	7.23±8.55	20451.14±17767.34
Site – 3 Edathua	BDL	BDL	BDL	1143.24±2067.23
Site – 4 Manarcad	BDL	BDL	1.89±3.75	16.62±42.83
Site -5 Athirampuzha	BDL	BDL	1.96±3.74	6516.62±715.09
Site-6 Fireworks Control	BDL	BDL	BDL	BDL

Table 6.3 Mean chlorate, pH and OC in soil before and after fireworks at different sites

Site name	Chlorate (n=5) (µg/kg)		pH		OC (%)	
	Before	After	Before	After	Before	After
Site – 1 Thrissur	BDL	159453.0	5.84	5.98	1.42	1.48
Site – 2 Palakkad	BDL	298780.40	4.96	5.10	1.52	1.50
Site – 3 Edathua	BDL	1780.72	6.81	6.90	1.27	1.38
Site – 4 Manarcad	BDL	1035.32	5.36	5.51	3.71	3.81
Site-5 Athirampuzha	BDL	10543.01	6.08	6.81	0.06	0.06
Site-6 Fireworks Control	BDL	BDL	6.22	6.33	2.46	2.48

Results were discussed based on site.

Site-1 (Thrissur fireworks display)

Perchlorate and chlorate in the samples before fireworks were BDL (Table 6.4). After fireworks, perchlorate values ranged from 1587.48 ppb (S1s) to 5330.10 ppb (G3s). Ground sample had maximum perchlorate and chlorate (Table 6.4). Variation of pH, chlorate and perchlorate in soil samples were found to be highly significant ($p<0.05$). In the case of water samples (Table 6.5 and 6.6), only pH and ammonium had significant variation ($p<0.1$). All other parameters were almost similar prior to and after fireworks. Perchlorate in water samples before and after fireworks was BDL only. No open wells were found in the nearby areas of the site.

Table 6.4 Perchlorate and other parameters in soil before and after fireworks, Site-1

Sl.No	**pH**		**OC (%)**		**Chlorate (µg/kg)**		**Perchlorate (µg/kg)**	
	Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**
S1s	6.40	6.68	1.62	1.42	BDL	63749.92	BDL	1587.48
S2 s	6.25	6.93	1.20	1.48	BDL	150606.90	BDL	4994.28
G1 s	5.24	6.08	1.60	1.69	BDL	84812.32	BDL	2273.42
G2 s	5.61	6.16	1.21	1.53	BDL	130707.30	BDL	1967.82
G3 s	5.70	6.48	1.48	1.62	BDL	367388.80	BDL	5330.10

Table 6.5 Perchlorate and other water quality parameters before fireworks display at Site-1

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
TBS1W	6.36	174.40	87.20	0.09	25.27	27.74	21.46	26.83	29.80	32.33	5.61	BDL	1004.16	BDL
TBS2W	6.20	328.0	164.0	0.23	78.44	24.78	31.26	43.81	34.88	58.24	12.19	BDL	BDL	BDL
TBS3W	6.30	249.0	124.70	0.12	34.97	22.85	34.06	38.44	26.95	47.72	11.67	BDL	379.76	BDL
TBS4W	6.43	153.50	76.80	0.08	27.16	18.42	21.69	29.74	11.25	27.42	5.941	BDL	BDL	BDL
TBS5W	6.35	365.0	182.40	0.18	46.89	39.69	42.27	48.94	33.85	102.21	10.16	BDL	BDL	BDL

Table 6.6 Perchlorate and other water quality parameters after fireworks display at Site-1

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
TAS1W	6.83	178.0	91.0	0.10	36.63	49.68	24.59	39.06	37.79	54.19	7.24	0.50	BDL	BDL
TAS2W	6.29	348.10	173.0	0.06	24.82	36.29	21.62	29.12	27.28	37.08	5.34	0.59	BDL	BDL
TAS3W	6.61	269.80	143.60	0.10	36.79	6.39	13.90	38.78	20.65	30.49	6.28	1.46	BDL	BDL

Site-2 (Palakkad Nenmara Vallangi Vela fireworks display)

None of the soil samples had perchlorate and chlorate before fireworks (Table 6.7). A spike of perchlorate and chlorate was observed after fireworks. Perchlorate values ranged from 450.30 ppb (S1s) to 42141.42 ppb (G1s) and chlorate ranged from 91786.0 ppb (G1s) to 586296.70 ppb (S2s). pH and OC varied slightly before and after fireworks, but the variation did not show any significance ($p>0.1$). At the same time perchlorate and chlorate showed highly significant variation before and after fireworks ($P<0.05$).

Before fireworks, water was free from chlorate and perchlorate (Table 6.8). After fireworks perchlorate ranged from BDL to 14.65 ppb (pond sample) (Table 6.9). Perchlorate was detected in S1W and pond sample, both lying within the site. Both chlorate and perchlorate showed highly significant variation before and after fireworks ($p<0.05$). No other water quality parameters had significant variation.

Table 6.7 Perchlorate and other parameters in soil before and after fireworks, Site -2

Sl.No	pH		OC (%)		Chlorate(µg/kg)		Perchlorate(µg/kg)	
	Before	After	Before	After	Before	After	Before	After
S1s	5.76	5.83	1.60	1.70	BDL	172773.0	BDL	450.30
S2s	4.65	4.69	1.80	1.80	BDL	586296.70	BDL	8580.68
G1s	4.92	5.02	1.60	1.30	BDL	91786.0	BDL	42141.42
G2s	4.68	5.39	1.20	1.30	BDL	426152.70	BDL	35528.58
G3s	4.81	5.63	1.40	1.40	BDL	216893.80	BDL	15554.70

Table 6.8 Perchlorate and other water quality parameters before fireworks display at Site-2

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
PBS1 W	5.26	87.0	43.50	0.05	16.39	0.18	1.20	15.54	19.18	13.91	6.40	BDL	BDL	BDL
PBS2 W	5.41	62.30	31.20	0.03	6.30	1.64	2.83	11.44	3.57	18.05	4.02	BDL	BDL	BDL
PBS3 W	6.02	511.0	256.0	0.25	87.45	1.45	45.49	138.79	12.73	104.07	20.62	BDL	BDL	BDL
PBS4 W	6.37	392.0	195.90	0.19	43.15	0.05	34.19	61.69	16.39	77.12	33.55	BDL	BDL	BDL
PBpond	6.59	167.90	83.90	0.08	23.91	0.11	4.71	42.32	8.40	34.17	8.362	BDL	BDL	BDL

Table 6.9 Perchlorate and other water quality parameters after fireworks display at Site-2

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
PAS1 W	5.28	89.0	49.0	0.05	17.36	0.47	2.55	2.29	19.09	7.93	0.04	BDL	148.64	19.46
PAS2 W	5.23	60.30	32.0	0.03	6.72	0.05	2.81	11.19	2.98	18.32	4.80	BDL	BDL	9.28
PAS3 W	6.08	329.0	169.0	0.22	73.11	1.63	14.44	47.19	13.33	36.33	25.51	BDL	495.92	BDL
PAS4 W	6.60	509.0	238.0	0.20	64.12	6.67	20.31	18.16	4.98	49.76	33.06	BDL	1632.4	BDL
PAS5 W	6.28	428.0	203.0	0.06	18.01	2.29	13.84	38.62	7.50	41.18	10.65	BDL	BDL	BDL
PApond	6.91	170.30	86.30	0.08	23.39	0.06	4.53	43.13	7.74	36.42	8.26	BDL	267.52	14.65

Site- 3 (Edathua fireworks display)

Perchlorate and chlorate in soil was BDL before fireworks at Edathua (site 3) (Table 6.10). After fireworks, perchlorate values in soil ranged from 49.30 ppb (S1s) to 4826.80 ppb (G1s) (Table 6.10). Chlorate in soil ranged from 741.60 ppb (G1s) to 2571.68 ppb (S1s). Both perchlorate and chlorate in soil samples had significant variation before and after fireworks ($p<0.05$). pH and OC did not show any significant variation.

Both perchlorate and chlorate in water samples were BDL before and after fireworks display (Table 6.11 and Table 6.12). Significant variation was observed ($p<0.1$) for salinity, chloride, sodium, calcium and magnesium and highly significant variation ($p<0.05$) was shown by nitrate and sodium. As the land is lying below the sea level, continuous influx of saline water could have resulted in the significant variation of water quality parameters.

Table 6.10 Perchlorate and other parameters in soil before and after fireworks, Site-3

Sl.No	**pH**		**OC (%)**		**Chlorate (µg/kg)**		**Perchlorate (µg/kg)**	
	Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**
S1 s	5.65	6.01	0.96	1.03	BDL	2571.68	BDL	49.30
S2 s	6.68	6.93	0.96	1.12	BDL	1500.16	BDL	112.30
S3 s	7.30	7.46	1.20	1.42	BDL	830.16	BDL	204.52
G1 s	7.12	7.48	1.61	1.89	BDL	741.60	253.9	4826.80
G2 s	7.31	7.63	1.61	1.93	BDL	3260.0	BDL	523.30

Table. 6.11 Perchlorate and other water quality parameters before fireworks display at Site-3

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
EBS1W	5.95	898.0	450.0	0.44	167.69	1.06	1.60	252.26	19.75	82.44	21.54	BDL	BDL	BDL
EBS2W	5.65	774.0	387.0	0.58	223.09	0.34	4.52	124.01	12.54	166.42	34.56	3.33	BDL	BDL
EBS3W	5.71	429.0	215.0	0.21	62.14	0.15	3.94	73.99	31.23	65.75	26.89	6.62	BDL	BDL
EBS4W	5.90	638.0	319.0	0.31	128.30	1.51	22.89	136.67	19.52	97.04	21.72	10.69	BDL	BDL
EBS5W	5.85	672.0	336.0	0.33	173.35	2.96	29.75	146.15	40.96	96.95	47.32	BDL	BDL	BDL
EBR1 W	6.03	34.0	16.99	0.02	6.70	BDL	2.0	8.48	3.70	6.70	2.59	0.14	BDL	BDL
EBR2 W	5.90	26.30	13.17	0.02	4.63	BDL	1.38	8.69	4.02	5.89	2.68	0.20	BDL	BDL

Table 6.12 Perchlorate and other water quality parameters after fireworks display at Site-3

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
EAS1W	5.63	902.0	469.0	0.12	39.02	12.39	12.53	29.39	7.97	28.98	5.20	0.06	BDL	BDL
EAS2W	5.78	836.0	402.0	0.02	2.47	0.05	1.40	3.81	8.34	9.58	1.99	BDL	BDL	BDL
EAS3W	6.01	442.0	368.0	0.20	58.59	14.18	28.93	71.30	14.88	88.93	13.61	5.28	BDL	BDL
EAS4W	5.98	609.0	323.0	0.30	117.51	4.82	95.22	105.55	36.25	112.80	42.54	1.33	BDL	BDL
EAS5W	6.13	683.0	246.0	0.18	50.99	12.67	21.55	43.86	18.16	35.84	11.35	0.39	BDL	BDL
EAR1W	6.08	54.20	23.08	0.02	6.30	5.47	3.18	8.36	4.08	8.37	2.64	0.19	BDL	BDL
EAR2W	6.06	46.90	32.13	0.03	5.29	5.03	2.65	7.67	3.66	6.40	2.21	0.18	BDL	BDL

Site-4 (Manarcad fireworks display)

None of the soil samples were contaminated with chlorate and perchlorate before fireworks (Table 6.13). After the display, chlorate was found to be the maximum in G1s (8952.08 ppb). Only ground samples showed perchlorate contamination after fireworks (Table 6.13) and the maximum value observed was 143.44 ppb (G1s). pH and OC of soil samples showed significant variation.

In the case of water, none of the samples had chlorate or perchlorate before fireworks (Table 6.14). But after the fireworks, perchlorate was detected in two samples with values 8.71 ppb (S4W) and 8.29 ppb (S5W) (Table 6.15). S4W lies in the site and S5W very close to the site. Significant variation was observed for chlorate and perchlorate in water samples ($p<0.1$).

Table 6.13 Perchlorate and other parameters in soil before and after fireworks, Site-4

Sl.No	pH		OC (%)		Chlorate (µg/kg)		Perchlorate (µg/kg)	
	Before	**After**	**Before**	**After**	**Before**	**After**	**Before**	**After**
S1 s	4.48	4.65	3.71	2.72	BDL	50.56	BDL	BDL
S2 s	5.17	6.84	3.44	3.80	BDL	BDL	BDL	BDL
S3 s	4.40	5.17	3.58	4.26	BDL	BDL	BDL	BDL
S4 s	5.36	5.61	3.67	5.21	BDL	222.96	BDL	BDL
S5 s	4.77	6.0	2.99	4.75	BDL	BDL	BDL	BDL
S6 s	5.04	4.53	4.75	4.08	BDL	154.88	BDL	BDL
S7 s	5.42	5.17	3.94	4.35	BDL	BDL	BDL	BDL
G1 s	4.01	5.69	3.49	3.67	BDL	8952.08	BDL	143.44
G2 s	3.92	4.75	4.35	4.17	BDL	862.72	BDL	23.94
G3 s	4.01	6.30	4.53	3.62	BDL	655.76	BDL	BDL
G4 s	4.07	5.92	2.40	5.62	BDL	489.52	BDL	15.48

Table 6.14 Perchlorate and other water quality parameters before fireworks display at Site-4

Sl.No	pH	EC(µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
MBS1W	4.40	69.10	34.60	2.0	23.45	4.57	7.77	18.11	6.86	4.01	2.11	3.75	BDL	BDL
MBS2W	4.58	82.20	41.10	5.0	19.68	17.64	11.88	17.93	10.68	8.88	3.34	11.22	BDL	BDL
MBS3W	5.31	106.30	53.20	3.0	13.39	18.94	18.95	14.67	10.78	27.50	5.24	2.61	BDL	BDL
MBS4W	5.08	85.20	42.60	2.0	BDL	BDL	BDL	15.34	4.90	26.02	3.27	6.17	BDL	BDL
MBS5W	5.98	232.0	116.0	5.0	15.79	7.55	36.80	17.82	12.34	95.93	7.64	2.72	BDL	BDL
MBS6W	5.77	183.70	91.80	6.0	20.25	7.83	30.91	21.80	10.32	66.0	7.02	5.18	BDL	BDL
MBS7W	4.79	65.0	32.50	7.0	11.90	15.42	8.91	11.71	4.79	14.27	3.23	5.72	BDL	BDL
MBS8W	4.51	101.0	50.50	4.0	43.99	14.82	1.89	36.45	6.32	8.56	3.54	12.05	BDL	BDL
MBS9W	4.73	83.70	40.50	4.0	24.87	10.54	7.71	24.92	5.34	11.80	3.03	5.85	BDL	BDL

Table 6.15 Perchlorate and other water quality parameters after fireworks display at Site-4

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
MAS1W	4.09	71.30	35.70	2.0	23.56	5.38	7.08	20.83	9.03	5.47	2.61	11.07	BDL	BDL
MAS2W	4.56	86.40	43.20	7.0	21.20	17.84	12.15	20.06	11.55	10.62	3.85	11.42	BDL	BDL
MAS3W	4.88	112.20	56.10	8.0	13.14	19.05	17.93	14.82	10.05	29.43	5.63	8.75	BDL	BDL
MAS4W	4.83	91.80	45.90	3.0	16.78	1.75	16.50	15.65	7.73	26.91	3.91	8.09	BDL	8.71
MAS5W	5.59	188.80	94.40	6.0	25.03	9.71	26.74	26.12	10.64	61.82	9.48	4.42	BDL	8.29
MAS6W	5.60	183.90	92.0	6.0	24.36	10.86	25.60	24.09	10.22	61.42	7.94	4.95	BDL	BDL
MAS7W	4.70	66.50	33.20	6.0	13.71	15.79	7.24	13.57	6.11	15.62	3.64	4.03	BDL	BDL
MAS8W	4.33	116.0	58.0	4.0	48.95	13.51	1.17	40.62	7.87	9.61	3.94	5.60	BDL	BDL
MAS9W	4.50	87.20	43.60	5.0	25.06	11.40	8.71	26.27	5.48	12.45	3.22	5.74	BDL	BDL

Site-6 (Control site)

Chlorate and perchlorate was not detected from the water and soil samples of fireworks control site before and after the display in the nearby site (Palakkad- site 2) (Table 6.16 to Table 6.18). Significant variation was seen for pH and EC of water samples only. No other parameters in water or soil had significant variation.

Table 6.16 Perchlorate and other parameters in soil set-1 and set-2, Site-6

Sl.No	pH		OC (%)		Chlorate(µg/kg)		Perchlorate(µg/kg)	
	Set-1	Set-2	Set-1	Set-2	Set-1	Set-2	Set-1	Set-2
S1 s	6.0	6.20	2.85	2.63	BDL	BDL	BDL	BDL
S2 s	6.10	6.19	1.93	2.40	BDL	BDL	BDL	BDL
S3 s	6.57	6.60	2.61	2.42	BDL	BDL	BDL	BDL

Table 6.17 Perchlorate and other water quality parameters in set-1 at Site-6

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
FCBSIW	6.50	292.0	146.0	0.14	49.36	0.07	22.93	57.02	7.71	37.91	40.95	BDL	BDL	BDL
FCBS2W	6.53	328.0	164.20	0.16	51.89	BDL	43.31	69.25	7.19	40.89	41.03	BDL	BDL	BDL
FCBS3W	6.58	378.0	189.10	0.18	60.38	BDL	28.12	65.66	9.97	59.79	48.86	BDL	BDL	BDL
FCBS4W	7.17	95.10	476.0	0.47	191.44	37.70	91.45	133.94	135.51	156.81	80.46	BDL	BDL	BDL

Table 6.18 Perchlorate and other water quality parameters set-2 at Site-6

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
FCAS1W	8.21	537.0	269.0	0.17	57.29	0.08	44.79	92.68	51.03	84.79	31.73	BDL	BDL	BDL
FCAS2W	7.11	396.0	197.80	0.16	53.67	0.06	30.32	73.16	7.70	46.88	42.41	BDL	BDL	BDL
FCAS3W	7.69	403.0	202.0	0.17	56.94	0.07	27.89	66.09	10.14	60.89	48.63	BDL	BDL	BDL
FCAS4W	7.94	1045.0	523.0	0.46	184.67	26.39	88.19	131.96	130.92	178.20	84.49	BDL	BDL	BDL

Variation of perchlorate in soil might be due to variation in the amount of fireworks used for the display. The increase in quantity of fireworks will result in more contamination. Also the perchlorate content in fireworks may vary with the type and the manufacturer. The spent out or unused perchlorate will increase when the content of perchlorate in firework increases. However the complete combustion of perchlorate is significant as the incomplete combustion results in the persistence of perchlorate in the environment. For example, 1000-2000 aerial shells weighing a total of 1,361kg, of which 40% is perchlorate, can contaminate an area (fireworks fall out area) around 3,600 m^2 (DEP, 2006). Hence the rate of combustion will determine the perchlorate influx into the soil or water environment.

In the case of water samples, perchlorate was detected from the wells, either situated within the site or very close to the site, in the windward direction. Munster *et al.*, (2009) showed that groundwater get contaminated to the tens of µg perchlorate per liter within 100 meters of fireworks display. But at site 1 (Thrissur) and site 3 (Edathua), we could not trace wells within or close to the display ground. Hence the unavailability of water sources (wells) may be the reason that no perchlorate was detected from the water samples collected from these sites after fireworks. Like perchlorate, chlorate in various forms is used in fireworks. Moreover, perchlorate during explosion gets converted to chlorate and chlorine, the free chlorine combines with other metals to give colors. Incomplete burning of the perchlorate will give rise to chlorate also. Only a few other parameters analyzed showed significant variation before and after fireworks in selected sites and might be owed to other geographical parameters. Except perchlorate and chlorate, none of the water quality parameters had significant variation in all sites and this points that other parameters does not reach water bodies immediately after fireworks or these might not get easily transported. This also pointed a chance of over use of perchlorate in the fireworks. Other parameters could have easily used up during the time of display. Perchlorate is usually used in large quantities compared to other parameters to increase the effect (height of explosion, flash and light effect etc.) of firework displays.

Transport of perchlorate

Perchlorate in soil samples and water samples were monitored continuously at Athirampuzha fireworks display site 5. Perchlorate and chlorate in soil and water samples before firework display was BDL while after fireworks the concentration increased especially in soil samples. Average wind velocity in the area ranged from 3.02 to 5.2 km/h during day time and from 0.66 to 2.03 km/h during night time. The wind direction was North- North East during night time and South- South West during day time.

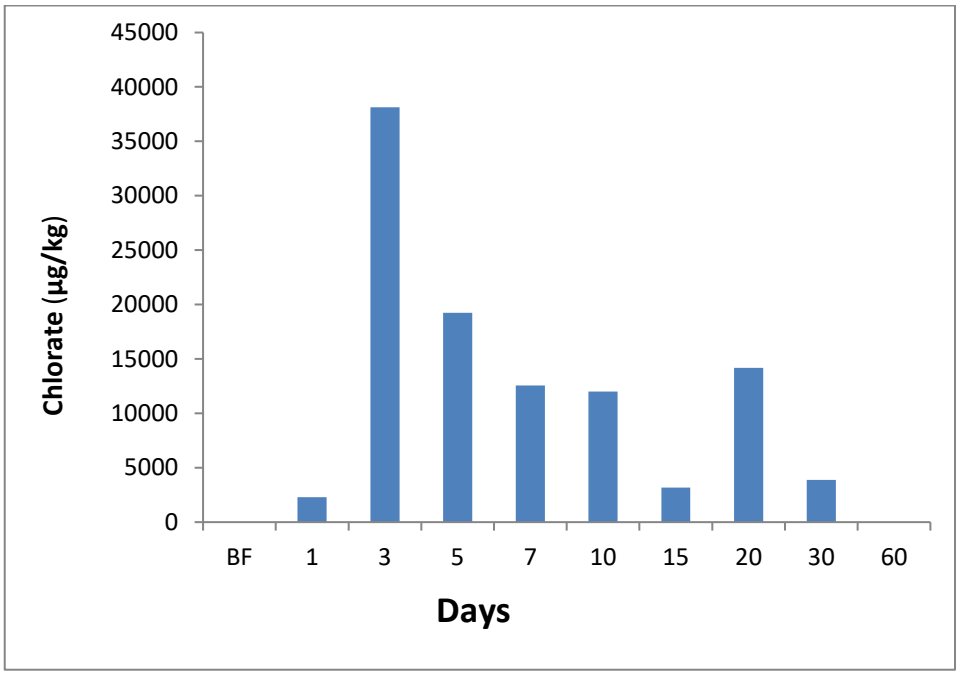


Fig. 6.2 Variation of mean chlorate (µg/kg) in soil at Site 5 (Athirampuzha)

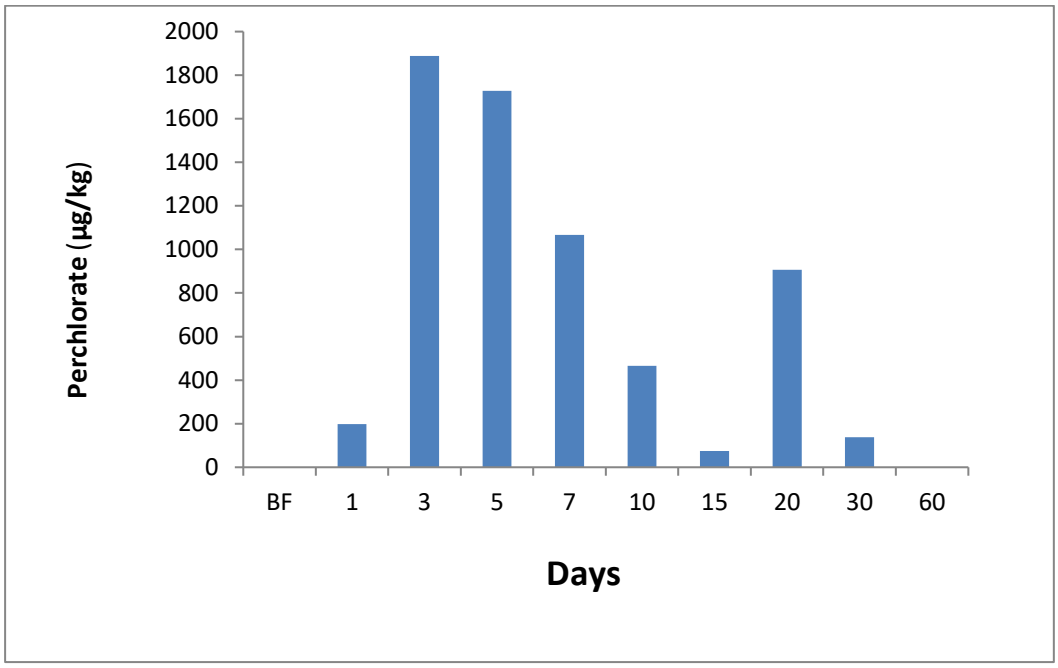


Fig. 6.3 Variation of mean perchlorate (µg/kg) in soil at Site 5 (Athirampuzha)

Soil analysis results at Athirampuzha (site 5) were given in Table 6.19 and 6.20. pH, chlorate and perchlorate showed significant variation before and after fireworks ($p<0.1$). After fireworks, perchlorate and chlorate values of soil samples had increased (Fig. 6.1 and Fig. 6.2). The maximum value was on the 3rd day after fireworks and then decreased till 15th day. The increase of perchlorate on day 3 might be due to the deposition of perchlorate released into the air during the display (Munster *et al.*, 2009).

On 14th day, there was a minor fireworks display at the same site and hence there was a marked increase of both perchlorate and chlorate on 20th day and then decreased to BDL on day 60. There was a heavy rainfall on day 5 and day 20 after fireworks. The temperature was high except during the rainy days. Both these factors might have together resulted in the degradation or removal of perchlorate. This also indicated that the degradation or removal of perchlorate and chlorate in soil was related to environmental conditions such as temperature and rainfall.

Table 6.19 pH and OC in soil at Site-5

Sl.No	Before fireworks		After fireworks	
	pH	**OC (%)**	**pH**	**OC (%)**
S1s	5.68	0.06	7.19	0.06
S2s	5.72	0.04	6.93	0.06
S3s	6.18	0.06	6.42	0.06
S4s	4.58	0.12	5.25	0.13
S5s	6.45	0.04	6.54	0.04
S6s	6.72	0.04	6.77	0.02
S7s	6.83	0.04	7.91	0.04
G1s	6.50	0.06	7.49	0.07

Continuous monitoring of soil samples

Perchlorate and chlorate before fireworks was BDL (Table 6.20). At Day 1, perchlorate in soil ranged from BDL to 831.76 ppb where as for chlorate it was 139.20 to 7743.68 ppb. Maximum value of perchlorate during Day 3 was 12580.10 ppb and that of chlorate was 189255.60 ppb whereas the minimum value was BDL for perchlorate and 2296.96 ppb for chlorate. Perchlorate value was maximum at G1s (9384.58 ppb) and minimum (BDL) at S1s on day 5. Here chlorate ranged from 550.40 ppb to 81230.32 ppb. On Day 7 ground sample showed highest perchlorate (7911.44 ppb) and chlorate (66602.16 ppb). Perchlorate values ranged from BDL to 381.08 ppb while chlorate values ranged from 451.76 ppb to 15314.72 ppb on 10^{th} day .The range of chlorate on 15^{th} day was 407.2 ppb to 56778.88 ppb and that of perchlorate was 38.96 ppb to 4589.32 ppb. Maximum value of perchlorate and chlorate on Day 30 was 550.76 ppb and 20023.36 ppb respectively and the minimum value was 54.08 ppb and BDL respectively. On 20^{th} day, chlorate value varied from 164.64 ppb to 69497.36 ppb and perchlorate value ranged from BDL to 2900.40 ppb. No perchlorate and chlorate was detected in any of the soil samples on Day 60.

Table 6.20 Perchlorate and chlorate in soil at Site-5

	Before		Day 1		Day 3		Day 5		Day 7		Day 10		Day 15		Day 20		Day 30		Day 60	
	ClO_3^- (µg/kg)	ClO_4^- (µg/kg)	ClO_3^- (µg/kg)	ClO_4^- (µg/kg)	ClO_3^- (µg/kg)	ClO_4^- (µg/kg)	ClO_3^- (µg/kg)	ClO_4^- (µg/kg)	ClO_3^- (µg/kg)	ClO_4^- (µg/kg)	ClO_3^- (µg/kg)	ClO_4^- (µg/kg)	ClO_3^- (µg/kg)	ClO_4^- (µg/kg)	ClO_3^- (µg/kg)	ClO_4^- (µg/kg)	ClO_3^- (µg/kg)	ClO_4^- (µg/kg)	ClO_3^- (µg/kg)	ClO_4^- (µg/kg)
S1s	BDL	BDL	1213.20	64.22	2296.96	204.90	1130.64	BDL	1559.28	34.16	712.71	39.64	2052.0	110.30	164.64	BDL	92.72	46.22	BDL	BDL
S2s	BDL	BDL	669.840	240.80	2719.12	107.26	2198.0	159.84	1263.44	62.16	1379.92	15.32	407.20	38.96	208.32	79.70	115.36	204.70	BDL	BDL
S3s	BDL	BDL	1819.76	62.22	4341.68	110.52	6476.56	199.76	1237.04	55.32	1620.48	44.40	1955.60	56.46	320.40	27.16	137.44	22.56	BDL	BDL
S4s	BDL	BDL	139.20	BDL	2158.56	55.20	550.40	52.18	370.32	26.86	201.84	30.84	436.24	42.38	2871.76	BDL	54.08	BDL	BDL	BDL
S5s	BDL	BDL	392.720	37.10	12384.80	220.98	3113.76	177.54	3356.96	102.50	3344.80	70.62	7781.92	266.44	3058.96	209.76	755.28	24.04	BDL	BDL
S6s	BDL	BDL	2288.80	73.36	13255.76	219.72	6229.76	118.40	6017.60	217.14	451.76	BDL	7192.80	190.64	1787.36	37.32	1674.88	31.66	BDL	BDL
S7s	BDL	BDL	482.08	26.22	5332.96	12580.10	10999.28	324.10	3531.60	48.56	2233.20	35.48	2016.48	185.16	2548.08	148.98	578.24	79.32	BDL	BDL
G1s	BDL	BDL	5921.36	831.76	189255.60	3287.90	81230.32	9384.58	66602.16	7911.44	3250.08	48.90	56778.88	4589.32	69497.36	2900.40	11415.52	287.14	BDL	BDL
G2s	BDL	BDL	7743.68	441.76	111301.0	2839.33	61115.68	5129.36	29161.76	1139.32	15314.72	381.08	49103.84	2681.90	27470.80	786.98	20023.36	550.76	BDL	BDL

Continuous monitoring of water samples

Mean perchlorate in the water samples before and just after fireworks was found to be BDL (Table 6.21). But chlorate was found in the water samples even before fireworks, which might be an after effect of disinfection process in the area, where sodium chlorate was used for the same. Mean perchlorate in the water samples ranged from BDL to 15.82 ppb after fireworks. Perchlorate was detected in some water samples on day 7, 10, 15 and 30 after fireworks (Table 6.21). The perchlorate was detected in the water samples only after 5^{th} day. Perchlorate from soil might have leached into water bodies due to the rainfall occurred in the area on 5^{th} day (Urbansky *et al.,* 2001; Ellington *et al.,* 2000) or might have deposited from the atmosphere. After day 20, heavy recurrent rainfall occurred in the area till 60^{th} day and no perchlorate content was observed in any of the water samples and this might be due to dilution. Another study also observed such variation in the perchlorate content in water samples. For example Backus *et al.,* (2005) had noticed the presence of perchlorate in surface water samples within 4 days after fireworks, but was absent after a week.

Table 6.21 Mean perchlorate in water before and after fireworks at site 5.

	Perchlorate (ppb)	
Day	**Range**	**Mean**
BF	BDL	BDL
1	BDL	BDL
3	BDL	BDL
5	BDL	BDL
7	BDL to 15.82	4.16
10	BDL to 7.14	1.02
15	BDL to 8.25	1.18
20	BDL	BDL
30	BDL to 32.6	11.24
60	BDL	BDL

Before fireworks, perchlorate in water samples was BDL but chlorate ranged from BDL to 482.64 ppb (Table 6.22). On Day 1 also perchlorate was absent in water and the maximum chlorate was 452.64 ppb and minimum of BDL (Table 6.23). The chlorate in water samples ranged from BDL to 812.80 ppb and perchlorate was BDL on Day 3 (Table 6.24). Perchlorate values of all water samples were BDL on Day 5 but chlorate values ranged from BDL to 599.44 ppb (Table 6.25). Perchlorate was detected in two water samples on Day 7- S4W (13.28 ppb) and S5W (15.82 ppb) (Table 6. 26). But chlorate was detected in one sample only S1W (1223.04 ppb). On Day 10 also perchlorate was present in S5W (7.14 ppb) but was BDL in all other samples (Table 6.27). Chlorate was again present in S1W only (321.92 ppb). Perchlorate was detected in S5W (8.25 ppb) and chlorate in S1W during 15^{th} day (Table 6.28). But on 20^{th} day perchlorate was absent in all water samples analyzed (Table 6.29) and chlorate was present in S1W and S3W. Again on 30^{th} day presence of perchlorate was noticed in S2W, S3W and S6W (Table 6.30). On 60^{th} day of sample collection, perchlorate and chlorate of all samples were BDL only (Table 6.31). Variation of perchlorate in different samples was clearly noticed. In some days perchlorate was detected from selected samples and in other day it was absent in those samples and was found to be present in some other samples. This was mainly due to the variation in the amount of perchlorate deposition, dilution, movement of perchlorate with ground water, etc. Only perchlorate showed highly significant variation before and after fireworks ($p<0.05$).

Table 6.22 Perchlorate and other water quality parameters at Site 5, before fireworks display

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
ABS1W	4.84	105.30	52.60	0.05	27.87	15.14	2.19	21.21	14.0	12.59	3.99	0.14	362.24	BDL
ABS2W	4.34	169.20	84.60	0.08	42.97	49.10	2.07	35.21	22.40	15.28	5.94	BDL	BDL	BDL
ABS3W	5.09	219.0	109.60	0.11	43.63	46.07	18.91	39.66	41.45	24.26	6.54	0.10	262.24	BDL
ABS4W	4.60	115.30	57.70	0.06	53.28	13.61	18.49	25.95	4.83	9.45	6.40	BDL	BDL	BDL
ABS5W	5.08	92.30	46.10	0.05	23.19	7.57	4.64	24.11	5.60	11.89	3.42	BDL	BDL	BDL
ABS6W	4.44	103.40	51.70	0.05	28.12	15.36	3.56	19.37	3.35	10.77	4.84	BDL	482.64	BDL
ABS7W	5.36	107.90	53.90	0.06	13.97	9.68	14.21	14.11	4.20	24.35	5.12	BDL	BDL	BDL

Table 6.23 Perchlorate and other water quality parameters at Site 5, Day 1

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
Day 1 S1W	5.53	203.0	10.14	0.10	1.50	0.24	1.79	27.25	13.17	49.67	5.06	BDL	452.64	BDL
Day 1 S2W	4.58	175.30	87.70	0.09	44.13	49.62	2.79	33.88	22.19	16.12	5.62	BDL	BDL	BDL
Day 1 S3W	5.16	217.0	108.50	0.11	42.66	48.53	17.68	39.16	40.04	23.06	6.28	BDL	85.36	BDL
Day 1 S4W	5.52	272.0	135.80	0.13	56.87	15.22	23.24	57.19	18.85	45.45	8.08	0.22	BDL	BDL
Day 1 S5W	4.87	97.70	48.90	0.05	22.94	7.87	7.957	23.37	5.07	5.34	9.15	BDL	BDL	BDL
Day 1 S6W	4.47	112.20	56.10	0.06	27.08	15.06	11.38	21.17	1.68	23.31	2.38	BDL	BDL	BDL
Day 1 S7W	5.20	90.90	45.50	0.05	10.69	5.63	13.66	13.31	4.14	18.69	5.25	BDL	BDL	BDL

Table 6.24 Perchlorate and other water quality parameters at Site 5, Day 3

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO^- (µg/L)
Day 3 S1W	5.61	231.60	50.21	0.09	23.65	22.79	10.77	25.92	6.90	32.32	4.75	BDL	812.80	BDL
Day 3 S2W	4.62	183.40	93.60	0.10	43.32	50.94	3.83	33.82	20.35	15.21	5.66	BDL	BDL	BDL
Day 3 S3W	5.06	211.30	126.30	0.11	42.78	48.97	18.13	40.97	42.35	24.24	6.63	BDL	90.56	BDL
Day 3 S4W	5.49	283.10	129.80	0.12	55.26	14.52	24.36	57.54	18.05	45.23	7.82	BDL	BDL	BDL
Day 3 S5W	4.92	106.20	65.10	0.06	22.64	7.94	5.83	22.85	5.36	13.17	3.44	BDL	BDL	BDL
Day 3 S6W	4.36	123.10	49.30	0.05	29.05	16.97	14.63	20.08	1.59	23.84	2.60	BDL	BDL	BDL
Day 3 S7W	5.19	88.20	61.80	0.05	11.59	9.34	16.84	13.15	3.91	21.39	5.08	BDL	BDL	BDL

Table 6.25 Perchlorate and other water quality parameters analyzed in samples at Site 5, Day 5

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
Day 5 S1W	5.59	226.30	49.30	0.10	22.01	32.55	21.27	28.47	9.26	50.21	4.73	BDL	599.44	BDL
Day 5 S2W	4.53	189.80	96.70	0.10	41.57	48.52	3.11	33.44	19.89	16.17	5.80	BDL	BDL	BDL
Day 5 S3W	5.12	242.60	133.40	0.12	42.78	48.43	16.53	38.67	39.95	22.62	6.10	BDL	180.24	BDL
Day 5 S4W	5.26	262.10	119.30	0.11	52.23	14.32	22.16	54.92	18.69	45.15	7.79	BDL	BDL	BDL
Day 5 S5W	4.98	126.30	73.10	0.07	22.03	7.95	7.56	22.25	5.16	12.79	3.21	BDL	BDL	BDL
Day 5 S6W	4.42	129.40	53.20	0.06	28.88	16.78	13.09	19.98	1.73	23.26	2.58	BDL	BDL	BDL
Day 5 S7W	5.08	92.60	69.60	0.05	13.14	14.13	23.37	13.17	3.99	22.65	4.66	BDL	BDL	BDL

Table 6.26 Perchlorate and other water quality parameters at Site 5, Day 7

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
Day 7 S1W	5.72	139.40	69.70	0.07	32.21	20.49	10.76	24.79	6.53	33.95	4.24	BDL	1223.04	BDL
Day 7 S2W	5.18	175.0	87.50	0.09	41.46	48.19	2.99	33.13	19.97	14.87	5.54	BDL	BDL	BDL
Day 7 S3W	5.30	217.0	108.50	0.11	41.56	48.33	17.28	38.76	40.0	23.14	6.24	BDL	BDL	BDL
Day 7 S4W	5.54	259.0	129.70	0.13	52.87	12.68	23.89	56.11	17.96	43.57	7.37	BDL	BDL	13.28
Day 7 S5W	5.28	93.70	46.90	0.05	21.98	7.965	6.01	23.21	5.01	12.49	3.10	BDL	BDL	15.82
Day 7 S6W	4.90	119.80	59.90	0.06	28.25	16.54	12.82	21.29	1.57	23.57	2.36	BDL	BDL	BDL
Day 7 S7W	5.36	78.40	39.20	0.04	8.96	1.44	8.13	12.30	3.60	13.47	5.48	5.48	BDL	BDL

Table 6.27 Perchlorate and other water quality parameters at Site 5, Day 10

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
Day 10 S1W	5.53	212.0	106.20	0.10	22.84	37.10	24.95	30.14	9.90	55.96	5.31	321.92	BDL	BDL
Day 10 S2W	4.80	172.80	86.40	0.09	42.31	49.17	1.70	33.02	20.49	16.37	5.75	BDL	BDL	0.07
Day 10 S3W	5.08	221.0	110.40	0.11	41.20	49.79	17.98	37.99	39.94	23.09	6.49	BDL	BDL	0.07
Day 10 S4W	5.33	256.0	128.20	0.12	53.71	14.23	22.18	54.07	18.81	44.04	7.74	BDL	BDL	0.11
Day 10 S5W	5.12	99.50	49.70	0.05	22.52	7.89	4.56	22.40	5.38	11.76	3.15	BDL	7.14	0.20
Day 10 S6W	4.73	120.60	60.30	0.06	29.26	16.91	12.15	20.18	1.86	23.20	2.51	BDL	BDL	0.10
Day 10 S7W	5.23	85.60	42.80	0.05	9.41	3.58	9.44	12.86	4.67	15.73	5.14	BDL	BDL	BDL

Table 6.28 Perchlorate and other water quality parameters at Site 5, Day 15

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
Day 15 S1W	5.52	221.0	110.40	0.11	23.44	41.59	26.81	30.71	10.72	62.53	5.27	0.06	104.16	BDL
Day 15 S2W	4.47	174.30	87.1	0.09	43.13	50.35	2.01	33.90	20.45	15.73	5.73	BDL	BDL	BDL
Day 15 S3W	4.94	215.0	107.70	0.10	40.94	47.29	16.46	37.06	38.62	22.48	6.20	0.07	BDL	BDL
Day 15 S4W	5.32	249.0	124.70	0.12	49.76	11.71	22.12	51.95	17.33	41.46	7.14	0.08	BDL	BDL
Day 15 S5W	5.13	93.40	46.70	0.05	21.37	8.01	4.61	23.16	4.75	12.95	3.12	BDL	BDL	8.25
Day 15 S6W	4.74	121.30	60.70	0.06	29.89	18.05	12.60	23.60	1.81	25.24	2.71	BDL	BDL	BDL
Day 15 S7W	5.12	94.20	47.10	0.05	10.67	7.85	15.19	13.99	4.06	20.59	5.34	0.08	BDL	BDL

Table 6.29 Perchlorate and other water quality parameters at Site 5, Day 20

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
Day 20 S1W	5.44	154.80	77.40	0.08	24.49	25.35	12.38	23.61	6.60	32.0	4.36	BDL	505.60	BDL
Day 20 S2W	4.74	170.90	85.40	0.08	52.73	52.66	2.28	31.05	18.69	15.20	5.38	BDL	BDL	BDL
Day 20 S3W	4.99	210.0	105.20	0.10	40.92	46.65	15.02	34.70	34.87	20.51	5.45	BDL	165.28	BDL
Day 20 S4W	5.33	237.0	118.70	0.12	51.41	10.64	20.99	46.95	15.73	36.86	6.64	BDL	BDL	BDL
Day 20 S5W	5.09	90.50	45.30	0.05	21.25	7.95	4.44	20.64	4.40	11.02	2.65	BDL	BDL	BDL
Day 20 S6W	4.68	123.10	61.50	0.06	30.09	17.46	12.58	21.45	1.52	23.09	2.40	BDL	BDL	BDL
Day 20 S7W	5.27	76.0	38.0	0.04	8.70	1.18	7.41	12.18	3.69	12.92	5.25	BDL	BDL	BDL

Table 6.30 Perchlorate and other water quality parameters at Site 5, Day 30

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
Day 30 S1W	5.58	194.30	97.10	0.10	24.45	34.98	17.19	28.19	8.23	44.37	4.63	BDL	1263.20	BDL
Day 30 S2W	4.50	174.80	87.40	0.09	44.40	52.43	3.58	36.46	19.91	17.86	6.39	BDL	BDL	30.22
Day 30 S3W	5.08	206.0	103.0	0.10	43.68	46.75	13.72	35.09	33.38	20.32	5.61	BDL	420.32	32.60
Day 30 S4W	5.41	233.0	116.40	0.11	44.77	9.60	20.19	47.53	16.11	36.54	6.38	BDL	BDL	BDL
Day 30 S5W	4.98	89.30	44.60	0.05	2098.0	8.87	4.78	20.59	4.80	12.71	2.71	0.06	BDL	BDL
Day 30 S6W	4.64	129.90	65.0	0.07	30.51	18.36	13.34	23.59	1.91	24.49	2.67	BDL	875.84	15.83
Day 30 S7W	5.31	77.30	38.60	0.04	9.60	1.56	7.30	12.35	4.01	12.99	5.43	0.11	BDL	BDL

Table 6.31 Perchlorate and other water quality parameters at Site 5, Day 60

Sl.No	pH	EC (µS/cm)	TDS (ppb)	SAL (psu)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (µg/L)	ClO_4^- (µg/L)
Day 60 S1W	5.83	206.30	101.80	0.12	27.37	40.62	13.19	0.56	0.53	1.59	0.21	0.11	BDL	BDL
Day 60 S2W	5.01	198.20	99.60	0.10	38.57	44.40	1.36	33.01	20.07	15.51	5.65	BDL	BDL	BDL
Day 60 S3W	5.12	216.10	113.30	0.11	37.48	42.09	11.32	36.23	34.	20.96	5.87	BDL	BDL	BDL
Day 60 S4W	5.56	249.90	126.80	0.13	23.57	3.97	8.18	25.91	9.95	17.52	0.39	BDL	BDL	BDL
Day 60 S5W	5.49	110.20	93.20	0.09	11.29	2.77	2.16	12.76	4.36	14.74	2.20	0.09	BDL	BDL
Day 60 S6W	5.03	134.50	100.60	0.09	29.35	18.24	14.49	27.21	2.24	25.15	2.65	BDL	BDL	BDL
Day 60 S7W	5.57	108.30	76.10	0.08	7.70	0.93	5.60	11.59	3.98	13.89	4.67	0.12	BDL	BDL

Sample wise data

Perchlorate and chlorate content in soil varied with sample points (Table 6.32 and Table 6.33). The highest amount of perchlorate and chlorate was detected from the firework display ground samples and this can cause high contamination in the nearby aquatic ecosystem. An increase had been noticed for the samples located in wind ward direction. This indicated that wind properties and direction might play a major role in environmental contamination due to perchlorate (Munster *et al.,* 2009). Least amount of

perchlorate and chlorate was measured in the samples which were distant from the site and also away from wind ward direction.

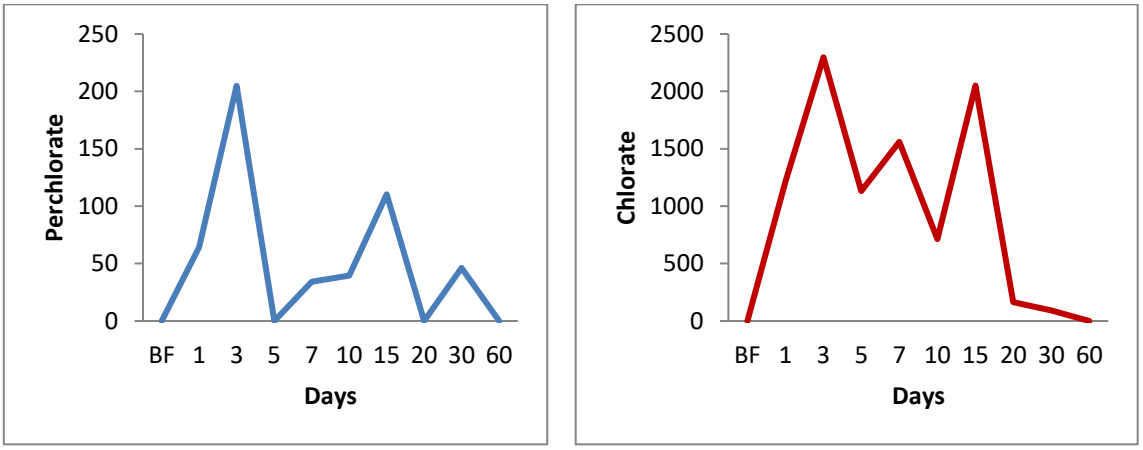
Table 6.32 Perchlorate (µg/kg) in soil at different sample points of Athirampuzha fireworks display site

DAY	S1	S2	S3	S4	S5	S6	S7	G1	G2	Mean
BF	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
1	64.22	240.80	62.22	BDL	37.10	73.36	26.22	831.76	5921.36	806.34
3	204.90	107.26	110.52	55.20	220.98	206.96	219.72	12580.10	189255.60	22551.20
5	BDL	159.84	199.76	52.18	177.54	118.40	324.10	9384.58	81230.32	10183.0
7	34.16	62.16	55.32	26.86	102.50	217.14	48.56	7911.44	66602.16	8340.03
10	39.64	15.32	44.40	30.84	70.62	BDL	35.48	48.90	3250.08	392.81
15	110.30	38.96	56.46	42.38	266.44	190.64	185.16	4589.32	56778.88	6917.62
20	BDL	79.70	27.16	BDL	209.76	37.32	148.98	2900.40	69497.36	8100.08
30	46.22	204.70	137.44	BDL	24.04	31.66	79.32	287.14	11415.52	1358.45
BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

Table 6.33 Chlorate in soil (µg/kg) at different sample points of Athirampuzha fireworks display site

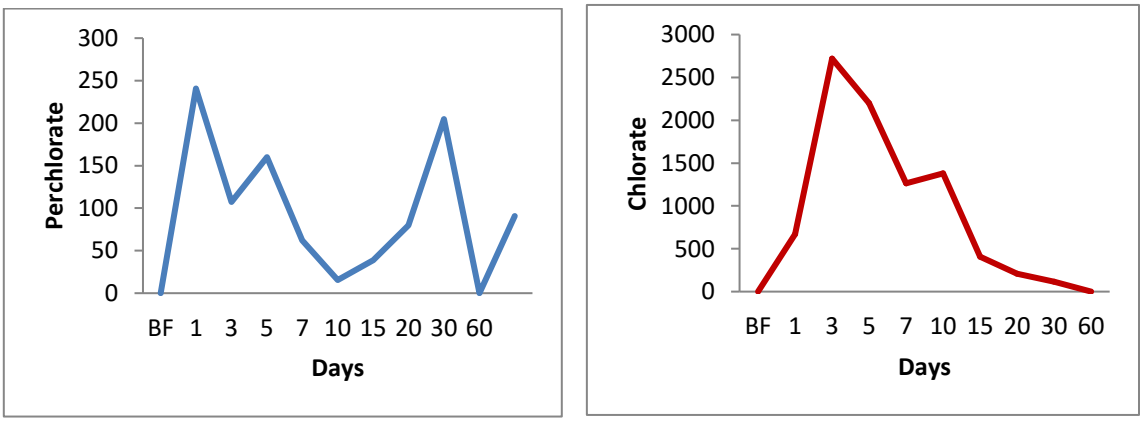
DAY	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**G1**	**G2**	**Mean**
BF	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
1	1213.20	669.84	1819.76	139.20	392.72	2288.80	482.08	5921.36	7743.68	2296.74
3	2296.96	2719.12	4341.68	2158.56	12384.80	13255.76	5332.92	189255.60	111301.0	38116.27
5	1130.64	2198.0	6476.56	550.40	3113.76	6229.76	10999.28	81230.32	61115.68	19227.16
7	1559.28	1263.44	1237.04	370.32	3356.96	6017.60	3531.60	66602.16	29161.76	12566.68
10	712.71	1379.92	1620.48	201.84	3344.80	451.76	2233.20	3250.08	15314.72	3167.72
15	2052.0	407.20	1955.60	436.24	7781.92	7192.80	2016.48	56778.88	49103.84	14191.66
20	164.64	208.32	320.40	2871.76	3058.96	1787.36	2548.08	69497.36	27470.80	11991.96
30	92.72	115.36	22.56	54.08	755.28	1674.88	578.24	11415.52	20023.36	3859.11
60	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL

In all the sample points, perchlorate was seen increasing to maximum during Day 3 to Day 5 and then decreased (Fig. 6.3 to Fig. 6.11). Again a rise in Day 15 was seen and it was due to the second firework display in the site. Chlorate also showed the same trend as of perchlorate. A small variation in perchlorate would arise due to the bias in sample collection. Also, perchlorate downfall would not be same, even in the same sample point. Moreover, the spent out fireworks would be seen in some places which would be absent in other sample points. Another problem faced during soil sample collection was that during the festival period (even after fireworks) a lot of people occupied the site and the soil would get mixed or downtrodden. This affected the precision of perchlorate in the soil.



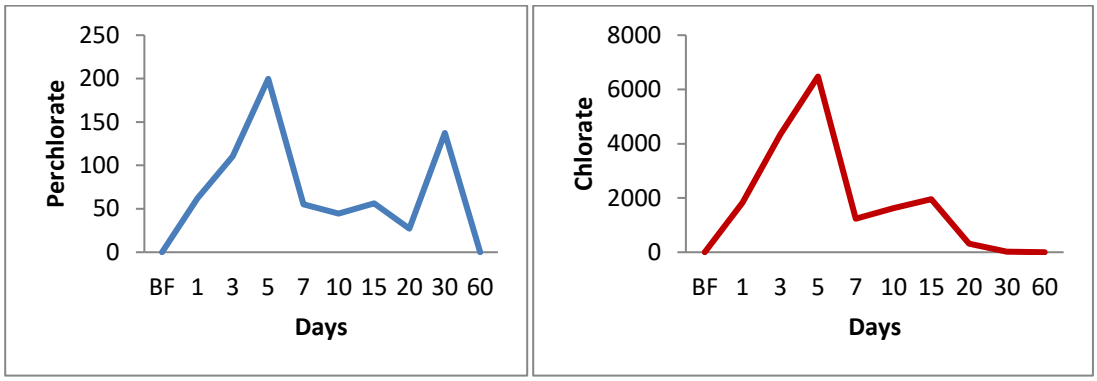
(a) (b)

Fig. 6.4 Variation of perchlorate (µg/kg) (a) and chlorate (µg/kg) (b) in soil at Athirampuzha-Sample 1



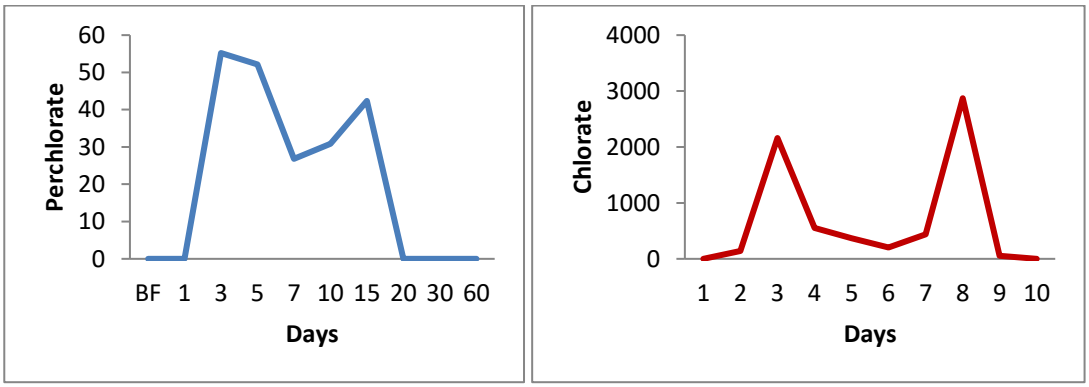
(a) (b)

Fig. 6.5 Variation of perchlorate (µg/kg) (a) and chlorate (µg/kg) (b) in soil at Athirampuzha-Sample 2



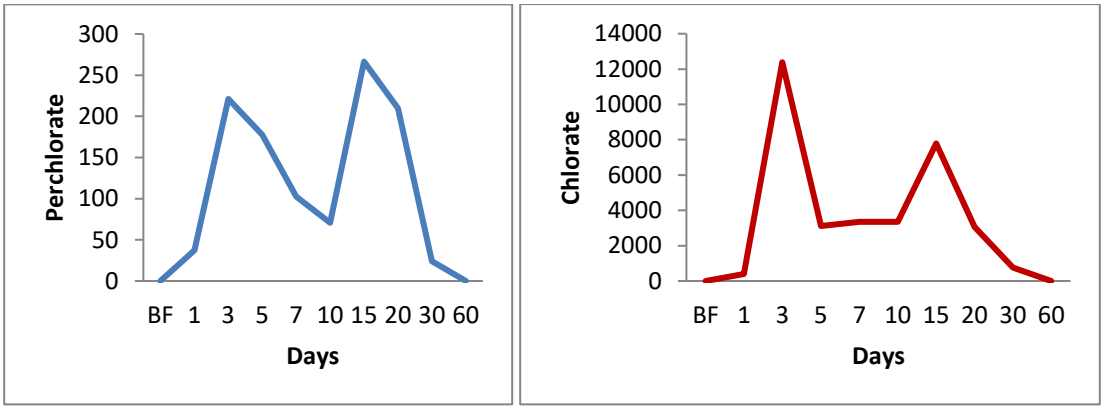
(a) (b)

Fig. 6.6 Variation of perchlorate (µg/kg) (a) and chlorate (µg/kg) (b) in soil at Athirampuzha-Sample 3



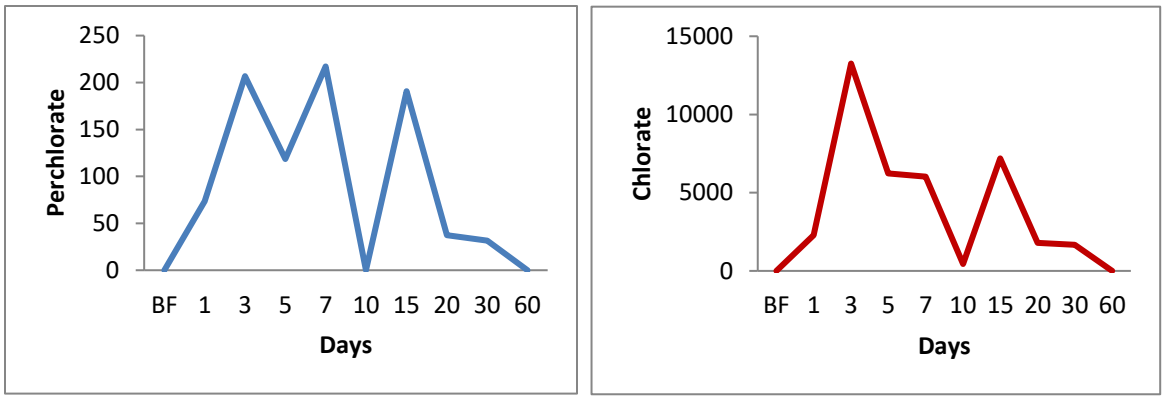
(a) (b)

Fig. 6.7 Variation of perchlorate (µg/kg) (a) and chlorate (µg/kg) (b) in soil at Athirampuzha-Sample 4



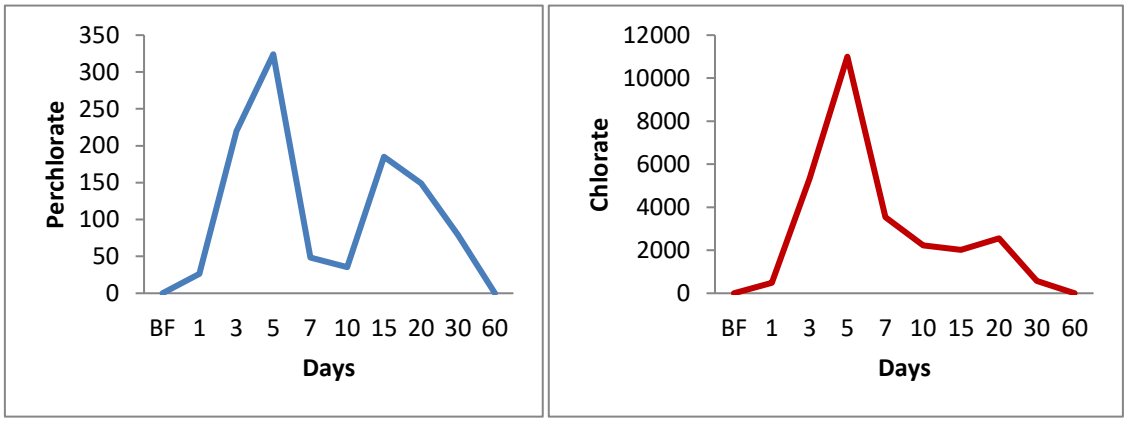
(a) (b)

Fig. 6.8 Variation of perchlorate (µg/kg) (a) and chlorate (µg/kg) (b) in soil at Athirampuzha-Sample 5



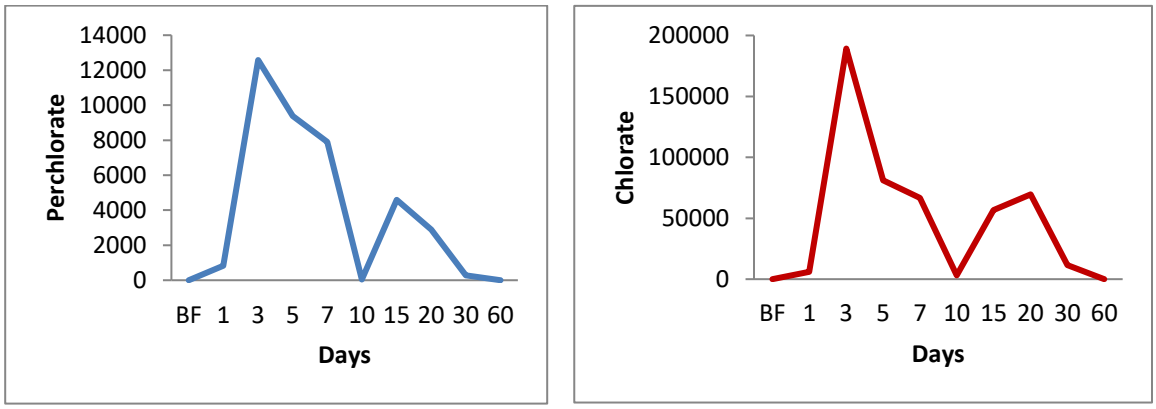
(a) (b)

Fig. 6.9 Variation of perchlorate (µg/kg) (a) and chlorate (µg/kg) (b) in soil at Athirampuzha-Sample 6



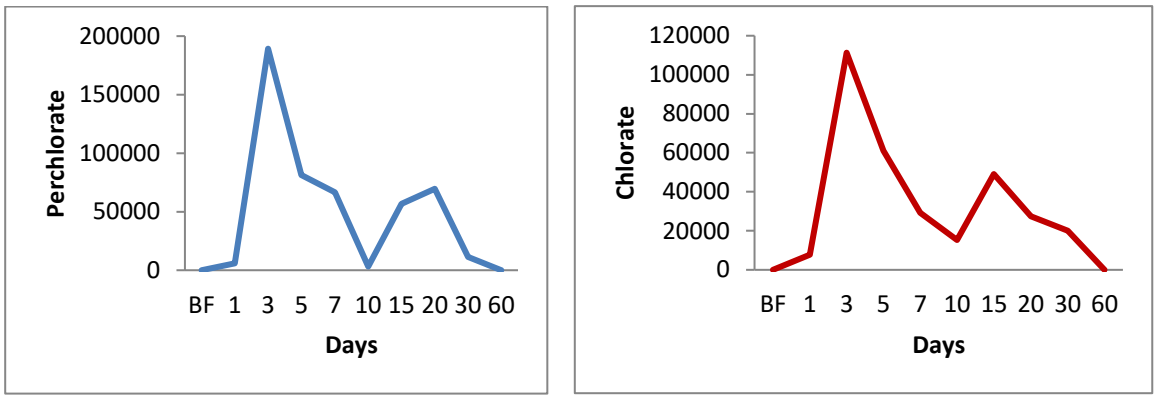
(a) (b)

Fig. 6.10 Variation of perchlorate (µg/kg) (a) and chlorate (µg/kg) (b) in soil at Athirampuzha-Sample 7



(a) (b)

Fig. 6.11 Variation of perchlorate (µg/kg) (a) and chlorate (µg/kg) (b) in soil at Athirampuzha-Ground Sample 1



(a) (b)

Fig. 6.12 Variation of perchlorate (µg/kg) (a) and chlorate (µg/kg) (b) in soil at Athirampuzha-Ground Sample 2

Correlation of perchlorate with other parameters

Correlation of perchlorate with other water quality parameters was also determined (Table 6.34). Only chloride and chlorate showed positive significant correlation with perchlorate. This showed that the chloride and chlorate in water might be either from the perchlorate which entered the water bodies or as a result of atmospheric deposition and run off after fireworks display. This also confirmed the fact that the analyzed cations and anions do not enter water bodies as a result of fireworks display.

Table 6.34 Correlation of perchlorate with water quality parameters, at Athirampuzha fireworks display site

	pH	EC	TDS	SAL	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	ClO_3^-	ClO_4^-
pH	1	.360	.655*	.646*	-.059	-.265	-.266	-.318	-.519	-.121	-.615	.551	-.195	.143
EC		1	.712*	.719*	-.127	.348	.515	.200	.058	.520	-.169	-.203	-.363	-.166
TDS			1	.899**	-.071	.265	.016	-.419	-.556	-.036	-.778**	-.087	-.404	-.071
SAL				1	-.110	.003	-.094	-.475	-.557	-.112	-.734*	-.090	-.379	-.139
Cl^-					1	.172	-.054	.082	-.220	.059	-.011	-.108	.845**	.933**
NO_3^-						1	.773**	.410	.189	.590	.058	-.250	.026	.146
SO_4^{2-}							1	.822**	.637*	.908**	.495	-.048	-.035	-.016
Na^+								1	.832**	.895**	.831**	.140	.210	.166
K^+									1	.663*	.929**	.025	-.031	-.183
Ca^{2+}										1	.583	.000	-.020	.119
Mg^{2+}											1	-.004	.201	-.004
NH_4^+												1	.161	.242
ClO_3^-													1	.844**
ClO_4^-														1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

Major factors driving environmental perchlorate contamination from fireworks

The present study confirmed the role of a number of factors such as quantity, manufacturer, type, environmental conditions etc. that caused perchlorate contamination after fireworks (Wu *et al.,* 2011).

Earlier works reported different factors influencing the perchlorate contamination from fireworks. In the case of surface water, overall amount of ignited fireworks, efficiency of perchlorate oxidation, and wind direction controls the perchlorate levels after fireworks (Wilkin *et al.,* 2007).

From the present study, factors affecting soil perchlorate contamination was found to be dependent on amount of fireworks ignited, combustion of perchlorate, type and manufacturer of fireworks, amount of spent or misfired fireworks, deposition of particles, wind direction, distance from the site, temperature, amount of rainfall, and slope of the area. Perchlorate in ground water was controlled by dilution, ground water movement and slope of the area, distance of well from the site, amount of deposition, rainfall etc.

6.5 Conclusion

Festivals and associated fireworks are a major reason for the perchlorate contamination in soil and drinking water. Perchlorate was detected in soil and water samples collected from different firework display sites. As the amount of firework usage is increasing, the probability of drinking water getting contaminated is also increasing. Perchlorate was transported from soil to water sources. There is also a chance for perchlorate to get into food chain from soil and water. Perchlorate was significantly correlated with chlorate and chloride in water samples. Present study revealed the role of fireworks in perchlorate and chlorate contamination of soil and water. It is therefore important to adopt safe firework manufacturing and display, eliminating the use of perchlorate.

Chapter- 7

Perchlorate contamination and its relation with thyroid disorder in Kerala -A health based survey

7.1 Introduction

Perchlorate is well known as a thyroid disruptor (Snyder *et al.,* 2003). It competes with iodide and reduces the production of thyroid hormones and increases thyroid stimulating hormone levels in blood (Lawrence *et al.,* 2000; Tonachera *et al.,* 2004), thus resulting in a condition known as hypothyroidism. Thyroid hormone plays a major role in the proper functioning of many of the metabolic processes, growth etc. Fetuses and infants may suffer from irrecoverable nervous and skeletal disorders (Haddow *et al.,* 1999; Alvarez *et al.,* 2000). Major exposure route of perchlorate is drinking water.

Perchlorate in groundwater, bottled water, surface water etc. were reported to be very high in Kerala and a risk of thyroid disorders in selected regions are reported (Anupama *et al.,* 2012). Present study aimed to correlate the increasing perchlorate content in drinking water and associated thyroid disorders in Kerala.

7.2 Objective

To assess the relation of perchlorate contamination of drinking water in Kerala with thyroid disorders in selected regions.

7.3 Methodology

Based on the water quality results, a health based survey was conducted at selected sites to study the relationship between perchlorate in drinking water and thyroid disorders (Fig. 7.1). The survey included the details such as age, gender, mean water intake from the source, mean body weight and thyroid status.

Mean daily intake was calculated using the following formula.

Intake (µg/kg body wt/day) = (CW x IR x ED)/ BW (Wu *et al.,* 2010; Wu *et al.,* 2011)

[CW= Chemical concentration in water (µg/L), IR= Intake rate (L/day), ED= Exposure duration (day), BW= Body weight (kg)]

Table 7.1 Thyroid survey sites

Site No.	**Site Name**
Site 1	APEP
Site 2	TERLS
Site 3	Paravur fireworks manufacturing site
Site 4	Kottayam fireworks manufacturing site
Site 5	Seasonal control site
Site 6	Thrissur fireworks display site
Site 7	Palakkad fireworks display site
Site 8	Edathua fireworks display site
Site 9	Manarcad fireworks display site
Site 10	Athirampuzha fireworks display site
Site 11	Fireworks display control site

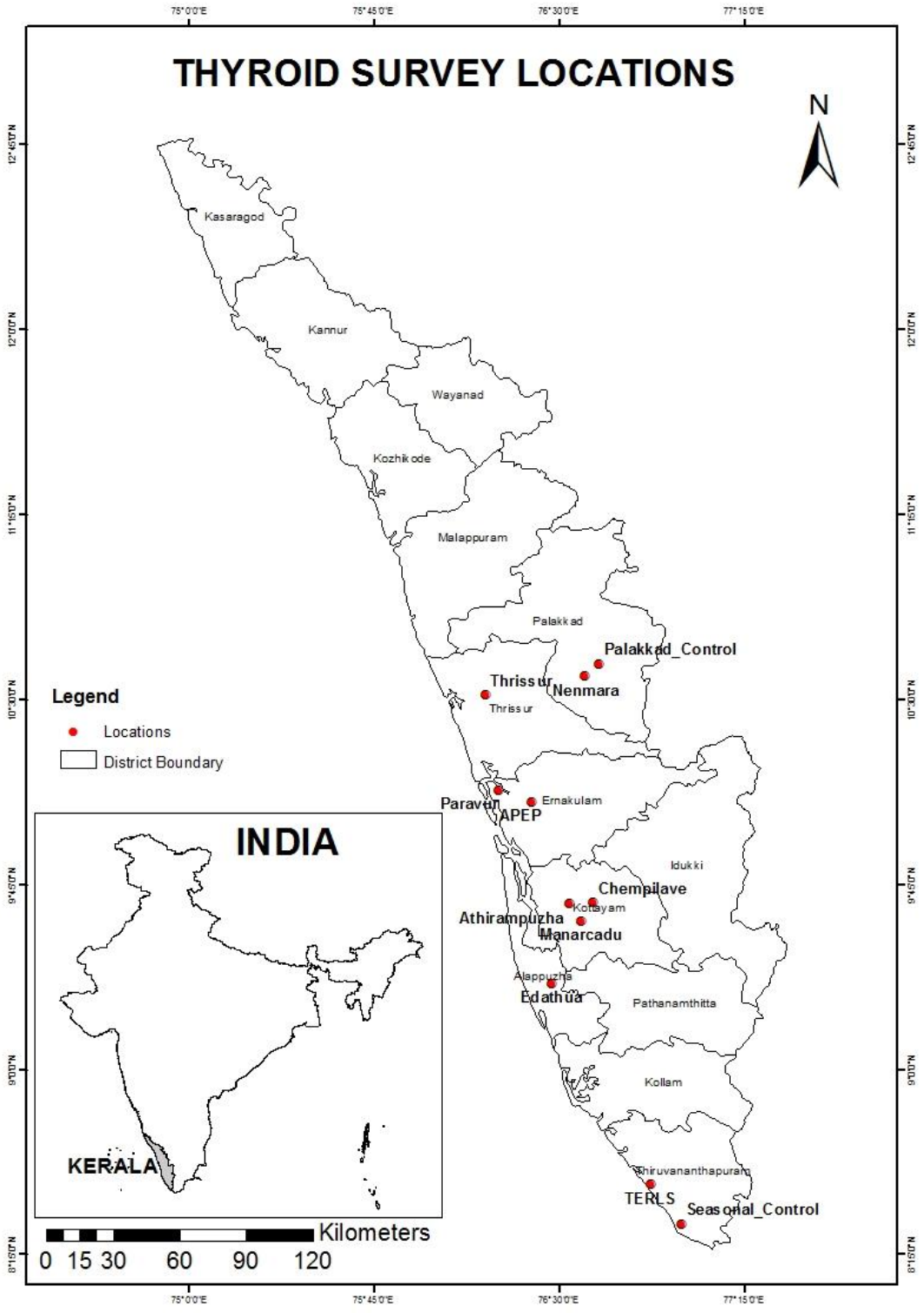


Fig. 7.1 Thyroid survey locations

7.4 Results and discussion

Perchlorate content in drinking water

LC/MS analysis of drinking water samples showed that the perchlorate concentration in drinking water ranged from BDL to 5094.87 ppb (Table 7.2 and 7.3).

Table 7.2 Mean seasonal values of perchlorate in drinking water (ppb)

Site Name	**Post-monsoon**	**Pre-monsoon**	**Monsoon**
Site 1 APEP	3760.15	5094.87	601.28
Site 2 TERLS	640.40	468.57	80.61
Site 3 Paravur fireworks manufacturing site	61.56	25.42	13.99
Site 4 Kottayam fireworks manufacturing site	1.03	BDL	20.72
Site 5 Seasonal control	BDL	BDL	BDL

At APEP and TERLS, mean perchlorate content exceeded in all the seasons (Table 7.2). At Paravur, during post-monsoon and pre-monsoon perchlorate was more than the permissible limit. Fireworks manufacturing site at Kottayam had perchlorate within the limit for all seasons. The control site did not show the presence of perchlorate in any environmental matrices. At firework display sites, perchlorate did not exceed the permissible limit. The values ranged from BDL to 7.23 ppb (Table 7.3)

Table 7.3 Mean perchlorate in drinking water around firework display sites (after fireworks)

Site Name	**Perchlorate (ppb)**
Site 6 Thrissur fireworks display site	BDL
Site 7 Palakkad fireworks display site	7.23
Site 8 Edathua fireworks display site	BDL
Site 9 Manarcad fireworks display site	1.89
Site 10 Athirampuzha fireworks display site	1.96
Site 11 Fireworks control site	BDL

The drinking water systems consisted of well and tap water. Some people used to drink well water throughout the year, whereas some others depended solely on tap water; and a few people used both tap and well water for consumption. Based on this, calculations were done separately to know the mean perchlorate intake from drinking water (i.e. well; tap; combination of well and tap) and the results were given in Table 7.3 and 7.4. Site 1 (APEP), site 2 (TERLS) and site 3 (Paravur fireworks manufacturing site) showed perchlorate in drinking water, levels more than the permissible limit of 24.5 ppb.

Table 7.4 Mean perchlorate (ppb) in drinking water systems

Site Name	Well	Tap	Well and Tap
Site 1 APEP	3666.40	19.52	3152.10
Site 2 TERLS	492.50	24.43	396.53
Site 3 Paravur fireworks manufacturing site	33.66	BDL	16.83
Site 4 Kottayam fireworks manufacturing site	6.70	3.64	7.25
Site 5 Seasonal control	BDL	BDL	BDL
Site 6 Thrissur fireworks display site	BDL	BDL	BDL
Site 7 Palakkad fireworks display site	7.23	BDL	3.61
Site 8 Edathua firework displays site	BDL	BDL	BDL
Site 9 Manarcad fireworks display site	1.89	BDL	0.94
Site 10 Athirampuzha fireworks display site	1.96	BDL	0.98
Site 11 Fireworks control site	BDL	BDL	BDL

Mean yearly perchlorate in well water ranged from BDL to 3666.40 ppb (Table 7.4), and that of tap water BDL to 24.43 ppb. In the combined state ie., well and tap water, mean perchlorate values ranged from BDL to 3152.10 ppb. APEP showed highest perchlorate in well (3666.40 ppb) and well and tap (3152.10 ppb) water whereas in tap water alone TERLS had the highest mean (24.43 ppb). Perchlorate values exceeded the permissible limit at APEP (well; well and tap), TERLS (well; well and tap) and Paravur (well water). All these were perchlorate manufacturing and handling sites only. In the case of firework display sites, none of the mean exceeded the permissible limit (Table 7.4).

Survey

Hypothyroidism was reported from almost all the regions except the control sites, where thyroid disorders were reported to be nil. In the fireworks display sites such as site 6 (Thrissur) and site 8 (Edathua), perchlorate in water samples were below detectable

limits, still hypothyroidism had been reported. This showed that perchlorate alone is not a factor for hypothyroidism. Other genetic, environmental and food behavioral problems add to thyroid disorders. Rate of thyroid disorders in the given regions ranged from 0% to 13.30% (Table 7.5). Hypothyroidism in male were reported from two sites only- Site 4 (Kottayam fireworks manufacturing site) and site 9 (Manarcad fireworks display site) (6.70%). In the case of females, site 2 (TERLS) showed maximum hypothyroidism rate (22.40%) (Fig. 7.2, 7.3 and 7.4). 13.3% hypothyroidism (in total) was reported from Manarcad (site 9) (20% in females and 6.7% in males), but out of 20% of females, 13.3% were reported with hereditary thyroid disorder and only 6.7% of women suffered hypothyroidism from other causes.

Table 7.5 Percentage of hypothyroidism in the survey sites

Place	Total	Female	Male
Site 1 APEP	2	4	0
Site 2 TERLS	11.50	22.40	0
Site 3 Paravur fireworks manufacturing site	6.70	12.50	0
Site 4 Kottayam fireworks manufacturing site	5.50	4	6.70
Site 5 Seasonal control	0	0	0
Site 6 Thrissur fireworks display site	5.90	10	0
Site 7 Palakkad fireworks display site	4	8.30	0
Site 8 Edathua fireworks display site	3.60	7.70	0
Site 9 Manarcad fireworks display site	13.30	20	6.70
Site 10 Athirampuzha fireworks display site	3.80	6.70	0
Site 11 Fireworks control site	0	0	0

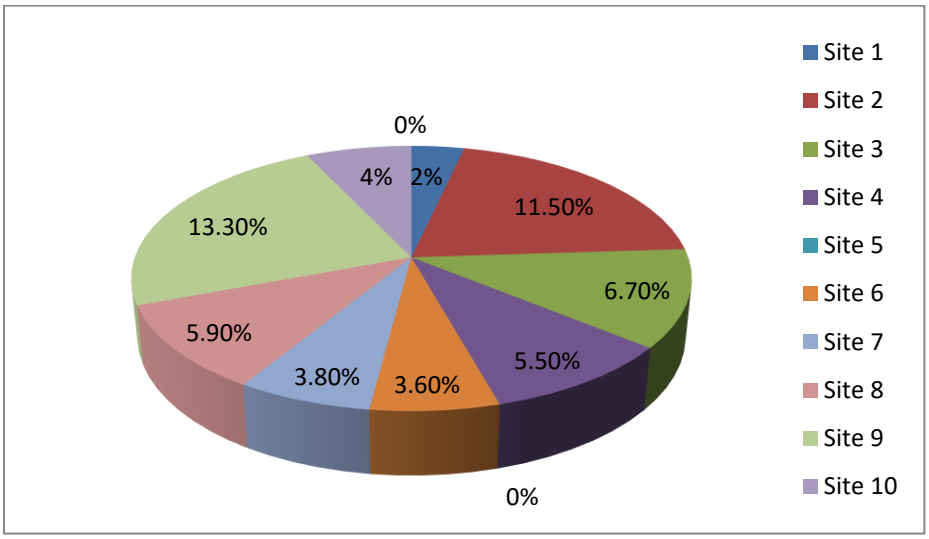


Fig. 7.2 Hypothyroidism in the study area

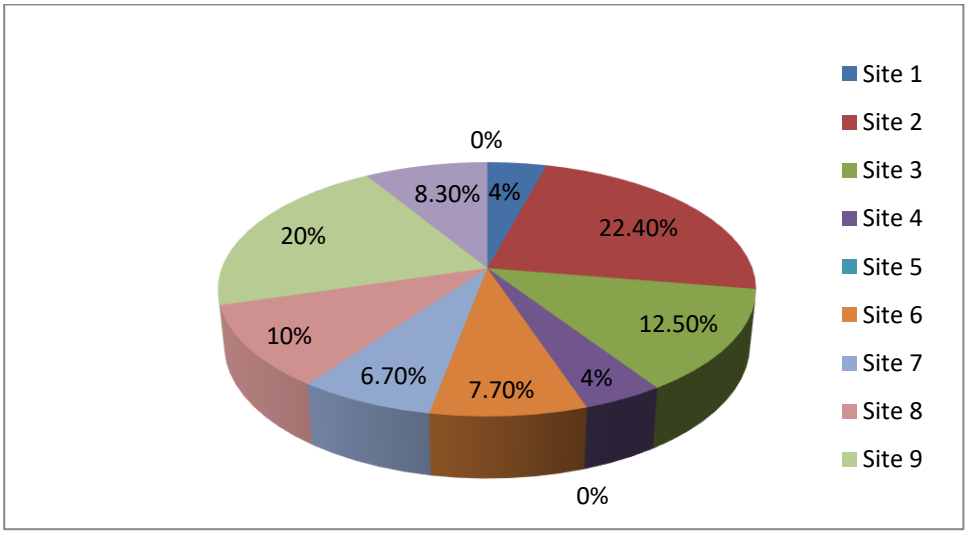


Fig. 7.3 Hypothyroidism in women in the study area

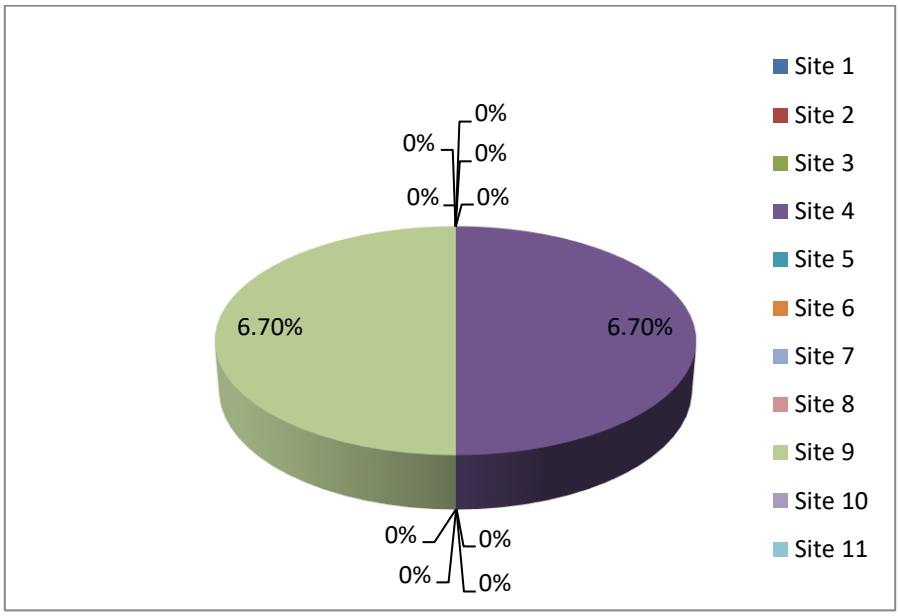


Fig. 7.4 Hypothyroidism in men in the study area

In Kerala, on a mean, around 6% of men and 11% of women suffered from thyroid disorders due to various factors (Menon *et al.*, 2009). When compared to men, women are more susceptible to hypothyroidism (Unnikrishnan and Menon, 2011). Based on the former study (Menon *et al.*, 2009), present study showed a significant increase of hypothyroidism in females at site 2 (TERLS) (22.40%), site 3 (Paravur) (12.50%) and site 9 (Manaracad) (20%- Here, majority (13.3%) was hereditary and no need to consider with perchlorate contamination in drinking water).

The mean intake of perchlorate was found to be high (more than 0.7 ppb, the health protective perchlorate dose per kg body weight per day) at site 2 (TERLS), and site 3 (Paravur) (Table 7.6).

Table 7.6 Mean perchlorate intake per kg body weight per day

Place	Range of perchlorate/kg body weight/day (ppb)	Mean perchlorate/kg body weight/day (ppb)
Site 1 APEP	0.30 to 0.9	0.50
Site 2 TERLS	0.70 to 131.0	18.0
Site 3 Paravur fireworks manufacturing site	0 to 5.40	2.50
Site 4 Kottayam fireworks manufacturing site	0.10 to 0.70	0.30
Site 5 Seasonal control	0	0
Site 6 Thrissur fireworks display site	0	0
Site 7 Palakkad fireworks display site	0.07 to 0.20	0.10
Site 8 Edathua fireworks display site	0	0
Site 9 Manarcad fireworks display site	0 to 0.70	0.10
Site 10 Athirampuzha fireworks display site	0 to 0.70	0.10
Site 11 Fireworks control site	0	0

At site 1 (APEP), most of the people depended either on tap or both well and tap for drinking purpose throughout the year. In the case of well and tap, people mostly depended on tap water and rarely did they use well water for drinking purposes. Government is providing the people around APEP with continuous supply of tap water. This made the reason for the minimum number of thyroid disorders reported even though the well water in the region had been contaminated with extreme levels of perchlorate. In the case of TERLS (site 2) too, a lot of people depended on both well and tap system. Here, tap water was used only for a few days i.e., during scarcity of well water and the rest of the times they were using well water which was heavily contaminated with perchlorate. The abnormal rate of hypothyroidism in women (22.4%) in site 2 (TERLS)

could be owed to the increase in perchlorate contamination of the drinking water in the given area. The people in the region were iodine sufficient too.

Hypothyroidism increases with age, especially in women with hypertension and post menopausal age (Menon *et al.,* 2011). In India, usually the maximum age before puberty is 14 years and the age of menopause is around 48 years. So the hypothyroid women in the area was classified into 3 age groups- Pre-puberty age (1-14 years), conceptional age (15-49 years) and menopausal age (50-70 years) (Table 7.7). No hypothyroidism was detected in the pre-puberty age group at any of the regions. Women in the entire regions (considering average of all sites except site 2 (TERLS) and site 3 (Paravur)) was having hypothyroidal rate of 67% at menopausal age and 33% at conceptional age (Fig. 7.5). At the same time in site 3 (Paravur) alone (Fig. 7.6), the rate of hypothyroidism in women at menopausal age was 67% and that of conceptional age was 33%. Perchlorate may be the one of the reasons for this. Whereas at TERLS, 82% of women suffering from hypothyroidism belonged to conceptional age and only 18% belonged to menopausal age (Fig. 7.7) and proved the role of some extra factors in the area to induce hypothyroidism and the perchlorate in drinking water might be the culprit. Furthur medical analysis (analysis of blood, urine etc.) is needed to confirm the fact.

Table 7.7 Hypothyroidism in women of different age groups at different sites

Age group	Classification	Other sites (Average)	Site 2	Site 3
1 to 14	Pre-puberty age	0%	0%	0%
15 to 49	Conceptional age	33.00%	82%	33%
50 to 70	Menopause age	67.00%	18%	67%

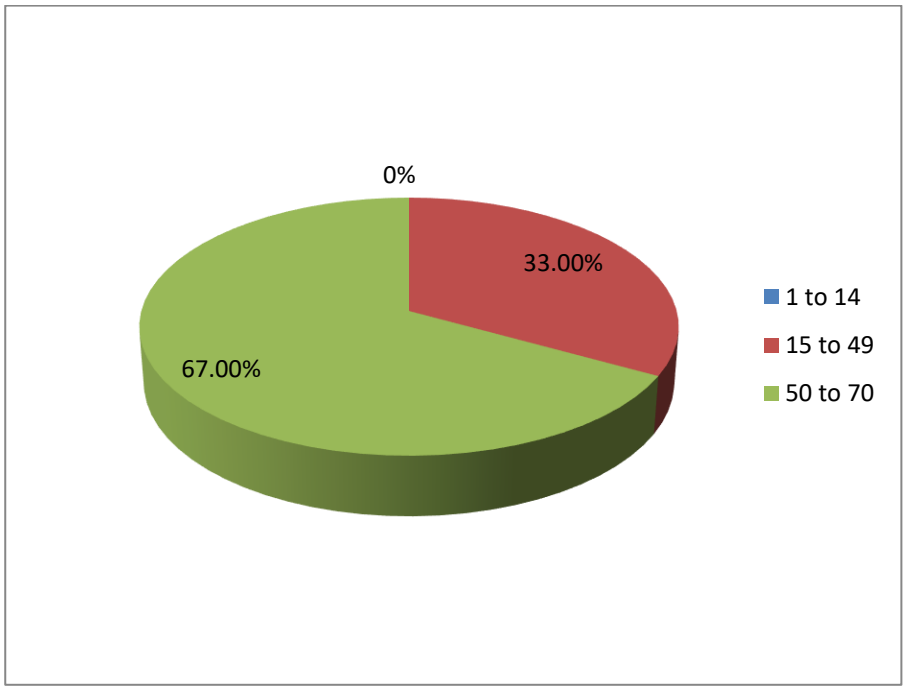


Fig. 7.5 Age group of women affected by hypothyroidism other than Site 2 and Site 3

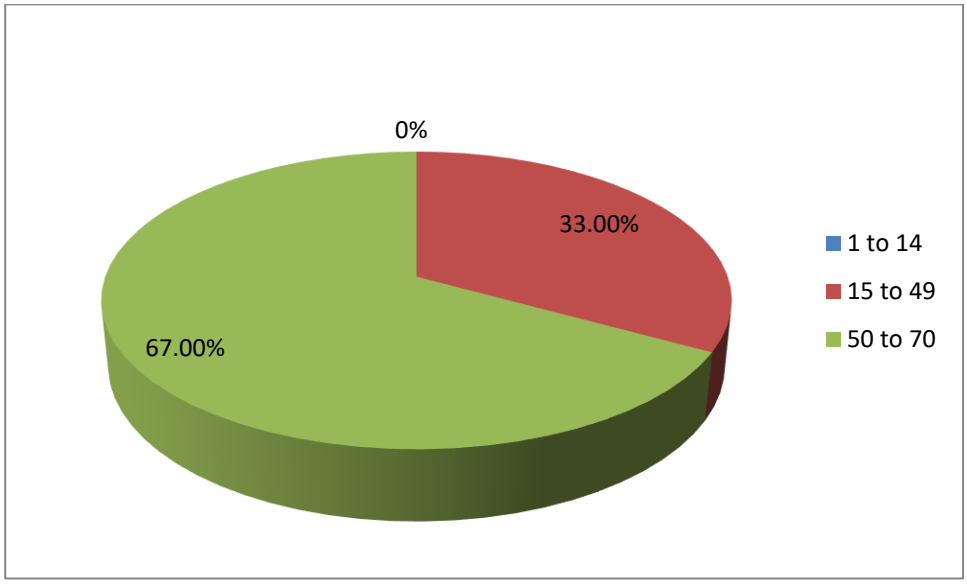


Fig. 7.6 Age group of women affected by hypothyroidism at Site 2

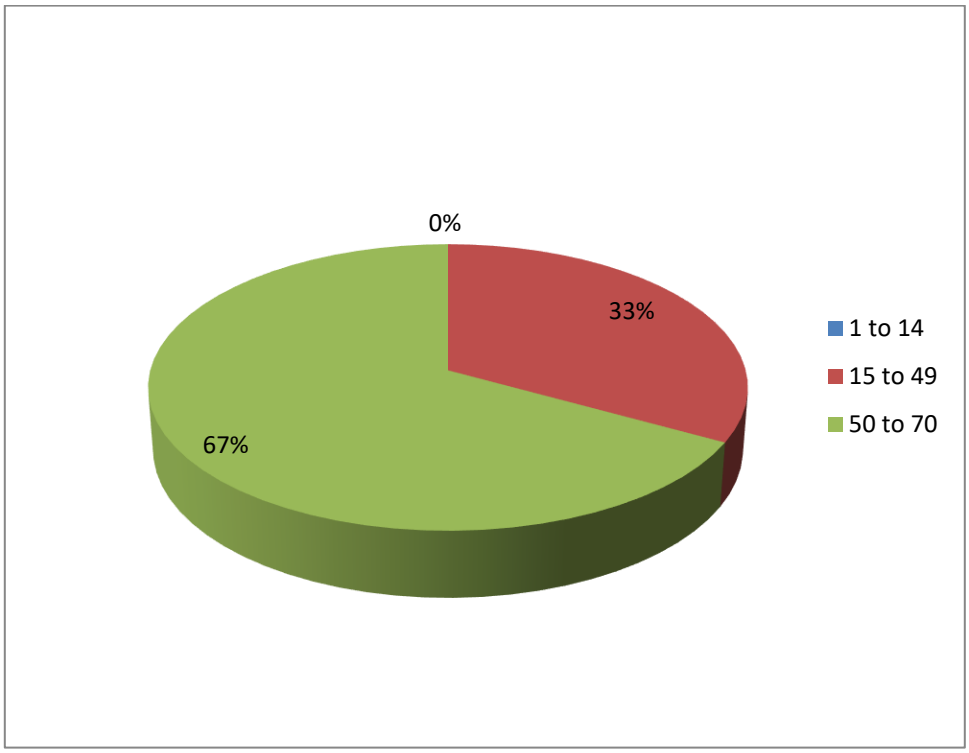


Fig. 7.7 Age group of women affected by hypothyroidism at Site 3

Relationship between perchlorate and thyroid disorder in selected regions

The rate of hypothyroidism and perchlorate contamination in drinking water could be related only at site 2 (TERLS) and site 3 (Paravur fireworks manufacturing site). All other sites were having thyroid disorder rate as comparable to former studies. Mean daily intake of perchlorate per kg body weight at site 2 (TERLS) was 18 ppb and that of site 3 (Paravur fireworks manufacturing site) was 2.5 ppb, which was far higher than the recommended health dose 0.7 ppb (Table 7.7). Women were found to be the culprit for perchlorate induced hypothyroidism.

Perchlorate risk depends on factors like thyroid status of mother during gestation, thyroid status of the fetus, maternal and infant iodine intake, exposure of each other, TH-disrupting chemicals etc. (Kirk, 2006). Women of reproductive age are to be served with adequate iodine intake (Brent, 2010). Once they are iodine deficient, perchlorate can easily take up the position and can result in hypothyroidism.

Fireworks display in the selected regions did not result in any kind of thyroid disorders as the spent perchlorate reaching the drinking water was less than the health protective limit.

Health protective perchlorate dose

Perchlorate in exceeding concentrations in the samples might have resulted in thyroid disorders, specifically hypothyroidism. 0.0007 mg/kg body weight/day (0.7 ppb/kg body weight/day) is the recommended health protective dose of perchlorate (Groef *et al.,* 2006), equivalent to 24.5 ppb perchlorate in drinking water. This reference dose is intended to protect even the sensitive one- fetus (Anderson *et al.,* 2006). In the present study mean intake of perchlorate was obtained to be from BDL up to 18 ppb per kg body weight per day. But daily intake of 2.5 ppb and above was found to be causing thyroid disorder. Below that, obtained values of mean daily intake of 0.1, 0.3 and 0.5 ppb/kg body weight were not found to be inducing hypothyroidism. Perchlorate in low concentrations alone could not result in hypothyroidism, rather in combination with other factors like iodine deficiency, thyroid hormone insufficiency etc. Low level perchlorate exposure did not affect thyroid function in iodine-deficient pregnant women (Pearce *et al.,* 2010). Children from the area with perchlorate in drinking water up to 24 ppb showed no evidence of abnormalities (Chang *et al.,* 2003). Perchlorate exposure up to 15 ppb in drinking water also had no effect on neonatal TSH levels for the first month of life (Li *et al.,* 2000).

7.5 Conclusion

Perchlorate was detected in drinking water samples from selected regions. Low concentrations of perchlorate in drinking water were inadequate to cause hypothyroidism. Rocket propellant manufacturing, testing and use can create an environment that is favorable for inducing thyroid disorder. Fireworks manufacturing in large scale can also lead to thyroid disorders in the near future. Fireworks display in any of the regions was not found to be a base for perchlorate induced thyroid disorder. Further, medical and toxicological studies are needed to find the extent of the role of perchlorate in resulting hypothyroidism.

Chapter-8

Perchlorate degradation using Advanced Techniques

8.1 Introduction

Perchlorate, a negatively charged, highly oxidized ion of chlorine, is one of the major emerging water contaminants (Urbansky, 2002; Wolff, 1998). Techniques like anion exchange, precipitation processes, chemical and electro chemical reduction reactions, biological and biochemical degradation can be employed for perchlorate remediation (Urbansky, 1998; Srinivasan and Viraraghavan, 2009; Sijimol *et al.,* 2015). The conventional water treatment methods failed to remediate perchlorate and at the same time techniques like carbon adsorption and ion exchange techniques are very expensive (Evans *et al.,* 2002). Bioremediation is considered as an advantageous option for perchlorate removal. Bioreactors are proved to be effective for the remediation of perchlorate (Miller and Logan, 2000; Kim and Logan, 2001; Logan and LaPoint, 2002; Nerenberg *et al.,* 2002; Xu *et al.,* 2003, Chung *et al.,* 2007). However the drawback is that anaerobic environment is necessary for the microbes to act upon perchlorate and hence it is time consuming.

Advanced oxidation processes (AOPs) and advanced reduction processes (ARPs) are other unutilized options for perchlorate remediation. AOPs are widely used for the degradation of organic compounds (Pang *et al.,* 2011) where the hydroxyl radical destruct most of the organic components. Based on the generation of hydroxyl radical, it can be classified into UV/ H_2O_2 photolysis (Sunil Paul *et al.,* 2013), photocatalysis, sonolysis (Nejumal *et al.,* 2014), electrochemical methods (Oturan *et al.,* 2008) etc.

Advanced Reduction Processes (ARPs) are used for reducing oxidized contaminants. When properly activated, chemicals like dithionite, sulfite, sulfide and ferrous iron may yield highly reactive species (Liu *et al.,* 2013). UV irradiation in combination with

reducing agents also results in the production of highly reactive reducing free radicals (Liu *et al.,* 2013). Preliminary studies were conducted on the usage of ARPs for the degradation of inorganic compounds like perchlorate (Vellanki *et al.*, 2013).

Distillation is a common procedure for the removal of chemicals that are having boiling points higher and lower to that of water. Distillation is mainly used for the separation of contaminants and can be used for treating wastewater (Koczka and Mizsey, 2009). The present study thus aimed to find the effectiveness of ARPs for perchlorate degradation.

8.2 Objective

To study the degradation of perchlorate using advanced reduction processes.

8.3 Methodology

Remediation study was tried using Sono reactor, UV photolysis, strirring method and double distillation method.

Sono reaction

The sonochemical degradation was carried out in a 500 ml reaction vessel; the ultrasound was introduced at the bottom of the vessel using an L3 ELAC Nautik ultrasound generator powered by an Allied Signal R/F generator (T & C power conversion, Model AG 1006). The degradation was carried outat 350 kHz and 80 W power at varying pH using perchlorate and sulfite. Experiments were done for 6 hrs and samples were collected every 1 hour.

Fentons reaction (Stirring method)

Perchlorate standards were stirred using magnetic stirrer in different pH conditions (acidic, neutral and basic). Three major experiments were done using this method. Perchlorate alone in different pH was first done and found that the experiment runs well in acidic pH. So experiments were continued in acidic conditions. Perchlorate was added with iron (II) sulphate and undergone stirring method. Finally, perchlorate standards were mixed with iron (II) sulphate and persulphate and then stirred. Samples were collected and perchlorate reduction was determined using LCMS.

UV photolysis

UV reaction between perchlorate and Iron (II) sulphate at various concentrations were studied. UV irradiation experiments were carried out on a photo reactor with 125 W medium pressure deuterium lamp inserted on the quartz vessel as the light source supplied by Scientific Aids & Instruments Corporation (SAIC, Chennai). For each experiment, about 150 ml of the sample solution was placed on the immersion well reactor, made up of borosilicate glass. The samples were removed from the immersion well reactor after different irradiation times by using a micropipette / syringe and were used for further analysis. Samples were taken at an interval of 1 hour and the whole experiments were carried out for 5hrs.

Double distillation

Double distillation (Lab-Sil double distillation apparatus) was used for the separation of perchlorate and to purify water. The perchlorate standard of 5ppm was prepared. 1L of the sample was added to the Input beaker (B1). The apparatus was switched on. Every 5 minutes around 250 ml of standard was added to B1. Samples were collected from B1 every 5 minutes. After 20 minutes second flask Boiler B2 was filled and the B2 was switched on. Then samples were collected every 5 minutes from B1, B2 and Output beaker (B3), till 1L of water was double distilled. The collected samples were then analyzed using LCMS.

8.4 Results and discussion

Perchlorate reduction was noticed in all the reactions ranging from 4.68 to 32.25% (Table 8.1 to 8.3). Highly significant variation ($p<0.05$) was noticed between the experiments.

Sono chemical degradation

The experiments were carried out for 6hrs and a degradation of 10.71% to 28.83% was observed (Table 8.1). Experiments conducted in acid pH (3) and neutral pH (7) showed almost similar rate of degradation whereas alkaline pH (10) showed only 10.71% reduction. In acid pH maximum degradation was observed when addition of sulfite done whereas in neutral pH, reduction was more without sulfite. Perchlorate degradation at

different experimental conditions was graphically represented (Fig. 8.1 & 8.2). Highly significant variation of perchlorate degradation was shown (p=0.01) when reaction was carried out in the presence of sulfite under varying pH.

Table 8.1 Experimental conditions and perchlorate reduction percentage using sonolysis (350 kHz; 80W)

Expt. No	Reactants(conc.)	pH	Time (hrs)	Perchloratereduction (%)
Expt. 1	ClO_4 = 5ppm	7	6	24.8
Expt. 2	ClO_4 = 5ppm	3	6	21.14
Expt. 3	ClO_4 = 5ppm Sulfite= 5ppm	7	6	23.15
Expt. 4	ClO_4 = 5ppm Sulfite= 5ppm	10	6	10.71
Expt. 5	ClO_4 = 5ppm Sulfite= 5ppm	3	6	28.83

Generally the sonochemical degradation was reported at acidic pH. Under acidic pH, the protonium ion was more formed and accumulated in the interface region of the cavitating bubble as reported before (Pegram and Record, 2006). Therefore the bubble becomes positively charged. Since the perchlorate ion was negatively charged, it could absorb here. The generation of more hydroxyl radical was also reported at acidic pH. This might be the reason for observing comparatively higher degradation at low pH.

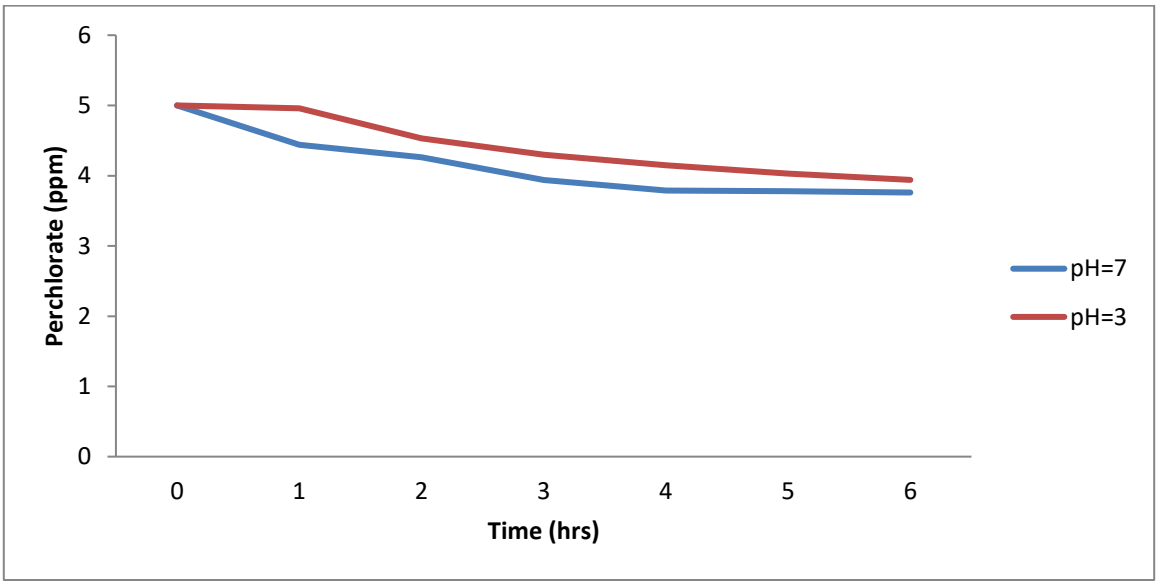


Fig. 8.1 Effect of pH (pH 7& 3) on sonochemical degradation of perchlorate

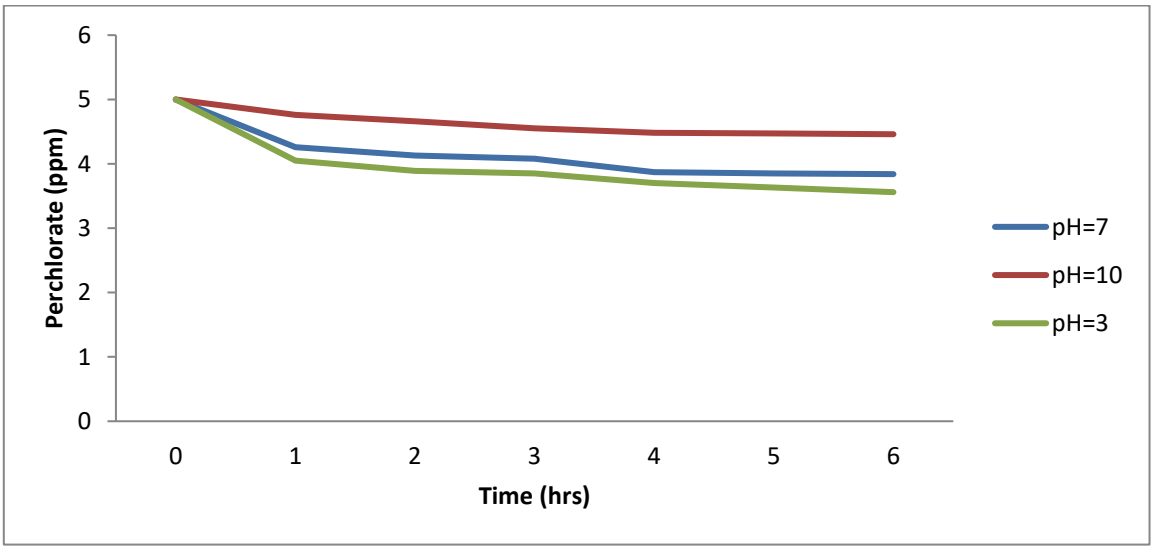


Fig. 8.2 Variation of perchlorate degradation using sonochemical method at varying pH (7, 10, 3) by adding sulfite as reducing agent.

Fentons type ($Fe^{2+}/S_2O_8^{2-}$) reaction

Degradation rate of perchlorate varied from 4.68% to 32.25% under different experimental conditions (Table 8.2). Maximum reduction was noticed under acidic condition (pH 3) whereas similar degradation rates were observed for both alkaline and

neutral pH (11 and 7 respectively) (Fig. 8.3 & 8.5). The degradation rate showed highly significant variation (p=0.01) when perchlorate was reacted with persulfate and iron (II) sulfate at different pH.

Table 8.2 Experimental conditions and perchlorate reduction percentage using fentons type reaction

Expt. No	Reactants(conc.)	pH	Time (hrs)	Perchloratereduction (%)
Expt. 6	ClO_4 = 5ppm S_2O_8= 3ppm Fe^{2+}= 1ppm	7	5	9.91
Expt. 7	ClO_4 = 5ppm S_2O_8= 3ppm Fe^{2+}= 1ppm	3	5	25.53
Expt. 8	ClO_4 = 5ppm S_2O_8= 3ppm Fe^{2+}= 1ppm	11	5	14.67
Expt. 9	ClO_4 = 5ppm S_2O_8= 3ppm Fe^{2+}= 2ppm	7	5	19.06
Expt. 10	ClO_4 = 5ppm S_2O_8= 3ppm Fe^{2+}= 2ppm	3	5	32.25
Expt. 11	ClO_4 = 5ppm S_2O_8= 3ppm Fe^{2+}= 2ppm	11	5	4.68
Expt. 12	ClO_4 = 5ppm Fe^{2+}= 3ppm	3	5	8.98
Expt. 13	ClO_4 = 5ppm Fe^{2+}= 5ppm	3	5	15.76
Expt. 14	ClO_4 = 5ppm S_2O_8= 5ppm Fe^{2+}= 5ppm	3	5	17.53

In this type of reaction, the ferrous ion reacts with persulfate ion to form sulfate radical ion. The sulfate radical oxidizes the ClO_4^- to ClO_4. The reaction involved in $Fe^{2+}/S_2O_8^{2-}$ are given below,

$Fe^{2+} + S_2O_8^{2-} \rightarrow SO_4^{\bullet-} + Fe^{3+}$

$ClO_4^- + SO_4^{\bullet-} \rightarrow ClO_4$

This reaction was more favorable under acidic pH. The persulfate ion decomposition was also very effective in acidic pH. At alkaline pH, the precipitation of hydroxides occurred and resulted in the deactivation of persulfate ion. Thus only small amount of oxidizing species were generated.

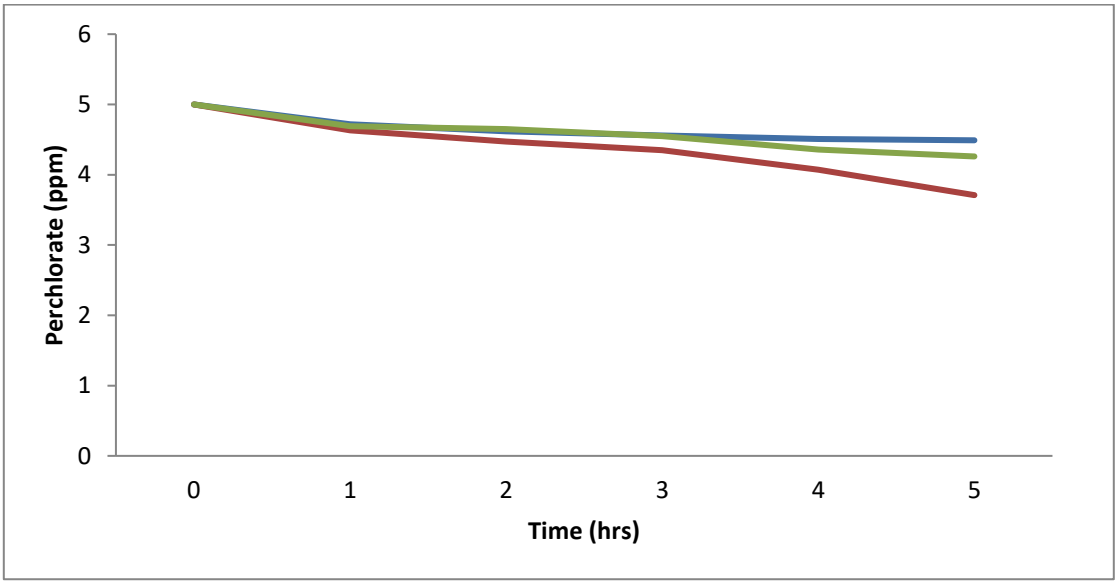


Fig. 8.3 Perchlorate degradation at various pH (7, 3 11) using 1ppm Fe (II) and 3ppm persulfate as reducing agents using fentons reaction.

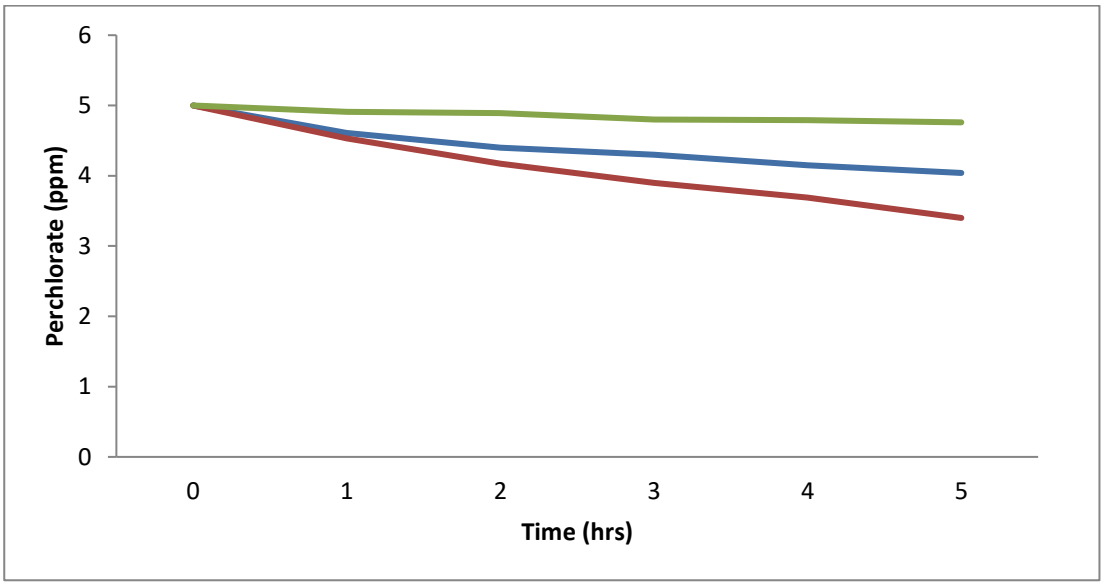


Fig. 8.4 Perchlorate degradation at various pH (7, 3, 11) using 2ppm Fe(II) and 3ppm persulfate as reducing agents using fentons reaction

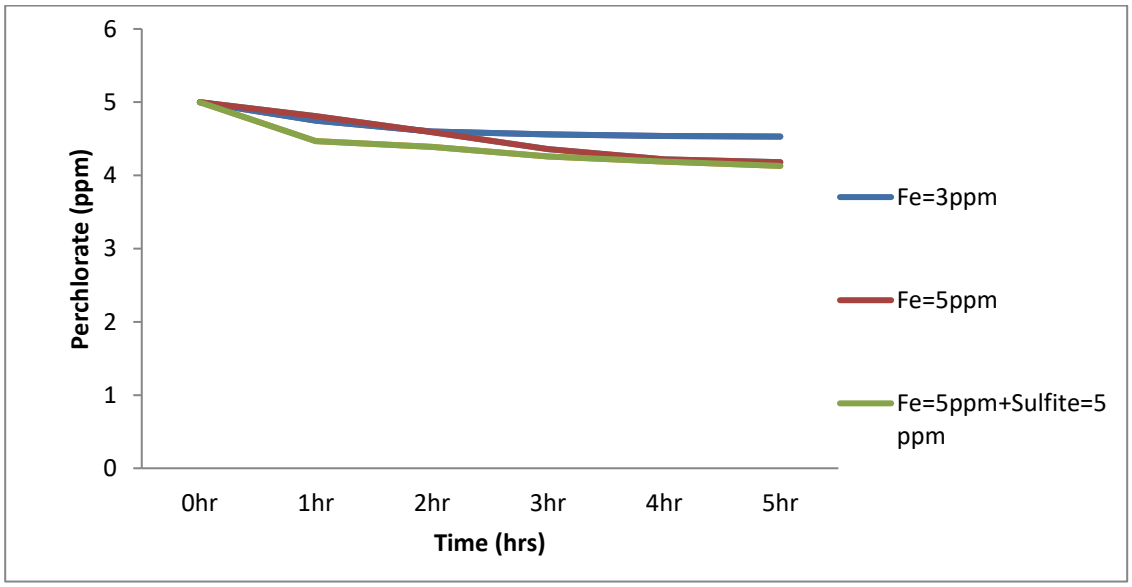


Fig. 8.5 Effect of varying concentration of Fe (II)- 3ppm and 5ppm, with and without the addition of persulfate in perchlorate degradation at pH=3 using fentons reaction

UV Photolysis

In UV photolysis 5.04% to 10.77% reduction of perchlorate was observed at varying conditions (Fig. 8.6 to 8.9) (Table 8.3). None of the experiments involving UV showed good amount of degradation and it seemed perchlorate was stable towards UV light.

Table 8.3 Experimental conditions and perchlorate reduction percentage using UV degradation (125W)

Expt. No	Reactants(conc.)	pH	Time (hrs)	Perchloratereduction (%)
Expt. 15	ClO_4 = 5ppm	3	5	6.22
Expt. 16	ClO_4 = 5ppm	7	5	6.68
Expt. 17	ClO_4 = 5ppm	11	5	6.63
Expt. 18	ClO_4 = 5ppm Fe^{2+}= 1ppm	3	5	6.73
Expt. 19	ClO_4 = 5ppm Fe^{2+}= 1ppm	7	5	10.77
Expt. 20	ClO_4 = 5ppm Fe^{2+}= 1ppm	11	5	8.81
Expt. 21	ClO_4 = 5ppm Fe^{2+}= 2ppm	3	5	7.08
Expt. 22	ClO_4 = 5ppm Fe^{2+}= 2ppm	7	5	7.52
Expt. 23	ClO_4 = 5ppm Fe^{2+}= 3ppm	7	5	7.58
Expt. 24	ClO_4 = 5ppm Fe^{2+}= 4ppm	7	5	7.54
Expt. 25	ClO_4 = 5ppm Fe^{2+}= 5ppm	7	5	5.04

Screening experiments using ARPs for perchlorate remediation was reported recently (Vellanki *et al.,* 2013). Negligible removal (0- 10%) of perchlorate was observed using UV and sonolysis involving sulfite and ferrous as reducing agents. Present study also

confirmed the fact that UV removal of perchlorate is only negligible (maximum 10.77%). However combination of ultra sound and sulfite gave 28.83% removal. Fenton type reaction showed maximum degradation (32.25%) when ferrous and persulfate combinations were used as reducing agents.

Perchlorate was removed by pilot-scale bioreactors (Evans *et al.*, 2002). Removal was successful to below 4ppb levels on day 106. It required reduction of dissolved oxygen, nitrate and addition of acetic acid and ammonium phosphate (Anaerobic biological perchlorate reduction). Perchlorate and chlorate in raw waste water and creek water was completely reduced using microbes in 4 to 7 days and 8 to 29 days. But substrates like acetate, lactate, citric acid or molasses needs to be added (Wu *et al.*, 2001). Aerobic conditions reduce the effectiveness of ARPs (Vellanki *et al.*, 2013). Also, at room temperature perchlorate degrades very slowly. This might be one of the reasons for the low removal of perchlorate. Analysis of strong reducing agents and their best suiting AOPs and various conditions (pH, concentration etc.) also posed a problem with the experiments.

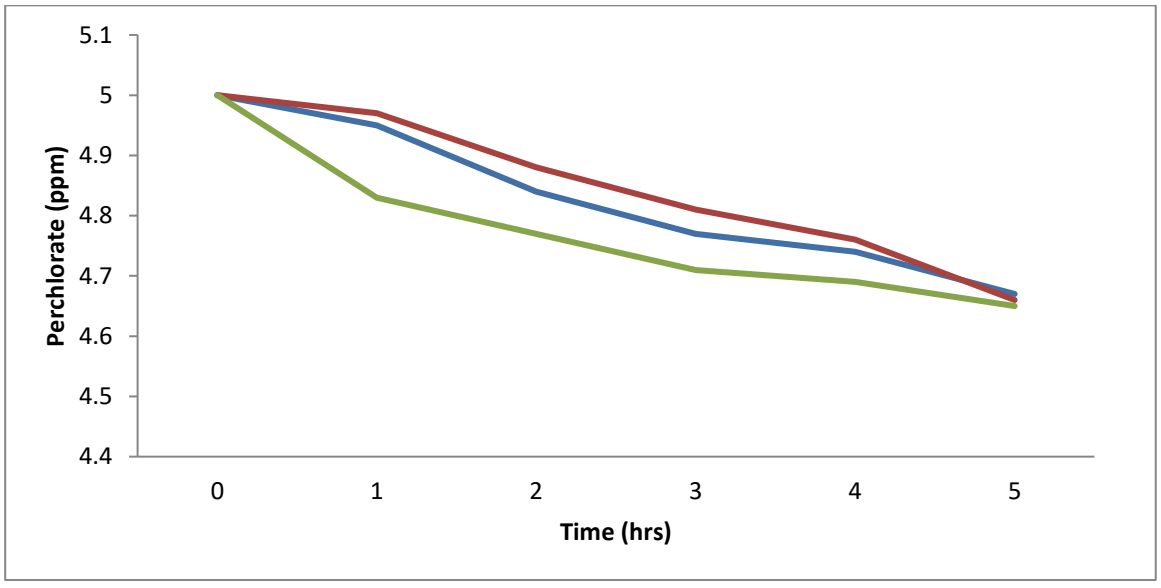


Fig. 8.6 UV degradation of perchlorate at different pH (3, 7, 11) without addition of reducing agents

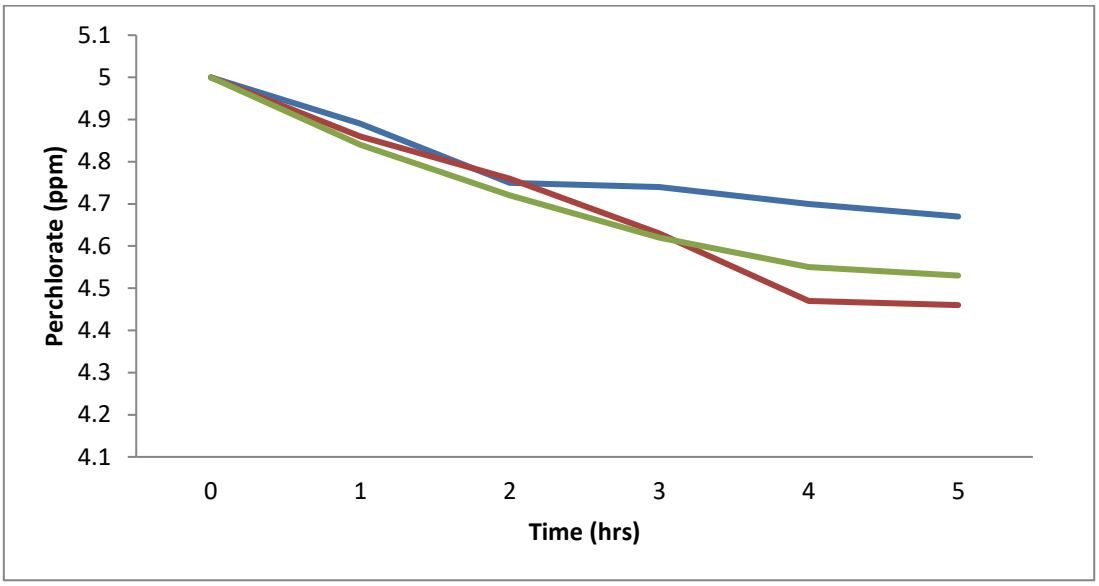


Fig. 8.7UV degradation of perchlorate at different pH (3, 7, 11) by addition of 1ppm Fe (II)

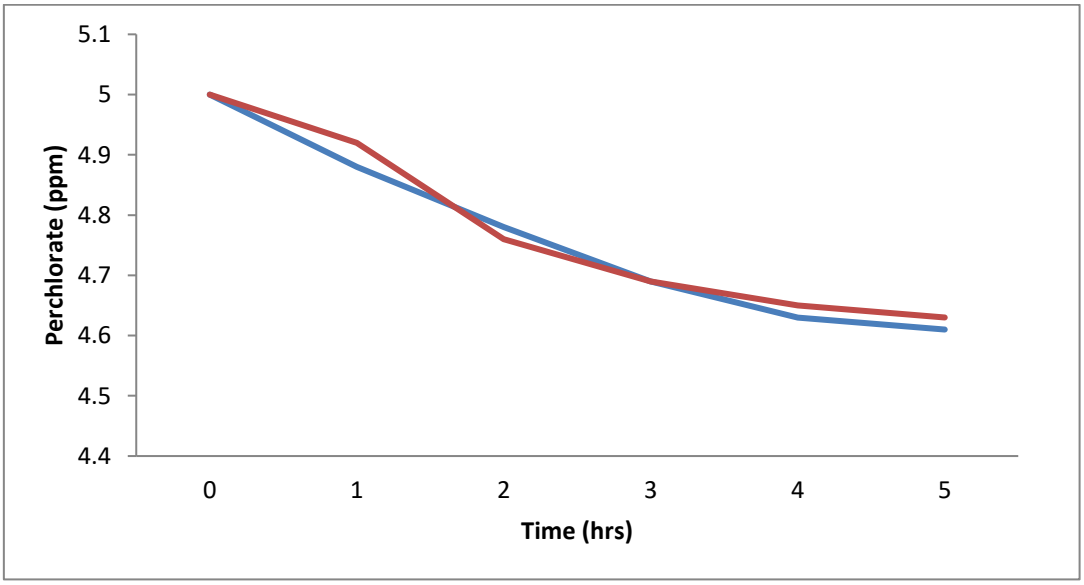


Fig. 8.8 UV degradation of perchlorate at pH 3 and 7 by addition of 2ppm Fe (II)

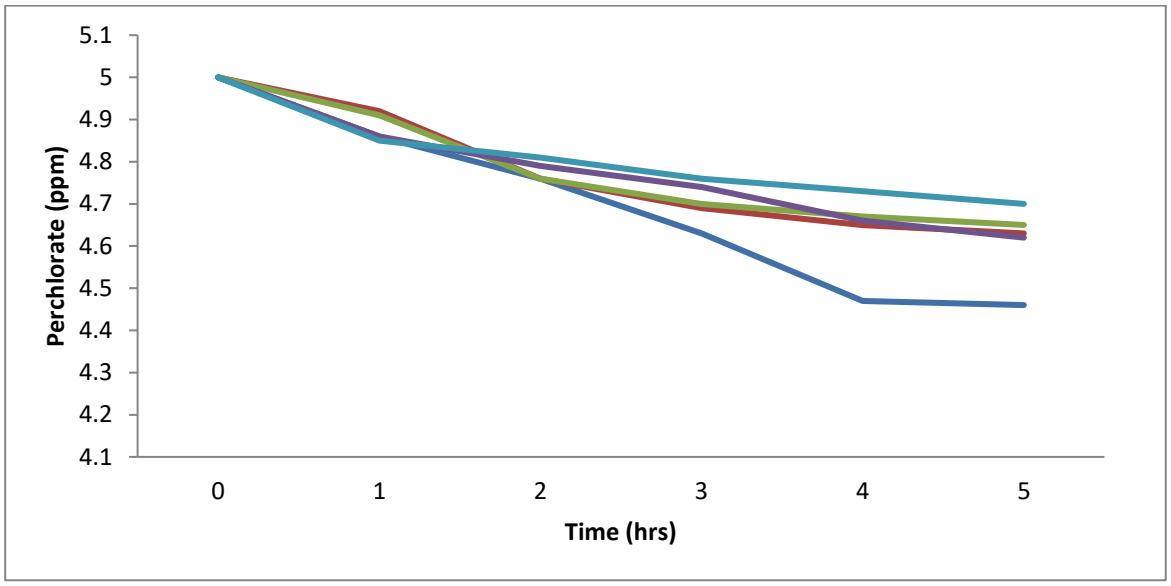


Fig. 8.9 UV degradation of perchlorate at pH 7 using different concentrations of Fe (II)

Distillation

Both single and double distilled water was checked for perchlorate. A complete separation of perchlorate in water was achieved using distillation process. It was found that even single distillation was enough for complete perchlorate removal. The perchlorate content in the input beaker was found to be gradually increasing (from 5 ppm to 16 ppm) with time during the experiment (50 minutes) (Fig. 8.10); still no perchlorate or chlorate was detected in the distilled water. This can be widely employed in industries for treating perchlorate contaminated waste water. The perchlorate contamination in ground water could be effectively controlled to a particular extent using this technology as the intrusion of perchlorate contaminated wastewater is the major reason of groundwater contamination near the industrial areas. The perchlorate salt in the input water could be recollected by undergoing complete distillation and then collecting and drying the salt. 1L of contaminated water was purified every 20 minutes during the experiment.

Distillation could also be used for treating drinking water contaminated with perchlorate. It was reported that drinking distilled pure water is better as it is less toxic, absorbs rapidly and prevents hydration (Misner, 2011).

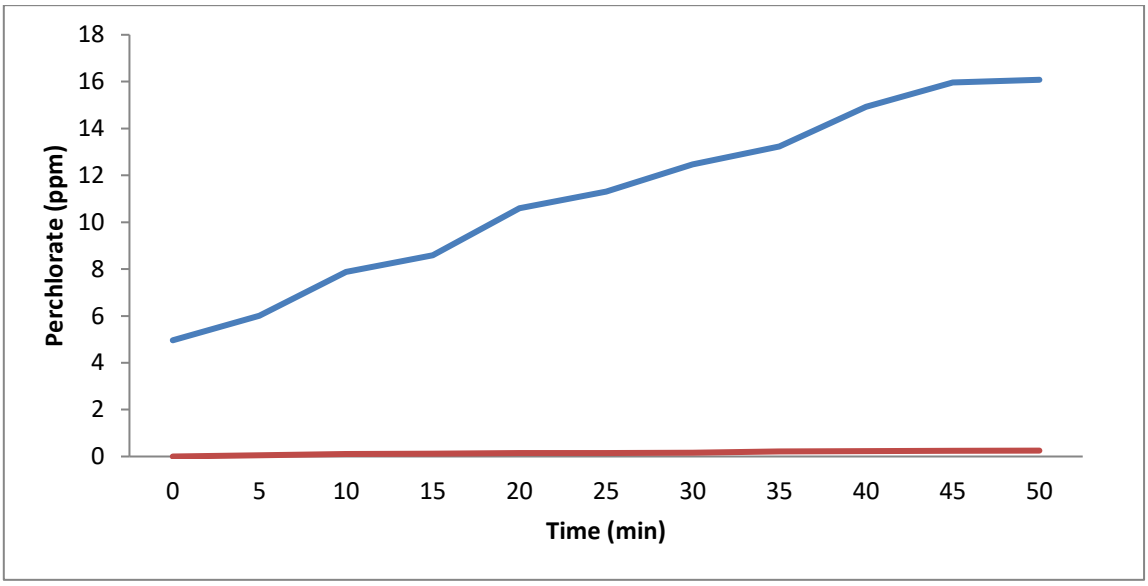


Fig. 8.10 Increase of perchlorate and chlorate in input beaker (B1) with time

8.5 Conclusion

Screening experiments using ARPs for perchlorate remediation points out that there is a possibility of complete degradation of perchlorate from environmental matrices. Further research is needed to find out the apt method of AOP and its corresponding best suitable reducing agents. Compared with other methods employed, ARPs are not time consuming. Distillation gave satisfactory results in separation of perchlorate from water. The present study indicated that the combination of ARPs, AOPs with other conventional methods could be a better option for the removal of perchlorate from water. More studies are needed in this regard.

Summary and Conclusion

Perchlorate is an emerging pollutant. It is an oxy anion of chlorine. The properties, uses, sources, fate and transport, toxicity and remediation of perchlorate are described in Chapter-1. The major salts such as sodium perchlorate, potassium perchlorate and ammonium perchlorate are widely used as oxidizers. Sodium and potassium perchlorates are used in fireworks and ammonium perchlorate is used mainly in rocket propellants. Perchlorate is formed both naturally and artificially. Natural production is very limited and the environment pollution by perchlorate is result of uncontrolled use of man-made salts. The soluble and persistent perchlorate salts enters the water bodies, soil and air and then reaches various life forms. Toxicity of perchlorate is mainly confined to hypothyroidism and the major victims are infants and women. In infants, perchlorate can result in permanent nervous disorders. Remediation of perchlorate is very difficult. Techniques like ion exchange, bioremediation, thermal reduction, electrolytic reduction etc. are employed for perchlorate degradation, still none gives complete results and studies are still being carried to remediate perchlorate completely.

Chapter 2 dealt with extensive literature review on perchlorate. The chapter reviewed the natural and anthropogenic sources around the world. The perchlorate contamination from artificial sources was reported from India, China, South Korea, US etc. The literature indicated the presence of perchlorate in soil, water, aquatic and terrestrial organisms, food crops etc. and reported to be contaminating river water, lakes, rain water, vegetation etc. Perchlorate was even found in breast milk, cow's milk, cord blood etc. Human saliva and urine also had perchlorate. Perchlorate can pass through amniotic fluid, placenta etc and make infants susceptible for thyroid disorders. Extensive study on toxicity of perchlorate was conducted in rats, rabbits, Japanese quail, Fathead minnow, fish, lamprey, goat etc. Based on various studies health protective dose of perchlorate is calculated as 0.7 ppb/kg body weight/day which is equivalent to a drinking water equivalent of 24.5 ppb. Different methods employed for perchlorate detection are

IC, IC/MS, IC/MS/MS, LC/MS, LC/MS/MS etc. The literature indicated the wide use of biological methods for remediation of perchlorate however it is time consuming and new methods are searched out like electrolytic method, hydrogen based reactors etc.

General methodology is detailed in Chapter 3. General sample collection and processing method for perchlorate in different matrices was explained. Water samples collected were filtered through 0.2µ nylon membrane filter paper and stored under 4ºC till it is analyzed using LCMS. Shimadzu LC/MS-2020 is used for the detection; Dionex AS-21 is the column used, Methylamine as the solvent. Soil samples were collected, weighed, added water in the ratio 1 soil: 2 water, vortex mixed, centrifuged, again vortex and filtered through 0.2µ nylon membrane filter paper. Chlorate was also detected using LCMS. Other parameters like anions and cations were detected using IC. pH was measured using pH meter, EC and TDS using conductivity meter. All the details of the instruments are mentioned in the chapter.

Perchlorate contamination of various drinking water sources like well water, bore well water, and tap water from selected regions of entire districts of Kerala was assessed and is described in Chapter 4. Samples were collected during pre-monsoon, monsoon and post monsoon. Well water was contaminated than bore well water and tap water. During pre-monsoon contamination has followed the pattern well water> bore well water> tap water; during monsoon it was well water> bore well water (perchlorate BDL in tap water); and in post monsoon well water> tap water (perchlorate BDL in bore well water). Region wise data followed the order Northern region> Southern region> Central region, for perchlorate. The results confirmed that the bottled water was also contaminated with perchlorate. A drawback of the purifying techniques used was elucidated. Presence of perchlorate was noticed in some rain water samples also. The study clearly showed that almost all the water sources in Kerala were contaminated with perchlorate.

Chapter 5 dealt with the seasonal variation of perchlorate around perchlorate handling industrial units and its correlation with other water quality parameters. Samples were collected in various seasons (pre-monsoon, monsoon and post-monsoon). All the

sites have showed perchlorate contamination except the control site during these seasons. Highest mean perchlorate was observed in site 1 (APEP) followed by site 2 (TERLS), site 3 (Paravur fireworks manufacturing site) and site 4 (Kottayam fireworks manufacturing site). Significant variation of perchlorate was not noticed between the seasons in site 1, site 2 and site 3 however it showed significant variation with control site. At site 4, perchlorate showed significant variation between the seasons and also with the control site. Non-monsoon samples had highest values of perchlorate and monsoon samples had minimum perchlorate but the contamination was widespread during monsoon. The perchlorate contamination around perchlorate manufacturing and handling industrial units were found to be site dependent. Well water samples were contaminated more than the tap water samples. Almost all the water quality parameters (except chlorate) were within the permissible limits only. Perchlorate contamination of drinking water in the study area was found to be dependent on amount of perchlorate manufactured and used, rainfall, geography of the site, depth of water table etc. General correlation table showed that perchlorate was significantly correlated with chlorate.

The role of firework displays in perchlorate contamination of the environment was studied in detail in the next chapter. The study focused five major fireworks display sites across Kerala. After fireworks soil samples were found to be more perchlorate contaminated than water samples. In selected sites water samples that were collected from wells or ponds within the site were contaminated with perchlorate. Variation of perchlorate in different sites owed to the variation in amount of perchlorate used spent or unused chemical, partial combustion of firework etc. Geographical factors like rainfall, wind direction, wind velocity etc. also determined the rate of perchlorate contamination. Continuous monitoring study proved that perchlorate can reach groundwater through runoff or atmospheric deposition. Perchlorate in water samples was significantly correlated with chlorate and chloride only.

Chapter 7 dealt with the role of perchlorate in causing thyroid disorder in selected regions of Kerala. Perchlorate was found to be exceeding in drinking water samples at APEP, TERLS and Paravur fireworks manufacturing sites. At APEP, as the government

provided drinking water, no thyroid disorder was reported. But at TERLS and Paravur average intake of perchlorate was far higher than the recommended dose and this might have resulted in hypothyroidism in humans. Women of conception age suffered the most in these two sites where as in all other sites the reported thyroid rate was less than the normal rate (except Manarcad fireworks display where majority was said to have hereditary thyroid disorder) and the women of post-menopausal age suffered from thyroid disorder. In short, some extra factors aided in inducing thyroid disorder at TERLS and Paravur and perchlorate might be the inducing factor. Along with perchlorate, other genetic, environmental factors also may add to the thyroid disorder.

Degradation of perchlorate using Advanced Reduction Processes (ARPs) was studied (Chapter 8). Perchlorate standards were treated with various concentrations of reducing agents under different pH. Techniques used were sonochemical methods, fentons reaction and UV photolysis. Distillation was used for the separation of perchlorate. In sonochemical degradation maximum reduction obtained was 28.83%, with the addition of sulfite to perchlorate standard at acidic pH. Fentons reaction gave the highest reduction among the studied reduction processes. 32.25% reduction of perchlorate was shown in acidic pH under the addition of persulfate and iron (II) sulfate. Very low degradation of perchlorate was noticed with UV photolysis experiments. Distillation proved to be very effective in separation of perchlorate and can be used for the recycling processes.

The major sources of perchlorate contamination of drinking water in Kerala were found to be from the manufacturing and usage of rocket propellants, fireworks manufacturing and display. Perchlorate was detected in well water, bore well water and tap water collected from all the districts of Kerala. Selected bottled water samples were also found to be perchlorate contaminated. Even some of the rain water samples had perchlorate. Perchlorate in drinking water varied with respect to seasons. More the rainfall less was the perchlorate contamination. Perchlorate in drinking water depended on slope of the area, dilution, distance from the source, usage of the chemical etc. Drinking water collected from around rocket propellant manufacturing and usage sites

had the maximum perchlorate. Fireworks display also resulted in perchlorate contamination of soil and water. The extent of contamination depended on the amount of fireworks cracked, combustion, amount of perchlorate usage in the fireworks etc. From soil perchlorate reached ground water. The health based survey showed that thyroid disorders were more than the usual around rocket testing site and fireworks manufacturing site. Only medical analysis of blood, urine samples etc. can confirm the fact. Remediation of perchlorate using Advanced Reduction Processes could not degrade perchlorate completely, however it can be considered along with other methods. More research on perchlorate contamination, toxicity and remediation is essential.

Chapter 10

Recommendations

Perchlorate is now considered as an emerging pollutant. The major sources in Kerala are mainly anthropogenic such as manufacturing and use of rocket propellants and fireworks. The soluble and persistent perchlorate salts enter the water bodies, soil and air and then reaches various life forms. Toxicity of perchlorate is mainly confined to hypothyroidism and the major victims are infants and women. The complete degradation of perchlorate is very difficult with any of the bioremediation techniques and hence it is necessary to regulate and manage the use of perchlorate.

The following recommendations are put forward based on our study;

1. Reduce the quantum of fire work especially during the celebrations in temple and churches.
2. Regulate major and minor fire work manufacturing centres. A number of small scale fire manufacturing centres are in Kerala which contributes perchlorate contamination at local scale.
3. The surrounding environment of industrial sites and rocket launching centres in Kerala are contaminated with perchlorate. Strict monitoring and management of industrial regions where perchlorate is producing/using. Proper water supply to the workers and their family to be provided from outside of the contaminated region and routine health check-up camps has to be organised
4. Perchlorate was detected in bottled water indicates the need of including perchlorate too in the list of parameters analysed before packing.
5. There is no permissible limit or any other drinking water quality standard for perchlorate in Kerala. Therefore, it is very urgent to include permissible limits for perchlorate along with other parameters. A value of 0.07 mg/L can be established as permissible limit in drinking water
6. The fate and transport of perchlorate especially in soil has to be studied in detail. It is highly significant as the perchlorate is reaching water bodies after atmospheric fall out is through soil.

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SURVEY FORM

For Ph.D work entitled "Perchlorate contamination of the drinking water in the selected regions of Kerala", by Sijimol. MR under the guidance of Dr. Mahesh Mohan, School of Environmental Sciences, Mahatma Gandhi University, Kottayam, Kerala

Station name:	**No.**	**Date**:

1. Name of house owner:
2. Address:

3. Details of people residing in the house

Sl. No.	**Name**	**Category** ***<1year:Newborns 1-4years:Infants 4-14years:Children 15-55years:Adult >55years:Old***	**Sex M/F**	**Age (in years)**	**Body Wt. (in Kg)**	**Amount of water consumed from the source per day (in L)**	**Any thyroid problem analyzed (Y/N)**	**Any symptoms of thyroid disorder (but not analyzed (Y/N)**
1.								
2.								
3.								
4.								
5.								
6.								
7.								

4. Source of drinking water: Well water/Tap water/ Bottled water/Purified water
5. Distance of water source from the main study station/site:
6. Any other problems due to the firework display/perchlorate manufacturing:

7. Do you prefer the fireworks display/perchlorate manufacturing in the site**:** **Yes/No**
8. Any feeding/pregnant women in the house: **Yes/No**
9. Any water treatment methods used: **Yes/No**……

Signature of house owner: Signature of surveyor:

To be filled after water sample analysis

1. Average amount of perchlorate in drinking water source:
2. Any observed thyroid problem:
3. Any need of milk/urine sample collection:
4. Amount of perchlorate intake/kg/day:

Category	Average intake (µg/kg/day)	Total intake per day (in µg)
Infants		
Children		
Adults		
Old		
Pregnant women		

5. Other notes to add:

PUBLICATIONS FROM THE PROJECT

Paper Published

1. Sijimol, M. R. and Mahesh Mohan (2014) Environmental impacts of perchlorate with special reference to fireworks—a review. ***Environmental Monitoring and Assessment***, 186:7203-7210. DOI 10.1007/s10661-014-3921-4, **Springer**

2. Sijimol MR, Jyothi S, Pradeepkumar AP, SHylesh Chandran MS, Shabin Ghouse S and Mahesh Mohan (2015) Review on fate, toxicity and remediation of perchlorate. ***Environmental Forensics*** 16(2): 125-134. DOI: 10.1080/15275922.2015.1022914, **Taylor & Francis**

3. Sijimol, M. R., Mahesh, M., and Dineep, D. (2016) Perchlortae contamination in bottled and other drinking water sources of Kerala, southwest coast of India. ***Energy Ecology and Environment***. DOI 10.1007/s40974-016-0018-7, 2016.**Springer**

4. Sijimol M. R., Mahesh Mohan, Gopikrishna V. G. and Dineep D. (2017). Perchlorate in drinking water around rocket manufacturing and testing facilities and firework manufacturing sites in Kerala, India. ***Energy Ecology and Environment*** ,DOI 10.1007/s40974-017-0055-x **Springer**

5. Sijimol, M. R., Aravindakumar, C. T., Manoj, P. R., Dineep, D., Nejumal, K. K., & Mohan, M. Perchlorate contamination of drinking water sources in Kerala, South India, and its degradation using advanced chemical treatment. Energy Ecology and Environment. 5(4):286–293, https://doi.org/10.1007/s40974-020-00163-5

6. Sijimol M R , Dineep D, Arun Sasi S, Abdul Shukkur M, Ashna Antony, and Mahesh Mohan. Fireworks Display and Perchlorate Contamination in Kerala, India. Environmental Forensics.

Papers Presented

1. Sijimol, M. R., Renju Kuttappan and Mahesh Mohan (2014) Fireworks: A disaster and an environment pollution source. In the proceedings of 2nd Diasaster Risk and Vulnerabilty Conference. A.P. Pradeepkumar, F.J. Behr, F.T. Illiyas and E. Shaji (Editors). Pg. No. 242-246. ISBN 9788192344928
2. Sijimol M.R., and Mahesh Mohan (2014). Perchlorate and its significance in Kerala. BCM college, Kottayam
3. Sijimol M.R. and Mahesh Mohan (2014). Fireworks and perchlorate contamination. St.Stephens college, Uzhavur
4. Sijimol M.R., Dineep D., and Mahesh Mohan (2014). Perchlorate contamination of bottled water in Kerala. NSE, MGU

5. Sijimol M.R., Dineep D., and Mahesh Mohan (2015). Perchlorate contamination of well water in Kerala. ICW, MGU
6. Sijimol M.R., and Mahesh Mohan (2015). Fireworks as a source of perchlorate contamination in the soil, Kerala University.
7. Sijimol MR, Mahesh Mohan and Dineep D (2015) Identification of perchlorate in environmental matrices using Liquid Chromatography Mass Spectrometry,, ICMS, MGU
8. Sijimol M.R., Dineep D., and Mahesh Mohan (2015). Perchlorate determination in environmental samples using Shimadzu LC-MS 2020, Chennai.
9. Sijimol M.R., Mahesh Mohan., and Nejumal K. K. (2016). Perchlorate degradation in drinking water- a lab scale study. ICW, MGU
10. Sijimol MR and Mahesh Mohan (2017) .Perchlorate contamination in kerala. Kerala Science Congress.

Papers submitted

1. Sijimol M R and Mahesh Mohan. Occurrence of thyroid disorders associated with perchlorate contamination in kerala- a preliminary health based survey. Environment Pollution and Protection.

Perchlorate contamination in bottled and other drinking water sources of Kerala, southwest coast of India

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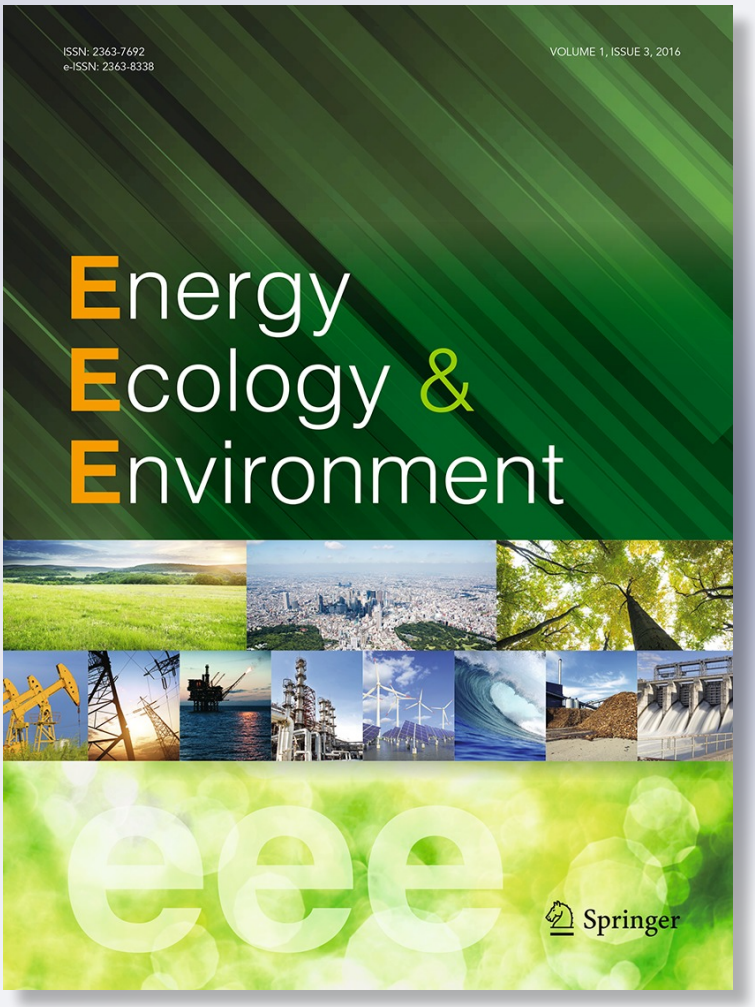
Energy, Ecology and Environment

ISSN 2363-7692
Volume 1
Number 3

Energ. Ecol. Environ. (2016) 1:148-156
DOI 10.1007/s40974-016-0018-7



Springer

Energ. Ecol. Environ. (2016) 1(3):148–156
DOI 10.1007/s40974-016-0018-7

RESEARCH ARTICLE

Perchlorate contamination in bottled and other drinking water sources of Kerala, southwest coast of India

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Received: 13 October 2015 / Revised: 22 February 2016 / Accepted: 25 February 2016 / Published online: 11 March 2016

Abstract Perchlorate and chlorate are inevitable components in rocket propellants, fireworks, water treatment, bleaching, textile industry, etc. Knowingly or unknowingly, wide use of these chemicals contaminates drinking water systems. The present study assessed the perchlorate and chlorate contamination of bottled water and other drinking well, tap, bore well, rainwater sources of Kerala and other parts of Peninsular India. Other drinking water samples were collected during the pre-monsoon, monsoon and post-monsoon from the 14 districts of Kerala and were analyzed for perchlorate and chlorate using liquid chromatography–mass spectrometry. Most of the locally available brands of bottled water were found to be contaminated with perchlorate and chlorate. Mean value of perchlorate was found to be 93.19 ppb, and that of chlorate was 3692.07 ppb, both exceeding the health reference level. The continuous consumption of water with high level of perchlorate content can cause high risk, and the probability of increasing thyroid disorders is high. Perchlorate was detected from well, tap and bore well water samples, and the maximum perchlorate was observed for the pre-monsoon season, whereas the minimum noticed in the monsoon samples. The high concentration of perchlorate detected in groundwater was mainly due to the industrial units and firework manufacturing and display sites.

Keywords Pollution · LC–MS · Bottled water · Chlorate · Thyroid disorders

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1 Introduction

Bottled water is one of the fastest-growing industries in India, and the rate is increasing on a more frequent basis, of 40–50 % annually. South India is the biggest consumer of bottled water, representing more than 50 % of the total market in India (The Economic Times 2012). In Kerala, one of the southernmost Indian states, around 0.8 million liters of potable water is sold amongurban communities per day and is increasing every year (IWR 2013). Hence, any contamination of bottled water may affect a large population. The present study aimed to investigate the drinking water contamination with perchlorate and chlorate.

Perchlorate (ClO_4^-) and chlorate (ClO_3^-), the inorganic anions of chlorine, are gaining attention because of their immense contamination in drinking water systems. Perchlorate is used as an oxidizer in solid rocket propellants (Tikkanen 2006), fireworks (Sijimol et al. 2014, 2015; Sijimol and Mahesh 2014; Isobe et al. 2012), munitions, signal flares (ITRC 2005; Urbansky 2002), etc. Perchlorate is highly soluble and is persistent in nature (Siglin et al. 2000; Motzer 2001). This results in the contamination of environment, especially aquatic systems, and is very difficult to treat (Logan 1998). Various studies reported perchlorate contamination of surface water, groundwater, tea, soft drinks, beverages, baby formulas, etc. (Snyder et al. 2006; Kannan et al. 2009; Anupama et al. 2012). The awe behind perchlorate contamination is that exceeding the limit of 24.5 ppb perchlorate in drinking water can result in thyroid disorders (Wolff 1998; Anderson et al. 2006; Sijimol et al. 2015).

Chlorate is widely used in matches, laboratories, herbicides, pulp, paper and textile industry, etc. The reduction of perchlorate can also result in chlorate production (USEPA

2008a). Sodium hypochlorite and chlorine dioxide are used in water treatment, disinfection of microorganisms, pesticide, bleaching, coir and textile industry. About 10 % of the applied chlorine dioxide is converted to chlorate. In hypochlorite solutions, chlorate is generated spontaneously. Like perchlorate, chlorate is also highly soluble (USEPA USEPA 2008a, b; AWWA 2014). It is included in the third Unregulated Contaminant Monitoring Rule (UCMR3) (AWWA 2014). In drinking water, the chronic dietary assessment for chlorate is estimated to be 0.69 mg/L (USEPA 2008a), whereas the estimated health reference level (HRL) for chlorate is 210 µg/L (AWWA 2014). Moreover, chlorate acts as a thyroid disruptor, resulting in thyroid gland follicular cell hypertrophy though not as strong as perchlorate (USEPA 2008a). It can also impair the oxygen-carrying capacity of blood and thereby ruptures red blood cell membranes in infants and fetuses (NAS 1987).

The major sources of perchlorate in Kerala are Ammonium Perchlorate Experimental Plant (APEP), Thumba Equatorial Rocket Launching Station (TERLS), firework manufacturing sites and innumerable firework displays (Sijimol and Mahesh 2014). Major industrial source of chlorate is Travancore Cochin Chemicals Limited where sodium chlorate is manufactured and used for ammonium perchlorate production at APEP (The Hindu 2013). The 800 tonnes of ammonium perchlorate produced by APEP is consumed by TERLS as rocket propellant. Sodium hypochlorite used in drinking water treatment plants can also act as a source of chlorate.

The literature indicates that a very few works have been carried out in India, to estimate the perchlorate contamination in drinking water (Kannan et al. 2009; Isobe et al. 2012; Anupama et al. 2012, 2015). Widespread occurrence of perchlorate in public drinking, open well and surface water sources was reported along the southwest coast of Kerala (Anupama et al. 2012). Hence, the present study aimed to understand the perchlorate and chlorate contamination of well water, bore well water, tap water, bottled water and rainwater in Kerala.

2 Materials and methods

2.1 Study area and sample collection

Kerala is situated along the southwest coast of India. Drinking water samples were collected from water supplies of selected towns from all the fourteen districts of Kerala. The 14 districts were classified into 3 regions—southern region (Trivandrum, Kollam, Pathanamthitta, Alappuzha), central region (Kottayam, Idukki, Thrissur, Ernakulam, Palakkad) and northern region (Kozhikode, Malappuram, Kannur, Kasaragod, Wayanad) (Fig. 1).

Drinking water samples (well, bore well and tap) were collected during April–May 2014 (before onset of monsoon); August–September 2014 (during monsoon) and December 2014–January, 2015 (after monsoon). Water samples were filtered using 0.2-µ nylon membrane filter paper and stored below 4 °C until the analysis performed.

Different brands (local and international) ($n = 31$) of bottled water were collected from different districts of Kerala. The number of samples from each district is given in Table 1. A few bottled water samples ($n = 5$) were randomly collected from other states also (Maharashtra, Andhra Pradesh, Tamil Nadu and Karnataka). The samples were filtered using 0.2-µ filter paper and stored in sterile polypropylene bottles, under 4 °C for the analysis.

Rainwater samples ($n = 15$) were collected during the summer season from selected towns of Kerala. Samples were then filtered and analyzed for perchlorate and chlorate.

2.2 Sample analysis

Liquid chromatography–mass spectrometry (LC–MS) (Shimadzu LCMS-2020) with Dionex AS 21 (250 mm × 4 mm diameter) column was used for perchlorate and chlorate analysis. Selective ion monitoring (SIM) technique was used for the detection. For perchlorate, *m/z* 101 (the isotopic mass of perchlorate *m/z* 99) was used for quantification, while hydrogen sulfate, $H^{34}SO_4$, the common anion in water, also had *m/z* 99. For the confirmation of a peak as of perchlorate, the ratio ^{35}Cl:^{37}Cl (*m/z* 99: *m/z* 101) was calculated and the ratio 3 ± 25 % was accepted. The method detection limit (MDL) was 2 ppb and the limit of quantification (LoQ) was 6 ppb for perchlorate, whereas those for chlorate were 4 and 10 ppb, respectively.

2.3 Risk assessment calculation

The established reference dose of perchlorate per kilogram body weight per day is 0.7 µg/kg/bw/day (USEPA 2008b). Risk assessment of perchlorate was calculated separately for entire Kerala (different seasons), regionwise (different seasons) and based on the type of drinking water.

$$\text{Intake } (\mu g/kg \text{ body wt/day}) = CW \times IR \times ED/BW,$$

where CW—chemical concentration in water (µg/L), IR—intake rate (L/day), ED—exposure duration (day), BW—body weight (kg) (Wu et al. 2010, 2011).

3 Results and discussion

3.1 Bottled water

Of the 36 brands of bottled water analyzed, 20 samples showed perchlorate (Fig. 2) and 32 samples showed

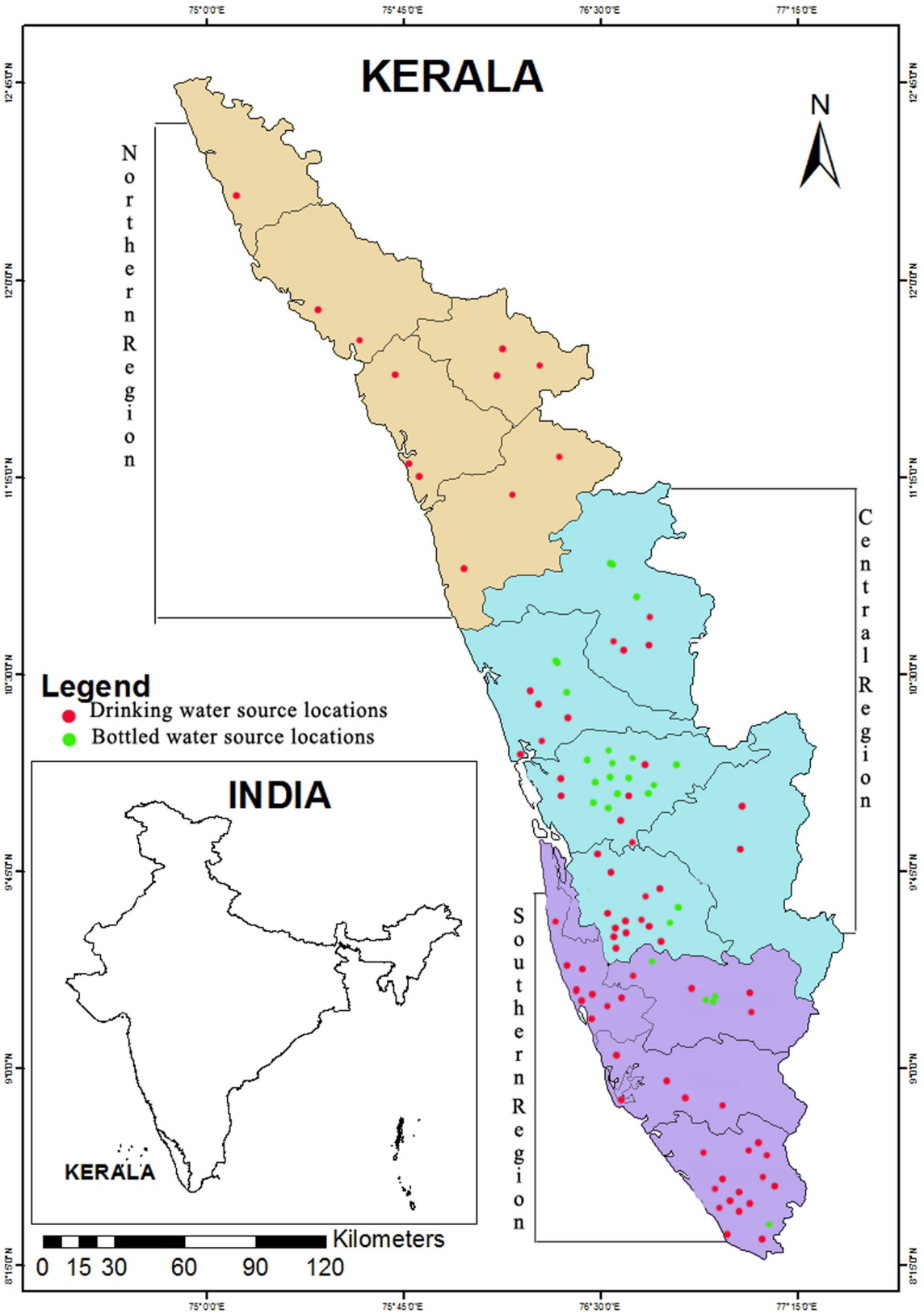

Fig. 1 Map showing bottled water and other drinking water source locations

Table 1 Mean perchlorate and chlorate concentration in different bottled water samples

Sample no.	Sample ID	No. of samples analyzed	Manufacturing place	Perchlorate (ppb)	Chlorate (ppb)
1	BW1	8	Ernakulam	1067.89	7328.89
2	BW2	6	Pathanamthitta	162.74	1821.96
3	BW3	5	Palakkad	19.77	101.2
4	BW4	1	Ernakulam	0	1304.64
5	BW5	6	Bangalore, Karnataka*	0	399.68
6	BW6	1	Pathanamthitta	90.34	3014.24
7	BW7	1	Thrissur	42.65	488.32
8	BW8	1	Thrissur	94.02	40,705.84
9	BW9	1	Thiruvananthapuram	126.17	20,500.16
10	BW10	1	Ernakulam	0	388.64
11	BW11	1	Ernakulam	0	1942.56
12	BW12	1	Kanchipuram, Tamil Nadu*	0	75.92
13	BW13	2	Pathanamthitta	0	120.8
14	BW14	1	Pathanamthitta	0	10,912.24
15	BW15	1	Hyderabad*	0	149.28
16	BW16	2	Ernakulam	17.14	487.36
17	BW17	2	Pathanamthitta	10.26	1007.76
18	BW18	3	Ernakulam	44.63	427.92
19	BW19	2	Thrissur	0	5644.4
20	BW20	2	Ernakulam	15.97	1090.08
21	BW21	1	Thiruvananthapuram	0	0
22	BW22	1	Palakkad	0	345.04
23	BW23	1	Mumbai*	0	0
24	BW24	1	Ernakulam	40.38	462.96
25	BW25	1	Andheri, Mumbai*	24.12	108.48
26	BW26	1	Ernakulam	0	1435.12
27	BW27	1	Ernakulam	19.05	3651.68
28	BW28	2	Ernakulam	16.05	2051.6
29	BW29	2	Ernakulam	13.12	7129.84
30	BW30	1	Ernakulam	9.51	521.92
31	BW31	1	Ernakulam	9.78	0
32	BW32	1	Kottayam	0	434.4
33	BW33	1	Ernakulam	32.2	0
34	BW34	2	Kottayam	0	1711.48
35	BW35	1	Ernakulam	7.91	430.88
36	BW36	2	Ernakulam	0	1950.88
			Mean	84.71	3281.84

* Samples manufactured outside Kerala

chlorate contamination (Table 1). Mean perchlorate content in bottled water was 84.71 ppb, whereas for chlorate was 3281.84 ppb. The observed perchlorate content in 9 samples was higher than the health reference level for chlorate content in drinking water given by USEPA (24.5 ppb). Twenty-one samples exceeded the health reference level for chlorate. Samples from Kottayam district, which is free from industrial sources, have perchlorate within below detectable limit (BDL < 6 ppb). More than 70 % of the samples from Ernakulam district showed perchlorate contamination. Perchlorate contamination was already reported from groundwater and surface water from Ernakulam district, near to APEP (Anupama et al. 2012). The source of surface water for bottled water manufacturing in Ernakulam district is Periyar River, which is the main reason behind the widespread perchlorate

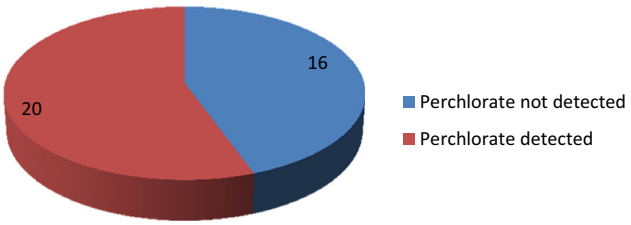

Fig. 2 Graph showing perchlorate detected and perchlorate undetected samples

contamination of bottled water from the region. The sample contaminated with perchlorate obtained from Trivandrum district is manufactured from Thumba nearby TERLS. Veli Lake is the source of water, which is contaminated with perchlorate (Anupama et al. 2012). The contamination at other districts can be owed to the firework manufacturing units as most of the districts in Kerala have licensed and unlicensed small-scale and large-scale units. It is interesting to note that out of 5 outside state samples analyzed, 4 samples are having perchlorate in BDL and the only one (from Mumbai) is having perchlorate (12.06 ppb) within the safe limit (Fig. 3). This shows either uncontrolled use and mishandling of the chemical or lacking of advanced systems for perchlorate removal in the study area. Perchlorate contamination of bottled water is thus found to be dependent on the source contamination.

Chlorate contamination is noticed in almost all samples, irrespective of their source of manufacturing. Both within state and outside state samples were contaminated with chlorate and found to be source independent. This may be owed to the disinfection processes using hypochlorites. In Kerala, sodium hypochlorite as such is used in treating large quantities of drinking water supplies (The Hindu 2008).

Almost all the samples underwent treatment processes such as reverse osmosis, microfiltration, UV irradiation before packaging, and the results suggest that those processes are inefficient in removing perchlorate and chlorate. Various studies reported the possibility of removing perchlorate using technologies such as physical separation (precipitation, anion exchange or membrane filtration, reverse osmosis and electrodialysis), chemical and electrochemical reduction, and biological or biochemical reduction (Urbansky 1998; Srinivasan and Viraraghavan 2009), but it is found that typical water treatment technologies cannot remove perchlorate (Logan 1998).

Various studies reported perchlorate and chlorate contamination of bottled water in different countries (Table 2). Global perchlorate values ranged from <0.02 to 2.01 ppb and chlorate values ranged from 5.8 to 343 ppb, with China being the topmost in both perchlorate and chlorate contamination. Perchlorate detected from bottled water in Kerala was found to be far above the values reported from other countries. But the measured perchlorate value from bottled water was comparable to the tap water (38.4 ppb), groundwater (34.1 ppb) and surface water (17 ppb) values in Kerala (Anupama et al. 2012).

3.2 Other drinking water sources

The analytical results of drinking water samples such as well, bore well and tap water are given according to regionwise and drinking water type (Table 4). Perchlorate content for the drinking water samples ranged from

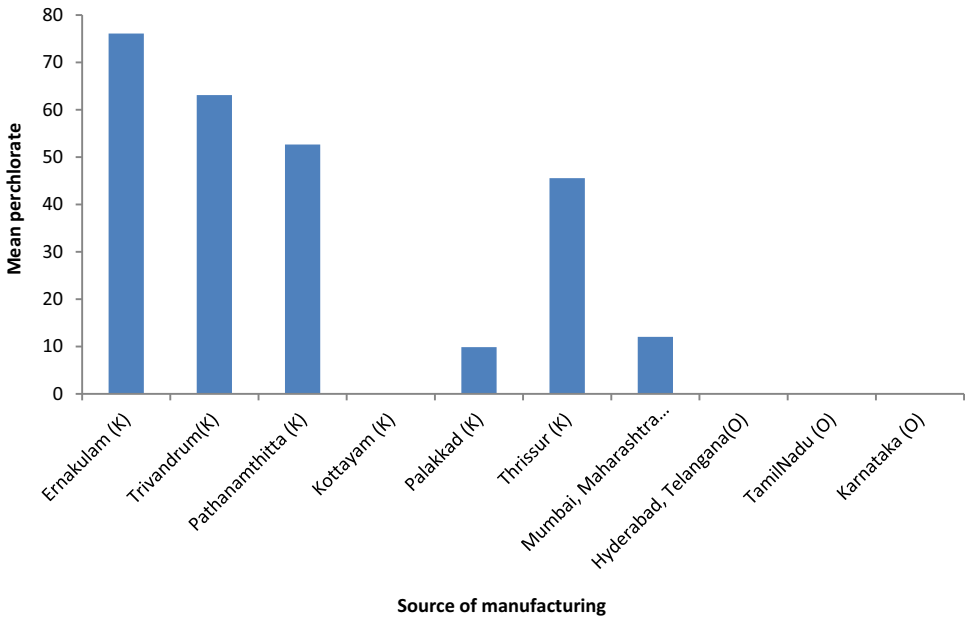

Fig. 3 Graph comparing the mean perchlorate of different sources [*K*—Kerala manufactured samples, *O*—outside state manufactured samples]

Table 2 Comparison of perchlorate in bottled water with other reported values

Country	Perchlorate (ppb)	Chlorate (ppb)	References
US	0.405	5.8	Snyder et al. (2005)
Japan	0.53	14	Asami et al. (2009)
China	2.013	343	Shi et al. (2007), Wu et al. (2010)
South Korea	0.07	–	Her et al. (2011)
Italy	0.075	–	Iannece et al. (2013)
India (7 states excluding Kerala)	<0.02 (quantitation limit)	–	Kannan et al. (2009)
Canada	–	6.9	Dabeka et al. (2002)

Table 3 Mean perchlorate (ppb) in well water samples from various districts of Kerala during different times in a year

Sl. no.	District	April–May 2014		August–September 2014		December 2014–January 2015	
		ClO_4^- (*n*)	ClO_3^-	ClO_4^- (*n*)	ClO_3^-	ClO_4^- (*n*)	ClO_3^-
1	Thiruvananthapuram	71.86* (*12*)	365.05	0 (13)	0	1.98 (13)	0
2	Kollam	14.45 (5)	99.07	0 (5)	0	27.45* (*5*)	33.71
3	Pathanamthitta	178.93* (5)	17.184	0 (5)	0	0 (5)	0
4	Alappuzha	1172.37* (*8*)	289.95	0 (9)	0	27.34* (*8*)	58.84
5	Kottayam	30.69* (*12*)	201.39	0.47 (13)	0	19.19 (13)	96.53
6	Idukki	102.19* (*20*)	0	5.82 (3)	0	19.3 (2)	0
7	Ernakulam	40.48* (*8*)	166.05	0 (8)	0	21.84 (8)	0
8	Thrissur	29.37* (*6*)	15.07	0 (6)	0	0 (6)	0
9	Palakkad	60.09* (*6*)	259.16	0 (4)	0	0 (4)	0
10	Malappuram	23.92 (3)	0	0 (4)	0	5.68 (5)	9.50
11	Kozhikode	39.09* (*2*)	0	0 (2)	0	64.68* (*3*)	28.08
12	Wayanad	121.04* (*2*)	0	0 (3)	0	0 (2)	0
13	Kannur	7.97 (1)	0	0 (1)	0	34.34* (*2*)	0
14	Kasaragod	254.14* (*1*)	154.56	0 (1)	0	95.72* (*1*)	0
	Total mean	153.33*	111.96	0.45	0	22.68	16.19

(*n*)—number of samples

Number of samples analyzed are given in italics

* Concentration exceeding the permissible level of 24.5 ppb

0.71 ppb (monsoon) to 78.45 ppb (pre-monsoon) with a mean value of 33.48 ppb. Maximum perchlorate was detected in pre-monsoon samples. Chlorate value ranged from 4.59 ppb (monsoon) to 247.19 ppb (pre-monsoon) with an average of 58.04 ppb.

The results are also discussed based on regionwise such as southern, central and northern parts of Kerala (Table 4). Southern part of Kerala showed a mean perchlorate content of 40.69 ppb and chlorate content of 211.07 ppb. High mean perchlorate content was observed for northern region (42.36 ppb), whereas minimum was noticed for central region (18.5 ppb). Chlorate was maximum at southern part and minimum at northern part (12.10 ppb).

The results were also compared based on the different types of drinking water such as well, bore well and tap water (Table 4). Well water showed high mean perchlorate and chlorate contents during pre-monsoon (153.33 ppb), whereas minimum was observed during monsoon (Table 3). The mean perchlorate and chlorate contents in well water samples from the entire Kerala were 58.82 and 42.72 ppb, respectively, and those varied from southern region (124.53 and 71.98 ppb) to central region (21.96 and 49.21 ppb) and northern region (43.10 and 12.81 ppb) (Table 4).

In the case of bore well water, average perchlorate and chlorate contents were 6.22 and 29.30 ppb, respectively, in Kerala. Perchlorate content was maximum at northern region (10.44 ppb), whereas maximum chlorate content was observed at southern region. Minimum mean perchlorate content was noticed at central region (1.74 ppb), and chlorate was in BDL at northern region. Tap water was also found to be contaminated with perchlorate and chlorate (Table 4). The mean concentration of perchlorate and chlorate in tap water in Kerala was 3.54 and 104.84 ppb, respectively. Central region had high mean perchlorate

Table 4 Mean perchlorate and chlorate in other drinking water samples (ppb)

	Other drinking water samples		Water type					
			Well water		Bore well water		Tap water	
	ClO_4^-	ClO_3^-	ClO_4^-	ClO_3^-	ClO_4^-	ClO_3^-	ClO_4^-	ClO_3^-
Kerala	33.48	58.04	58.82	42.72	6.22	29.30	3.54	104.84
Southern region	40.69	211.07	124.53	71.98	6.56	74.54	3.19	231.08
Central region	18.85	67.99	21.96	49.21	1.74	22.44	7.36	108.68
Northern region	42.36	12.10	43.10	12.81	10.42	0	0	0

Table 5 Average perchlorate intakes from well, bore well and tap water in different regions

Water	Category	ClO_4^- (ppb)	Intake (μg/kg/day)
Other water sources	Kerala	33.48	1.12*
	Southern region	40.69	1.36*
	Central region	18.85	0.63
	Northern region	42.36	1.41*
Well	Kerala	58.82	1.96*
	Southern region	124.53	4.15*
	Central region	21.96	0.73*
	Northern region	43.1	1.44*
Tap	Kerala	3.54	0.12
	Southern region	3.19	0.11
	Central region	7.36	0.25
	Northern region	0	0
Bore well	Kerala	6.22	0.21
	Southern region	6.56	0.22
	Central region	1.74	0.06
	Northern region	10.42	0.35

* Higher than the permissible intake of 0.7 μg/kg/day (USEPA 2008b)

content (7.366 ppb) than the other regions, whereas chlorate was high at southern region (231.08 ppb). Perchlorate and chlorate contents in tap water in the northern region were found to be below the detectable limit.

Out of the 15 rainwater samples analyzed, two samples showed the presence of perchlorate and the values ranged from 6.9 to 12.8 ppb, while chlorate was not detected in any of the samples. This might be the effect of firework residuals in the air as the samples were collected during summer, the festival time of Kerala when lots of fireworks occur. Earlier studies also showed the presence of perchlorate in rainwater samples of other parts of India (<0.02 ppb) (Kannan et al. 2009), but it was very low when compared with the mean perchlorate in rainwater samples of the present study (9.85 ppb).

3.3 Risk assessment

The recommended health protective dose of perchlorate is 0.0007 mg/kg body weight/day (0.7 μg/kg body weight/day) (USEPA 2008b; Groef et al. 2006), which is equivalent to 24.5 ppb perchlorate in drinking water. Average daily perchlorate intake was calculated with respect to regionwise and sample type (Table 5). The calculation considered the intake of drinking water as 2 L and the average body weight of a healthy adult in Kerala as 60 kg (Shome et al. 2014). The whole water samples showed a higher risk value (1.12 μg/kg body weight/day) than the safe limit of 0.7 μg/kg body weight/day. High risk was observed for northern region followed by southern region, whereas central region is under safe limit. Tap water and bore well water were also within the safe limit, but the well water samples (0.73–4.15 μg) were higher than the safe limit.

Widespread drinking water contamination in Kerala can be accounted for the use of rocket propellants and fireworks manufacturing. Further research is needed to confirm the role of natural perchlorate formation, as a source in the study area (Rajagopalan et al. 2006; Anupama et al. 2012).

4 Conclusion

The present study noticed a high perchlorate contamination of the drinking water sources such as bottled water and other drinking water, which urges immediate action in this regard. Both perchlorate and chlorate showed values above the reference levels. This shows that water is not properly treated or the treatment is ineffective before they are packed and sold. The results clearly indicated the role of perchlorate manufacturing industries and firework manufacturing and displaying processes in contamination of water resources. The perchlorate and chlorate in exceeding amounts than the health reference levels point to a probability of increasing thyroid disorders in the future, if chronic exposure to such levels occurred.

Acknowledgments The authors acknowledge the financial support from Department of Environment and Climate Change, Government of Kerala, through a major project. The financial support from DST-FIST and DST-PURSE, Government of India, for developing instrumental facility is gratefully acknowledged. The first author also acknowledges the Junior Research Fellowship from UGC, Government of India.

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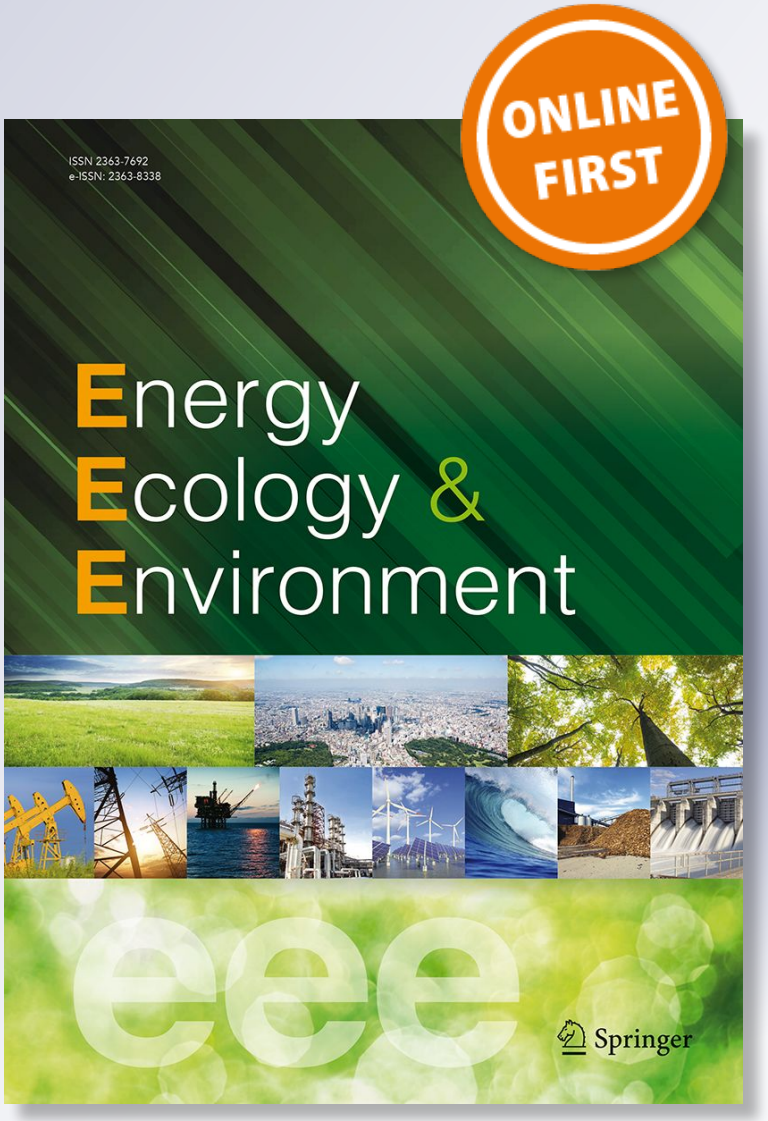
Energy, Ecology and Environment

ISSN 2363-7692

Energ. Ecol. Environ.
DOI 10.1007/s40974-017-0055-x



Springer

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DOI 10.1007/s40974-017-0055-x

ORIGINAL ARTICLE

Perchlorate in drinking water around rocket manufacturing and testing facilities and firework manufacturing sites in Kerala, India

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Received: 5 October 2016 / Revised: 28 February 2017 / Accepted: 2 March 2017

Abstract Perchlorate is used as an oxidizing agent in rocket propellants, fireworks, munitions, etc. This results in perchlorate contamination of drinking water sources in the nearby areas. The present study was carried out in Kerala, southwest coast of India, where exist rocket propellant manufacturing site (Ammonium Perchlorate Experimental Plant), rocket propellant testing facility (Thumba Equatorial Rocket Launching Station) and several fireworks manufacturing sites. Perchlorate contamination in drinking water was monitored during post-monsoon, pre-monsoon and monsoon seasons around these sites. Liquid chromatography–mass spectrometry was used for perchlorate quantification in drinking water. Mean perchlorate in drinking water ranged from 1.03 to 3760.16 ppb in post-monsoon, <6 to 5094.87 ppb in pre-monsoon and 13.99 to 601.28 ppb in monsoon. The perchlorate contamination is found to be varied with season, site and the type of drinking water.

Keywords Pollution · LCMS · Health · Thyroid

1 Introduction

Perchlorate is a colorless, odorless chemical, and its salts are highly soluble and mobile in water (Motzer 2001; ATSDR 2008; Sanchez et al. 2005). The perchlorate anion (ClO_4) in water remains highly stable and unreactive and may take decades to degrade (Siglin et al. 2000; Srinivasan and Viraraghavan 2009; Motzer 2001). The major sources are rocket propellants, fireworks manufacturing and display, blasting agents, military munitions, etc. as it is a good oxidizing agent (Tikkanen 2006; Sijimol and Mohan 2014; Sugimoto et al. 2012). Perchlorate could reach the aquatic ecosystem by a number of ways such as runoff and direct deposition (Logan 1998). Perchlorate contamination was noticed in rain water, raw and treated drinking water, groundwater, bottled water, open well and surface water resources from different parts of the world (McLaughlin et al. 2011; Anupama et al. 2012; Snyder et al. 2005).

The perchlorate could enter human body through drinking and may get either eliminated through urine (Cheng et al. 2008) or transmitted to the thyroid gland, saliva (Kannan et al. 2009), placenta (Steinmaus et al. 2010) or mammary glands (Dohan et al. 2007) through sodium iodide symporter (NIS). It is one of the most potential inhibitors of T_4 release (Hornung et al. 2010). It inhibits uptake of iodide at the cellular level (Soldin et al. 2001; Kirk 2006). Hence, it is important to study the perchlorate contamination of drinking water which will help in assessing the potential risk. Risk assessment of perchlorate among the inhabitants of the contaminated place can be done only by assessing the seasonal variation. The present study assessed the temporal variation of perchlorate around rocket propellant manufacturing and testing facilities and selected firework manufacturing sites in Kerala, India, which is not yet reported.

Electronic supplementary material The online version of this article (doi:10.1007/s40974-017-0055-x) contains supplementary material, which is available to authorized users.

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Published online: 13 March 2017

2 Materials and methods

2.1 Study area and sample collection

The samples were collected seasonally (post-monsoon, October–January; pre-monsoon, February–May; and monsoon, June–September) from the selected locations of Kerala, southwest coast of India (Fig. 1). The major perchlorate contamination sources such as Ammonium Perchlorate Experimental Plant (APEP), where 800 tones of ammonium perchlorate is manufactured per year (site 1); Thumba Equatorial Rocket Launching Station (TERLS) (site 2); and firework manufacturing sites—two firework manufacturing sites from central part of Kerala (sites 3 and 4)—were selected to monitor perchlorate contamination. A control (site 5) was also selected where 5 km surrounding area is free from any perchlorate handling activities. Well water (total—87 samples; 18 from sites 1 to 4 and 15 from site 5) and tap water (9 samples: 3 samples each from sites 1, 2 and 4) samples were collected in sterile polypropylene bottles and filtered immediately using 0.2-μm nylon membrane filter paper. There is a possibility for perchlorate to undergo microbiological degradation under anaerobic conditions. Hence, the samples were stored in the bottle by keeping one-third portions empty that will reduce the potential for degradation by any remaining anaerobic organisms. In the laboratory, samples were kept below 4 °C until analysis. The analysis was completed within 28 days after collection (EPA 331.0).

2.2 Parameters analyzed

Apart from perchlorate, parameters such as pH, electrical conductivity (EC), total dissolved solids (TDS), salinity (SAL), anions such as chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{2-}) and chlorate (ClO_3^-), and cations such as ammonium (NH_4^+), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}) were measured.

2.3 Instrumental analysis

pH was measured using digital pH meter. EC, TDS and salinity of the samples were analyzed using conductivity meter. Ion chromatography (Dionex 1100) was used for the detection of anions (except chlorate and perchlorate) and cations. Perchlorate and chlorate were detected by LCMS (Shimadzu 2020) (EPA Method 331.0). The column used was Dionex AS-21 and methylamine as eluent. Selective ion monitoring mode was applied for the quantification of perchlorate. Perchlorate has an *m/z* of 99 and an isotopic *m/z* of 101. Groundwater usually contains an ion of sulfate ($H^{34}SO_4$) at *m/z* 99. Both *m/z* 99 and *m/z* 101 were measured, and peak area having a ratio of *m/z* 99 to *m/z* 101 as 3:1 ± 25% was accepted as of perchlorate and *m/z* 101 was selected for quantification. Chlorate was detected and quantified at *m/z* 83. For perchlorate, method detection limit was 2 ppb and limit of quantification was 6 ppb, and for chlorate method detection limit was 4 ppb and limit of quantification was 6 ppb.

3 Results and discussion

3.1 Temporal variation of perchlorate

Perchlorate was detected in drinking water samples in all the seasons (except during pre-monsoon at site 3 firework manufacturing site) (Table 1). At sites 1 and 2, mean perchlorate levels in all the seasons were more than 24.5 ppb. At site 1, perchlorate in drinking water ranged from <6 ppb to 24,132.71 ppb during post-monsoon, 19.2 to 32,602.6 ppb during pre-monsoon and 30.18 to 4171.78 ppb during monsoon. The range of perchlorate in water samples from TERLS (site 2) ranged from 8.09 to 4913.77 ppb during post-monsoon, 14.68 to 3133.05 ppb during pre-monsoon and 8.06 to 410.86 ppb during monsoon season. Firework manufacturing sites also showed variation in perchlorate content during different seasons. The values ranged from <6 to 369.38, 16.22 to 51.74 and <6 to 35.08 ppb during post-monsoon, pre-monsoon, monsoon, respectively, at manufacturing site (site 4), whereas in site 3 the maximum variation was observed during monsoon (<6 to 40.66 ppb). Perchlorate was not found in control site during all the seasons.

The perchlorate concentration at various sites during different seasons is presented in Fig. 2. Very high values were observed at sample 1 of site 1 during all the seasons (24,132.71, 32,602.6, 4171.78 ppb) and sample 2 of site 2 during post-monsoon (4913.77 ppb). High perchlorate concentrations were observed for sites 1 and 2 during all the seasons compared with other sites. During the pre-monsoon and post-monsoon, high variability was observed for site 1 and site 2, respectively. However, site 3 showed high variability in post-monsoon. All the sites showed the presence of perchlorate during the monsoon and post-monsoon seasons. The average values showed that at site 1, the maximum concentration was noted during pre-monsoon followed by post-monsoon. The results clearly indicate that the industrial sites (sites 1 and 2) are highly contaminated than the firework manufacturing sites (sites 3 and 4). This might be due to the high usage of materials during the operations. In the case of tap water, perchlorate value at site 1 ranged from 19.2 ppb during pre-monsoon to 39.37 ppb during monsoon and below detectable limit (BDL) during post-monsoon. At site 3, only monsoon

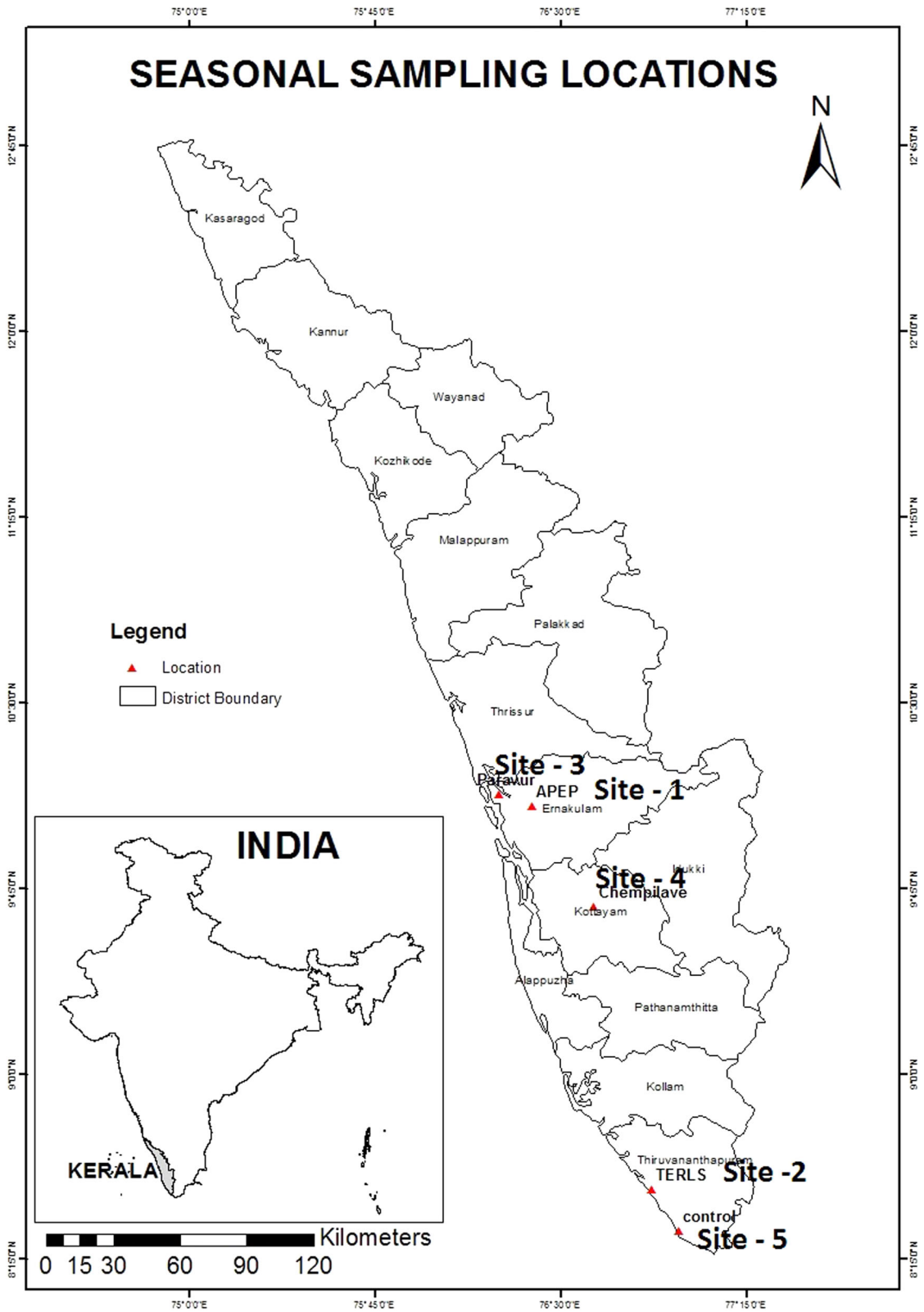

Fig. 1 Location map with sampling sites

Table 1 Mean perchlorate content in the study area during different seasons

Site	Season	Mean perchlorate (in ppb)
Site 1	POM	3760.16 ± 9007.53
	PRM	5094.87 ± 12,159.55
	MON	601.28 ± 1360.64
Site 2	POM	640.4 ± 1727.04
	PRM	468.57 ± 1174.97
	MON	80.61 ± 146.04
Site 3	POM	1.03 ± 2.72
	PRM	BDL
	MON	17.76 ± 14.25
Site 4	POM	61.56 ± 150.80
	PRM	25.42 ± 13.44
	MON	13.99 ± 16.90
Site 5	POM	BDL
	PRM	BDL
	MON	BDL

BDL below detectable limit

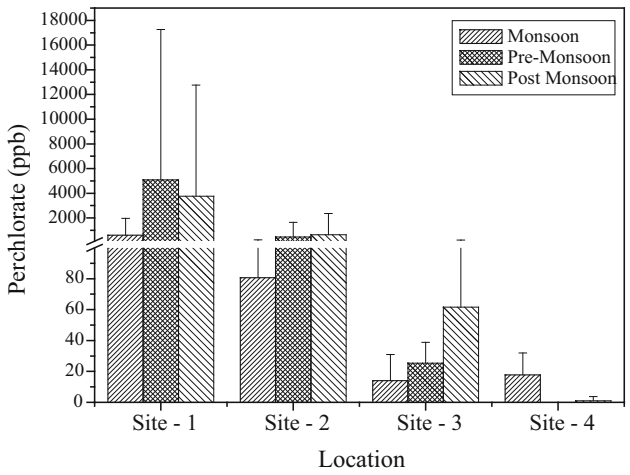

Fig. 2 Perchlorate content in water samples during various seasons

sample had a perchlorate of 20.72 ppb. Tap water from site 2 was found to be contaminated with perchlorate during all seasons, ranging from 8.09 to 25.08 ppb. The results of other water quality parameters (pH, EC, TDS, salinity, chloride, nitrate, sulfate, calcium, magnesium, sodium, potassium and chlorate) are given in Table 2. All the parameters except a very few parameters of sites 1 and 2 are within the permissible limit (WHO 2011; BIS 2012). During pre-monsoon, the high concentration was observed for chlorate (site 1), nitrate and calcium (site 2), whereas in post-monsoon and monsoon, sulfate and chlorate (site 2) and nitrate, respectively. Chlorate was high during the non-monsoon seasons for both industrial sites.

3.2 Correlation of perchlorate with other parameters

The interrelationship between perchlorate and other water quality parameters was tested with Pearson's correlation analysis. Water samples analyzed from APEP in all seasons showed significant positive correlation between perchlorate and chlorate ($p = 0.01$). Correlation analysis of samples from APEP further showed positive significant correlation between perchlorate and sodium, nitrate and sulfate during post-monsoon and with pH, EC, TDS, SAL, chloride, nitrate and magnesium during monsoon ($p = 0.01$). Samples from TERLS showed highly significant correlation between perchlorate and chloride during post-monsoon ($p = 0.01$), and no other parameters showed correlation with perchlorate in any of the seasons. At Paravur, perchlorate in water samples showed significant positive correlation with magnesium during post-monsoon and with sulfate during pre-monsoon ($p = 0.01$). Perchlorate was significantly correlated ($p = 0.01$) with sulfate and ammonium during post-monsoon at fireworks manufacturing site (site 4). A general correlation was done combining all seasons and all sites. It showed that perchlorate is correlated with chlorate and with no other parameters. Variation of correlation in different sites may be due to the change in general flushing of salts from the land surface or unsaturated zone to water table by means of precipitation–irrigation–evaporation cycles (Rajagopalan et al. 2006).

Use of perchlorate in rocket installations is found to be the major reason for perchlorate contamination of drinking water (ITRC 2005), and the present study also confirms the role of rocket installations in perchlorate contamination. Perchlorate may enter groundwater from the highly concentrated brine solution buried near rocket motor washout facilities (Flowers and Hunt 2000). The present study has proved that the major reason for drinking water contamination by perchlorate in Kerala is rocket propellant manufacturing (APEP) and rocket testing facilities (TERLS). An earlier study (Anupama et al. 2012) observed a concentration of 1.33–91.4 ppb of perchlorate in drinking water during post-monsoon (during the year 2009) which is lower than the concentration detected in the present study. In another study by Anupama et al. (2015), perchlorate content varied from 2.76 to 7270 ppb during pre-monsoon (in the year 2012) and is also lower than the concentrations observed in this study (BDL to 32,602.6 ppb). Anupama et al. (2015) studied the perchlorate contamination in four sites, which are not concentrated around the particular industrial site, during pre-monsoon. They did the analysis of drinking water samples from points which are located a few kilometers away from the industrial units. The present study was focused mainly around the industrial sites, and the sampling points are 500 m around the source at

Table 2 Mean values of physicochemical parameters in the study area during different seasons

Site	Season	pH	EC (μS/cm)	TDS (ppb)	SAL (ppt)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	NH_4^+ (mg/L)	ClO_3^- (μg/L)
Site 1	POM	5.9	66.8	33.4	0.03	14.8	7.05	3.31	17.08	4.40	9.66	3.02	BDL	664.59
	PRM	5.8	60.58	30.3	0.03	9.48	7.06	1.38	11.6	2.68	15.1	2.7	BDL	1362
	MON	7.6	62.7	31.1	0.03	9.17	10.8	1.17	10.3	1.89	5.17	1.35	BDL	168.6
Site 2	POM	5.97	445.8	186.0	0.18	61.01	61.6	58.7	105.9	34.6	27.5	20.4	112.6	894.0
	PRM	6.32	476.9	238.4	0.23	146.2	151.5	67.4	125.1	35.3	102.4	17.0	4.05	479.73
	MON	7.56	367	183.6	0.17	56.8	64.5	25.4	74.6	20.3	64.9	9.92	5.07	BDL
Site 3	POM	5.2	44.8	22.40	0.02	7.29	4.7	3.58	8.90	4.38	4.43	2.33	0.46	BDL
	PRM	4.7	33.3	16.8	0.02	6.34	2.12	1.28	7.57	2.63	4.33	2.51	BDL	46.09
	MON	8.13	39.4	19.7	0.02	6.61	5.37	1.25	6.44	2.48	4.80	1.78	0.09	13.49
Site 4	POM	6.7	257.4	128.6	0.12	4.3	4.51	51.0	81.5	18.9	56.5	1.9	104.8	BDL
	PRM	6.26	255.3	127.7	0.12	199.5	8.85	70.1	69.1	14.6	61.9	23.7	11.3	35.2
	MON	7.15	288.8	144.4	0.14	71.17	8.26	36.9	87.2	9.62	47.0	13.9	1.72	32.98
Site 5	POM	5.4	141.8	70.8	0.07	34.4	13.1	2.92	34.7	12.7	6.7	3.52	BDL	23.9
	PRM	5.9	131.4	65.7	0.06	41.7	14.0	1.55	40.9	15.3	8.30	5.17	BDL	97.10
	MON	7.5	136.3	68.1	0.06	42.7	15.19	1.74	35.8	14.2	6.5	3.65	0.10	BDL

different directions. This might be the reason for high perchlorate concentration observed in this study. In the present study, the concentration observed at APEP industrial region (maximum 32,602.6 ppb, mean 5094.87 ppb) is higher than in the earlier study (maximum 7270 ppb; mean 7230 ppb) (Anupama et al. 2015). The same trend is also observed at TERLS, i.e., high concentration in the present study (mean 468.57 ppb) compared to the earlier study (mean 300 ppb) (Table 3). This clearly shows the high concentration of perchlorate in the surrounding environment of the industries. This may be due to the slow rate of degradation along with industrial output, and this may enhance the concentration or accumulate the perchlorate in this region. Wastewater from perchlorate manufacturing companies dispersed into water bodies causes widespread perchlorate contamination (Hogue 2003). The present study also established the role of firework manufacturing units in perchlorate contamination of water bodies. Groundwater contamination due to firework manufacturing has been reported from other parts of the country (Isobe et al. 2013). Also in China, firework production and display accounts for the perchlorate contamination in groundwater, tap water, surface water and bottled water (Shi et al. 2007). The present study showed the contamination of drinking water sources nearby firework manufacturing units. At site 3, the higher concentration was observed during monsoon, whereas at site 4 it was during post-monsoon. Site 3 is located at an elevated region and rainfall could bring down the perchlorate from the soils to aquatic systems of lower lands, whereas site 4 is located in a plain land and is surrounded by wetlands. Hence, the seasonal variation could be owed to the geography and local climatic conditions of the region.

The maximum range of perchlorate in all sites was observed during post-monsoon, whereas widespread contamination was noticed during monsoon season besides the low perchlorate values compared to other seasons. Runoff during monsoon season might have resulted in widespread contamination and dilution of the chemical. Well water samples showed more perchlorate than tap water (perchlorate remained BDL in tap water samples from majority of sites), thus proving the source of contamination as the

Table 3 Comparison of perchlorate content (ppb) with an earlier study

	APEP			TERLS		
	No. of samples	Maximum value	Mean value	No. of samples	Maximum value	Mean value
Anupama et al. (2015)	2	7270	7230	2	300	300
The present study	7	32,602.6	5094.87	7	3133.05	468.57

selected sites itself. Perchlorate contamination is found to be site dependent. At TERLS, perchlorate was detected from tap water samples also. When city water supply fails to provide water in the area, water is supplied from the TERLS water supply, which uses a large well within the rocket ground testing site, which might be the reason for the presence of perchlorate in tap water samples. No perchlorate was detected in the water samples collected from the control site in any of the seasons, and it again confirms that the perchlorate contamination is source dependent. The health safe reference dose of perchlorate in drinking water is 24.5 ppb. Above this can result in thyroid disorders. However at APEP and TERLS, perchlorate dosage in drinking water is far above 24.5 ppb in all the seasons. Since perchlorate is exceeding the limit in all seasons, it may result in thyroid disorders in the area. The chances for thyroid disorders and abnormal growth of breast milk-consuming infants cannot be neglected (Renner 2008). In Arizona, perchlorate-contaminated Colorado River resulted in causing abnormal thyroid functions of newborns, and in California the same happened because of gestational exposure (Brechner et al. 2000; Schwartz 2001). Also perchlorate may reach vegetation, fishes, insects, mammals, etc. through water (Smith et al. 2005; Park et al. 2007; Smith et al. 2001). Perchlorate was found in fish, amphibians, aquatic insect larvae, etc. (Smith et al. 2001; Park et al. 2007). Further survey and detailed studies are needed to finalize the same in this part of the world also.

Data gaps exist on the presence of any natural perchlorate in the site. Elaborate study is essential to differentiate the natural and man-made perchlorate in all the sites. The studies on health impacts are important, and it may need further survey and other studies such as blood sample analysis and urine sample analysis. More research on perchlorate degradation using latest chemical treatment methods, which uses minimum time, has to be carried out for the drinking water supplies in the contaminated areas.

4 Conclusion

The present study assessed the perchlorate contamination of water resources of selected sources in Kerala. The results showed that the adjacent aquatic ecosystems of the industries which are manufacturing and using were contaminated with perchlorate. The contamination of perchlorate is found to be site dependent. Also the contamination in drinking water varied with season and source. The results indicated that rocket propellant manufacturing and consumption and fireworks manufacturing are found to be the major sources of perchlorate in Kerala. Firework manufacturing sites are located in almost all districts of Kerala. Hence, there may be a chance of widespread contamination of perchlorate in drinking water. The result of the present study is significant and urges a detailed investigation in this regard. Also elaborate research is needed to detect the thyroid disorders in this area.

Acknowledgement The financial support from DoECC, Government of Kerala, through a project is gratefully acknowledged. Also acknowledges DST-FIST and DST-PURSE, Government of India, for supporting instrumental facility. First author also acknowledges the Junior Research Fellowship from UGC, Government of India.

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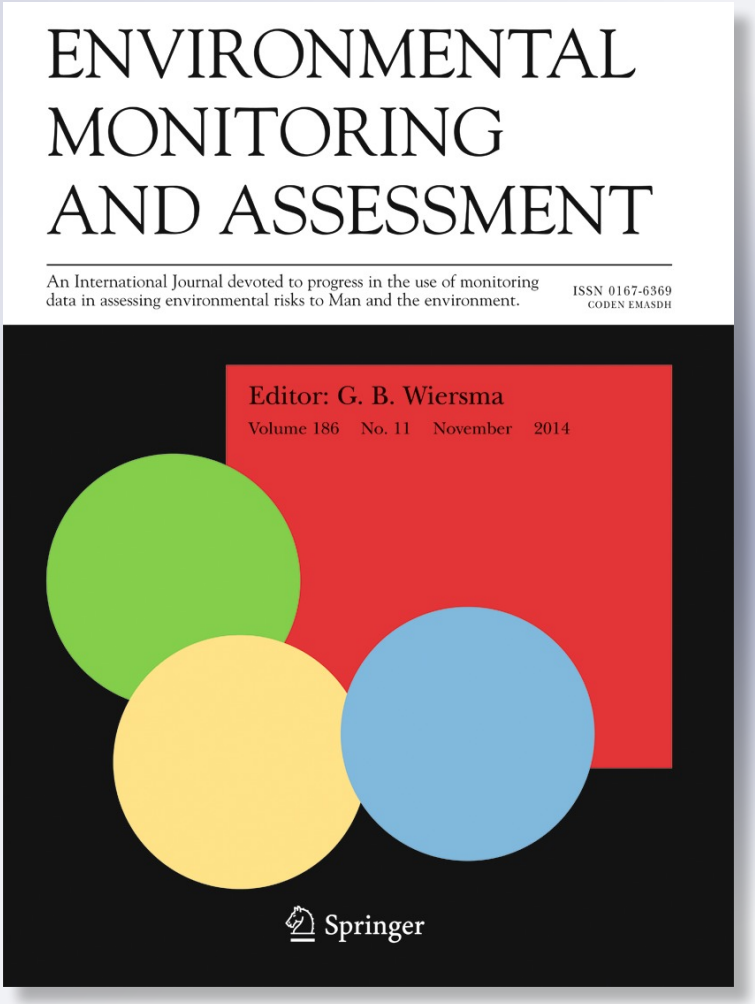
Environmental Monitoring and Assessment
An International Journal Devoted to Progress in the Use of Monitoring Data in Assessing Environmental Risks to Man and the Environment

ISSN 0167-6369
Volume 186
Number 11

Environ Monit Assess (2014)
186:7203-7210
DOI 10.1007/s10661-014-3921-4



Springer

Environ Monit Assess (2014) 186:7203–7210
DOI 10.1007/s10661-014-3921-4

Environmental impacts of perchlorate with special reference to fireworks—a review

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Received: 8 January 2014 / Accepted: 30 June 2014 / Published online: 10 July 2014

Abstract Perchlorate is an inorganic anion that is used in solid rocket propellants, fireworks, munitions, signal flares, etc. The use of fireworks is identified as one of the main contributors in the increasing environmental perchlorate contamination. Although fireworks are displayed for entertainment, its environmental costs are dire. Perchlorates are also emerging as potent thyroid disruptors, and they have an impact on the ecology too. Many studies have shown that perchlorate contaminates the groundwater and the surface water, especially in the vicinity of fireworks manufacturing sites and fireworks display sites. The health and ecological impacts of perchlorate released in fireworks are yet to be fully assessed. This paper reviews fireworks as a source of perchlorate contamination and its expected adverse impacts.

Keywords Perchlorate · Fireworks · Disaster · Water · Soil · Pollution · Thyroid · Toxicity

Introduction

Perchlorate is an oxy-anion of chlorine. It is negatively charged and is composed of one chlorine atom surrounded by four oxygen atoms arranged in tetrahedral geometry. The perchlorate anion combines with cations like sodium, potassium, ammonium, etc., to form perchlorate salts like sodium perchlorate, potassium perchlorate, and ammonium perchlorate. Perchlorate occurs both in natural and manufactured compounds (Dasgupta et al. 2005). Apart from lightning, the reaction between the sodium chloride present in the evaporated sea water and ozone also results in the natural production of perchlorate (Dasgupta et al. 2005; Jackson et al. 2003). Perchlorate also occurs naturally within the extensive caliche deposits of the Atacama Desert in Chile (Ericksen 1983; Schumacher 1960). Natural formation has also been recorded from Antarctica (Kounaves et al. 2010), where the perchlorate content of soils is about 1,100 μg/kg. Orris et al. (2003) has detected perchlorate in seaweed (Kelp).

Perchlorate content in fireworks

Fireworks are one of the sources of perchlorate contamination in the environment (SERDP 2005; White 1996; Dasgupta et al. 2006). Fireworks are used worldwide to celebrate popular events like festivals and official celebrations (Puri et al. 2009) and are one of the most unusual sources of pollution (Vecchi et al. 2008). Fireworks contain chemicals such as potassium nitrates, potassium chlorate, potassium perchlorate, charcoal, sulfur, manganese, sodium oxalate, aluminum and iron dust powder, strontium nitrate, and barium nitrate, etc. (Ravindra et al. 2003; Wang et al. 2007; Mclain 1980). Ignited fireworks release pollutants like sulfur dioxide, carbon dioxide, carbon monoxide, suspended particles, and several metals like aluminum, manganese and

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cadmium, etc. These generate dense clouds of smoke that contain a black powder made up of potassium nitrate, charcoal, and sulfur (Liu et al. 1997; Dutcher et al. 1999; Mandal et al. 1997; Kulshrestha et al. 2004; Drewnick et al. 2006). These are associated with serious health hazards (Dockery et al. 1993; Pope et al. 1995). Firework particles are acidic in nature (Wang et al. 2007; Urbansky 1998) and aid the process of acid rain and climate change (www.scienceinschool.org/repository/docs/issue21_fireworks.pdf). This paper reviews the environmental contamination of perchlorate due to fireworks.

Fireworks vary greatly in their type, composition, and perchlorate content. They also have a complex anatomy (www.pbs.org/wgbh/nova/fireworks/anat_flash.html). Perchlorate is used to make loud explosions, colored flames, and bright light (SERDP 2005; Thompson and Potter 2000). Potassium perchlorate and ammonium perchlorate are the commonly used ingredients in fireworks production (Wu et al. 2011; Motzer 2001). These are used preferentially because of the higher availability of oxygen per unit weight, higher stability, and lesser sensitivity to mechanical action (Zoeller and Rovet 2004). The released free chlorine from perchlorate combines with barium, strontium, or copper to produce characteristic green, red, and blue hues, respectively (Conkling 1990). Some components contain up to 70 % ammonium perchlorate or potassium perchlorate, and there are fireworks that contain little or no perchlorate (Conkling 1985; Zhang et al. 2010). During production and display of fireworks, the potential exists for perchlorate to be released into the air, which will be later deposited along with precipitation (Munster et al. 2009). But the actual amount of perchlorate released to the environment due to fireworks is unknown (Rajagopalan et al. 2009; Munster et al. 2009). The venue of many pyrotechnic displays are near surface water bodies, presumably for visual impact and safety reasons, but this increases the potential for perchlorate impacts on water sources (SERDP 2005).

Perchlorate salts serve as oxidizing agents in the manufacturing of solid rocket propellants, explosives, fireworks, signal flares, and matches (ITRC 2005; Trumpolt et al. 2007). These are also used in vehicle air bag inflators, electronic tubes, lubricating oils, leather tanning and finishing processes, electroplating and aluminum refining, paint and enamel production, production of chlorate-based herbicides, bleaching agents, etc. (Urbansky 1998; Burns et al. 1989). In the case of munitions, perchlorate is used in training simulators, smokes or obscurants, pyrotechnics, grenades, signals and flares, and fuses. Some types of simulators contain relatively high perchlorate concentrations as do most of those with solid rocket motors (ITRC 2005). Quite a few studies have detected perchlorate content in groundwater, surface water and drinking water (Snyder et al. 2005; Crawford-Brown et al. 2006; Rajagopalan et al. 2006; Stetson et al. 2006; Kimbrough and Parekh 2007; Kosaka et al. 2007; Quinones et al. 2007; Wagner et al. 2007; Asami et al. 2009; Kannan et al. 2009; USEPA 2008), sea water (Her et al. 2011; Martinelango et al. 2006), tea and soft drinks (Asami et al. 2009), milk (Dyke et al. 2007), saliva (Oldi and Kannan 2009), and waste water effluent (Quinones et al. 2007; Kim et al. 2009). Perchlorate has also become one of the biggest challenges currently being faced by the drinking water industry (Srinivasan and Sorial 2009) because drinking water acts as one of the major sources of human exposure to perchlorate (Wu et al. 2010).

Perchlorates are readily water soluble salts, and in aquatic systems, it readily dissociates into perchlorate anion and the corresponding cationic ligands (Urbansky 1998). Perchlorate anion then remains stable for long periods under ambient environmental conditions. Perchlorate from soil may either leach into water bodies or may be absorbed by the plants through soil moisture and accumulate in plant tissues (Urbansky et al. 2001; Ellington and Evans 2000) or may be held in solution in the vadose zone by capillary forces. The half-life period of perchlorates in soil was estimated to be 52 h (Robles 1999). In the case of highly concentrated perchlorate brine solution, as released from rocket motor washout facilities at locations where perchlorate has been buried, the density effects control the movement of the brine (Flowers and Hunt 2000) and with the density contrast between the brine and groundwater, the brine moves vertically with minimal influence by groundwater movement. These brine pools may form on top of confining layers, and significant perchlorate mass may move into low-permeability confining layers by diffusion (ITRC 2005). Perchlorate contamination is reported from surface water and groundwater in USA, Korea, Japan, India, and China (Gullick et al. 2001; Kosaka et al. 2007; Quinones et al. 2007; Kannan et al. 2009; Wu et al. 2010). Through water, it may reach plants, insects, mammals, fishes, etc. (Smith et al. 2001, 2005; Park et al. 2007). Perchlorate has been detected in numerous wild plant and animal species including

amphibians, fish, and small mammals near perchlorate manufacturing and handling sites (Smith et al. 2001; Anderson and Wu 2002).

Perchlorate is a potent thyroid disruptor. Perchlorate competitively inhibits the uptake of iodide by the thyroid gland and results in the decreased production of thyroid hormones—thyroxin and triiodothyronine (Tonachera et al. 2004; Saito et al. 1983) and thereby increases the thyroid stimulating hormone (TSH) levels in blood (Lawrence et al. 2000; ITRC 2005). Thyroid hormones are essential for proper protein expression, neuronal differentiation, migration, and myelination of the fetus, who obtains it from the mother right from the first trimester of gestation (Haddow et al. 1999; Dowling et al. 2000; Alvarez et al. 2000). If TH deficiency occurs, it may result in characteristic functional deficits, especially difficulty in processing visual—spatial information, poor sensorimotor coordination, and memory/attention deficits (Rovet 2002). Perchlorate adversely affects fetal and neonatal development by reducing maternal TH available during gestation, TH production by the fetal thyroid, and the iodide content of breast milk (Clewell et al. 2003). Perchlorate also gets selectively transferred to the mammary gland (Dasgupta et al. 2008).

A fairly extensive database of animal toxicity studies was built in keeping with risk assessment guidelines to determine the health effects of perchlorate in humans. Immunological effects in mice (Keil et al. 1999), developmental effects in rats and rabbits (York et al. 2001, 2003), two-generation reproductive studies in rats (York et al. 2004), etc., has been undertaken to assess the risk of exposure to perchlorate. Siglin et al. (2000) conducted a 90-day perchlorate mode-of-action study in rats, and the entire animal study database collectively supported the mode-of-action for perchlorate and the competitive iodide uptake inhibition. Perchlorate has been shown to induce brain morphological changes in rats, at dosages down to 10 μg $kg^{-1}day^{-1}$ (ARL 2001). Peak blood levels of perchlorate were reported after a 3-h exposure in rats, and the half-life was approximately 8 h (Wolf 1998). Retention time of perchlorate is different for different mammalian tissues (Yu et al. 2002). In Sprague-Dawley rats, T3 concentrations were significantly altered by low doses of perchlorate (0.01 mg $kg^{-1}day^{-1}$) (Siglin et al. 2000). Even though low levels of perchlorate are not sufficient to affect hormone profiles, it may affect the thyroid gland through production of hypertrophic cells and colloid tissue (Becker et al. 1995). When perchlorate was given at around 100 μg/L, for 30 days, fish developed increased thyroid follicular hyperplasia, hypertrophy, and colloid depletion (Bradford et al. 2005; Theodorakis et al. 2006). In amphibians, perchlorate was shown to alter the metamorphosis and sex ratios (Goleman et al. 2002a, b). It was also noticed that infusion of perchlorate in large doses in goats causes major reduction of iodide expression in milk (Mountford et al. 1987). Perchlorate also inhibits larval development in amphibians (Brown 1997), disrupts iodide accumulation in lamprey (Manzon and Youson 1997), and results in hermaphroditism in fish (Bernhardt et al. 2006).

Remediation of perchlorate is an important aspect. Bioremediation is the promising method for perchlorate degradation than physicochemical methods (Logan 1998). It is found that microaerophilic or anaerobic microorganisms can be effectively used for bioremediation of perchlorate (Coates and Achenbach 2004; Logan 1998; Rikken et al. 1996; Wu et al. 2001; Holdren et al. 2008). Phytoremediation also proves to be an efficient method (Tan et al. 2004; Cope et al. 1967).

How fireworks display causes environmental impacts

Fireworks-resultant perchlorate residue can contaminate soil and water over a wide area. But the extent of contamination depends on the number of displays, types of fireworks involved, amount of misfiring and its disposal, and the duration of the display (ITRC 2005; MADEP 2005). Fireworks residue consists of fine particles of burnt black powder, paper debris, and residue, where perchlorate in paper residue alone ranges from 302 to 34,200 μg/kg (DEP 2006). It is assumed that 1,000–2,000 aerial shells weighing a total of 1,361 kg, of which 40 % is perchlorate, can contaminate an area (fireworks fall out area) of around 3,600 m^2 (DEP 2006). The aerial deposition of perchlorate from fireworks display has ranged from 670 to 2,620 g/ha (Wu et al. 2011), and in the USA, the yearly deposition of perchlorate from fireworks ranges from 0.7 to 2.6 kg (Wu et al. 2011). Deposition rates vary with the amount of fireworks used, area covered by the display, etc.

Ecological impacts

Perchlorate contamination due to fireworks was reported from Canada (Backus et al. 2005), USA (Munster et al. 2009), India (Isobe et al. 2012), China (Shi et al. 2007), etc. Fireworks impact may either be direct or indirect. Direct contamination of lake water due to fireworks display was caused increased surface water perchlorate concentration (Backus et al. 2005; Wu et al. 2011; Wilkin et al. 2007). Munster et al. (2009) showed that groundwater gets contaminated with tens of micrograms perchlorate per liter within 100 m of fireworks display.

The sites of where fireworks are manufactured may also have significant soil and groundwater contamination. Perchlorate concentration in groundwater around a firework manufacturing site at Sivakasi and Madurai in Tamil Nadu state, India was found to be significantly higher than that in the groundwater in other locations (Isobe et al. 2012). In China, perchlorate was detected in ground water, surface water, tap water, and bottled water (Wu et al. 2010), and it was high in groundwater followed by surface water. Surface water near a firework manufacturing area had a perchlorate level of 54.4 μg/L (Wu et al. 2010). Indirect impacts are mainly through human exposure and atmospheric particulate emission because fireworks display influences the perchlorate levels in atmospheric particulate matter. Mean concentration of perchlorate in air increases during fireworks display, and Shi et al. (2007) showed several tens of nanograms per cubic meter concentrations of perchlorate in the atmospheric particulate emissions. The studies conducted at Long Island, New York indicated an increase in concentration of perchlorate content in the total deposition after fireworks display (Munster et al. 2009). The major factors influencing the perchlorate concentration from fireworks fallout are amount and type of fireworks ignited, efficiency of perchlorate oxidation, wind direction and velocity, volume of water, rainfall, and evaporation (Wu et al. 2011; Munster et al. 2009). In China, the largest fireworks manufacturing country, the presence of perchlorate in groundwater, tap water, surface water, and bottled water (Shi et al. 2007) is attributable to the large production and display of fireworks.

Human exposure to perchlorate-contaminated fine particles emitted from fireworks display may take place through inhalation, dermal exposure, and dust ingestion (Wu et al. 2011). In China, perchlorate was detected in blood samples of infants, toddlers, and adults from Nanchang City, where manufacturing of fireworks is done in large quantity (Zhang et al. 2010). Also, in Japan, fireworks are suspected to be one of the reasons behind the increased amount of perchlorate in cow's milk (Dyke et al. 2007).

Fate of firework particles

The fate of perchlorate, following fireworks display, is affected by natural attenuation, at sites with appropriate biogeochemical conditions (Wilkin et al. 2007). Wind properties and storm direction plays a major role in the final settling of perchlorate, and it goes on increasing as we move away from the display site, in the windward direction (Munster et al. 2009). Perchlorate in dust may also be picked up by wind, transported and deposited as dry deposition (Munster et al. 2009; Rao et al. 2007). The rate of decay of perchlorate is correlated with temperature (Wu et al. 2011), as temperature increases the rate of degradation also increases. Aerobic conditions may result in slow degradation of perchlorate (Wu et al. 2011; MDEP 2006).

Perchlorate concentration decreased at a first-order kinetic degradation rate, at an average half-life of 29 days (Wu et al. 2011). Various studies have showed the degradation of perchlorate in water after fireworks in 1 week (Backus et al. 2005), 20–80 days (Wilkin et al. 2007), etc. Maximum concentration of perchlorate in water after fireworks display was found to be in 4 days (Backus et al. 2005). But concentrations were above the background values even 90 days after the fireworks display (Wu et al. 2011).

Data gaps existing

A lot of data gaps need exploration in relation to fireworks display and manufacturing. The impacts of fireworks on groundwater and surface water need to be explored (MDEP 2006). Further studies are needed to assess human exposures to perchlorate through inhalation of particles released during fireworks displays (Wu et al. 2011). In China and Japan, perchlorate was found in blood samples and dairy milk. This raises concern on the health impacts on infants. Also, perchlorate deposition on surface water can result in accumulation of perchlorate in aquatic organisms and plants. All these are yet to be assessed. In short, there exists a knowledge

gap regarding the relationship between fireworks displays and the environmental occurrence of perchlorate.

Go green

Fireworks can be "greened" by the application of nitrogen-rich compounds (Steinhauser and Klapotke 2008). High-nitrogen energetic salts can be used in pyrotechnics by replacing perchlorate (Klapotke et al. 2010a). Alkali metal and alkaline earth metal salts of nitrogen-rich compounds like bis (1H-tetrazol-5-yl) hydrazine (BTH) is found to be environment friendly (Ebespacher et al. 2009). Other suitable additives that may be used are salts of 1H-tetrazole (Klapotke et al. 2008), strontium tetrazolate pentahydrate (Klapotke et al. 2010b), and barium tetrazolate (Thiele and Ingle 1895; Klapotke et al. 2010a).

Conclusion

Fireworks display end up in environmental contamination. Most of the people are unaware about the potential impacts of this "exotic" display. The epidemiological and ecological impacts we can expect from fireworks display are numerous. There exist data gaps in many areas regarding fireworks display, which are yet to be explored. Above all, there are options for safe enjoyment by replacing perchlorate in fireworks with other oxygen-rich compounds.

Acknowledgments The financial support from DST-FIST, Government of India is gratefully acknowledged. The authors are grateful to the anonymous reviewers for their valuable suggestions and guidance in shaping this article. First author also acknowledges the Junior Research Fellowship from UGC, Govt. of India.

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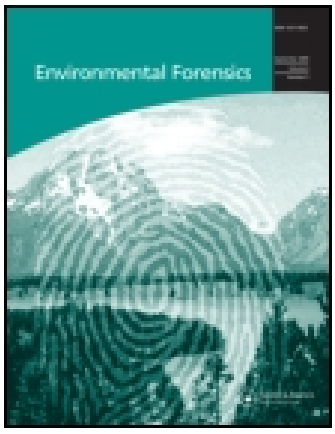

Environmental Forensics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uenf20

Review on Fate, Toxicity, and Remediation of Perchlorate

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Published online: 10 Jun 2015.

Environmental Forensics, 16:125–134, 2015

ISSN: 1527-5922 print / 1527-5930 online
DOI: 10.1080/15275922.2015.1022914

Taylor & Francis
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Several issues regarding the adverse impacts of the chemical—perchlorate—have been identified recently. Perchlorate is a persistent chemical, and remains in water and soil, thereby accumulating in plants and animals. Fetuses suffer the most from perchlorate contamination. There are ongoing debates about the impacts, toxicity and health effects of perchlorate. Many studies have been conducted on its ecotoxicity and its effects, but standards do not exist for perchlorate. This study aims to review the sources, impacts, fate, transport and remediation of perchlorate.

Keywords: pollution, water, ecotoxicology, thyroid disorders, bioremediation, perchlorate

Perchlorate Overview

Perchlorate is a non-labile, monovalent, oxy-anion (Sterner and Mattie, 1998; Bao and Gu, 2004). It consists of a tetrahedral array of oxygen atoms around a central chlorine atom, where perchlorate is in +7 oxidation state (Urbansky, 2002; Wolff, 1998). Perchlorate, as salt, is a colorless, odorless chemical (Agency for Toxic Substances and Disease Registry [ATSDR], 2008; Sanchez et al., 2005a), a good oxidizing agent (Srinivasan and Viraraghavan, 2009) and is explosive at high concentrations in acid (Wolff, 1998). The major chemical forms are perchloric acid, ammonium perchlorate, potassium perchlorate and sodium perchlorate (Interstate Technology and Regulatory Council [ITRC], 2005). Perchlorate salts are highly soluble and mobile in water (Motzer, 2001; ITRC, 2005). Perchlorate anion (ClO_4^-) is produced when these salts dissolve in water (Motzer, 2001) and the anion is highly stable, unreactive and persistent in nature (Siglin et al., 2000; Srinivasan and Viraraghavan, 2009). Once it reaches water, it takes decades to degrade (Motzer, 2001). Perchlorate belongs to a group of anions that possesses antithyrotoxic activity (Wolff, 1998) and it threatens human health as it interferes with iodide uptake, resulting in decreased thyroid hormone production (Charnley, 2008; Urbansky, 2002; Stetson et al., 2006). This review aids in understanding the major sources of perchlorate, how it affects the environment, its impacts on health and recent advances in remediation.

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Sources

Perchlorate is found both naturally and artificially (Snyder et al., 2006; Murray et al., 2008) (Table 1), with the former being generated under certain specific climatic conditions, such as arid environments, caliche-containing soils, and evaporate deposits (Murray et al., 2008). Natural perchlorate has been reported from the hyper-arid Atacama Desert salts (Bao and Gu, 2004; Ericksen, 1983), Antarctic dry valleys (Kounaves et al., 2010), Martian soil (Hecht et al., 2009) and various parts of the United States, including California, New Mexico, and Texas (Rajagopalan et al., 2006; Ericksen et al., 1988; Orris et al., 2003; Jackson et al., 2005; Snyder et al., 2005; Plummer et al., 2005). The use of nature-derived nitrate fertilizers, from Chilean salt deposits and potash ores, are also found to be sources of perchlorate in certain regions (Srinivasan and Viraraghavan, 2009; Susarla et al., 1999). Atmospheric deposition is another natural source of perchlorate (Rajagopalan et al., 2006). The presence of perchlorate in atmospheric aerosols and precipitation further proves the natural production of perchlorate (Murphy and Thomson, 2000; Dasgupta et al., 2005).

Anthropogenic source of perchlorate is associated with production and use of perchlorate containing salts (ITRC, 2005). Environmental perchlorate contamination is associated with military installations, rocket propellant manufacture and testing facilities (Tikkanen, 2006), fireworks manufacturing and display (Sijimol and Mohan, 2014; Sugimoto et al., 2012), blasting agents, and military munitions, for example (Massachusetts State Department of Environmental Protection [MassDEP], 2005; Srinivasan and Viraraghavan, 2009; Urbansky, 2002; Gullick et al., 2001), where it is used as an oxidizing agent (Murray et al., 2008). Perchlorate is also formed as an oxidation product in sodium hypochlorite (Sanchez et al., 2009). Lesser amount of perchlorate is used in matches, gas drying

Table 1. *Natural and anthropogenic sources of perchlorate in the environment*

Natural sources	Anthropogenic sources
1. Geogenic sources- examples are following **a.** Hyper arid Atacama desert **b.** Antarctic dry valleys **c.** Martian soil **d.** Chilean salt deposits **e.** Potash ores **2.** Atmospheric deposition	**1.** Military installations **2.** Military munitions **3.** Rocket propellant manufacturing and testing facilities **4.** Fireworks manufacturing and display **5.** Blasting agents **6.** Matches **7.** Gas drying applications **8.** Seismic charges **9.** Highway safety flares

applications, seismic charges and highway safety flares (Rajagopalan et al., 2006). Natural and anthropogenic sources of perchlorate can be differentiated using stable isotope forensic technique, which involves the identification of perchlorate by analyzing the oxygen and chlorine isotopes (ITRC, 2005; Bao and Gu, 2004; Sturchio et al., 2012; Petrisor and Wells, 2008).

Fate and Transport

Perchlorate was detected in natural waters (rain water), raw and treated drinking water, groundwater, bottled water, open well and surface water in the United States, India, England, and Wales, China, South Korea, Japan, and Canada (Srinivasan and Viraraghavan, 2009; Tikkanen, 2006; Stetson et al., 2006; Kannan et al., 2009; McLaughlin et al., 2011; Anupama et al., 2012, Snyder et al., 2005; Crawford-Brown et al., 2006; Rajagopalan et al., 2006; Stetson et al., 2006; Kimbrough and Parekh, 2007; Kosaka et al., 2007; Quinones et al., 2007; Wagner et al., 2007). In the United States, perchlorate detection in 26 states, including Puerto Rico, Mariana Islands, and in the public water systems resulted in the discontinuation of the use of most of the perchlorate-contaminated sources (Brandhuber et al., 2009).

Perchlorate could reach the aquatic ecosystem by a number of ways such as runoff, direct deposition etc. and it is chemically stable in water under normal conditions (Logan, 1998). Perchlorate in ground water moves freely, by advection (Motzer, 2001). Once perchlorate reaches soil, it gets dissolved in the available moisture and thus reaches the water bodies (ITRC, 2005). Perchlorate does not bind to soil particles appreciably (Trumpolt et al., 2007; Robles, 1999; ITRC, 2005). But widespread perchlorate contamination has been found in soil even in 40-m deep vadose zones (Tikkanen, 2006; Robles, 1999; Gal et al., 2008).

Perchlorate in soil and sediment may either get degraded or get accumulated in plants (Tipton et al., 2003; Nozawa et al., 2005; Simon and Weber, 2006). Perchlorate was observed in high concentration in soybean sprouts (*Glycine max* L. Merr), water dropwort (*Oenanthe stolonifera* DC), and lotus root (*Nelumbo nucifera* Gaertn [Yang and Her, 2011]). The wetland plants like *Eichhornia crassipes*, *Acorus calamus* L., *Thalia dealbata* and *Canna indica* show perchlorate accumulation (He et al., 2013). Edible cole crops (*Brassica* sp.) and lettuce (*Lacuta sativa* L.), irrigated with perchlorate-contaminated water from the Colorado River, have been found to accumulate trace levels of the chemical (Sanchez et al., 2005a; 2005b; 2007). Irrigation of citrus plants (lemon, grapefruit, and orange) with perchlorate-contaminated water in the United States resulted in the uptake of perchlorate by these plants, especially in leaves and fruits (Sanchez et al., 2006). Using stable-isotope tracer of perchlorate, the metabolism and re-translocation in plants were studied. No significant movement of perchlorate from older leaves into new leaves or roots has been observed. Metabolism and re-translocation were also absent indicating the persistency of perchlorate in leafy produce and this also indicates the fact that the primary mode of transportation is through the xylem of higher plants (Seyfferth et al., 2008b). Even though accumulation of perchlorate is observed in plants, experiments with Soybean sprouts, showed decreased bioconcentration factor (Yang and Her, 2011).

The perchlorate content in plants may be the reason for its accumulation in animals. Perchlorate was detected in deer and mice (*Peromyscus maniculatus*) and half-lives in these animals were found to be 9.12 and 7.25 hours (Cheng et al., 2008). Fish and frog samples were found to contain perchlorate and these samples also exhibited thyroid disruption (Theodorakis et al., 2006). Food chain transfer of perchlorate may also occur in water bodies but unlike plants, no bioconcentration was reported in animals (Park et al., 2005). Blount et al. (2008) observed a transfer of an average of 23% of the perchlorate into eggs, when chicken ingested perchlorate-containing feed and this also resulted in decreased iodide levels in eggs. Perchlorate in dairy feed, such as corn silage, alfalfa hay, and Sudan grass, can result in contamination of milk and subsequent exposure to humans (Rice et al., 2007). Perchlorate contamination in milk was also reported from the United States and Japan (Capuco et al., 2005; Dyke et al., 2007). Studies have also revealed that certain ruminant animals can degrade perchlorate in their digestive system (Capuco et al., 2005).

Studies have revealed high concentrations of perchlorate in supplements recommended for pregnant women and also in other food sources (Snyder et al., 2006). Once perchlorate

enters the human body, either it gets eliminated through urine (Cheng et al., 2008), or it is transmitted to the thyroid gland, saliva (Kannan et al., 2009), placenta (Steinmaus et al., 2010) or mammary glands (Dohan et al., 2007) via NIS (sodium iodide symporter). Active translocation of perchlorate by NIS in epithelial mammary cells, results in perchlorate accumulation in milk (Dohan et al., 2007; Dasgupta et al., 2008).

Toxicity

As the perchlorate salts dissociate freely in water, the practical toxicity of each salt may be the same under similar environmental conditions (Sterner and Mattie, 1998). But the impacts can differ from species to species.

Impacts on Animals

Perchlorate is known to disrupt the thyroid axis of many terrestrial and aquatic species (McLanahan et al., 2009). Thyroid follicle cell height increases as the mean water perchlorate concentration increases (Theodorakis et al., 2006). A 30-day exposure of sodium perchlorate at concentrations 0, 0.1, 1, 10, 100, and 1000 mg/L resulted in decreased whole body thyroxine (T_4) concentration, increased follicular epithelial cell height, hyperplasia and hypertrophy in mosquito fish, *Gambusia holbrooki* (Bradford et al., 2005). Perchlorate was found to interfere with the expression of nuptial coloration, courtship behavior and normal sexual development in the fish species, three spine stickleback (*Gasterosteus aculeatus*). The study also revealed that perchlorate produces androgenic effects and it is capable of inducing functional hermaphroditism in non-hermaphroditic vertebrates (Bernhardt et al., 2006). When sodium perchlorate was administered to zebra finch (*Taeniopygia guttata*) on post-hatch days (3–14), at environmentally relevant concentrations (0, 10, 100, or 1000 μg/g body mass) for 72 days, it exhibited a dose-dependent alteration of multiple growth and behavioral end points (Rainwater et al., 2008). In the larvae and embryos of South African frog *Xenopus laevis*, a dosage level of 59 ppb and 14,140 ppb ammonium perchlorate (minimum and maximum concentration of perchlorate reported from South African surface water bodies) for 70 days inhibited the forelimb emergence, the percentage of animals completing tail resorption, and the hind limb development (Goleman et al., 2002). Even the minimum concentration (59 ppb) of ammonium perchlorate resulted in significant hypertrophy of the thyroid follicular epithelium. Sex ratios were skewed, significantly reducing the percentage of males at metamorphosis (Goleman et al., 2002). The inhibition of metamorphosis to mortality was observed in the larvae of southern leopard frogs (*Rana sphenocephala*) when it was exposed to 15 mg/L and 30 mg/L perchlorate, respectively (Ortiz-Santaliestra and Sparling, 2007). Environmental perchlorate at concentrations in the low mg/L range has negative effects on thyroid histology, thyroxine production and metamorphosis but have low lethal toxicity to amphibians (Sparling and Harvey, 2006).

In a rat study, the model simulations predicted a significant transfer of perchlorate through milk after maternal exposure (Clewell et al., 2003a; 2003b). When daily maternal doses of perchlorate (0.1–10.0 mg) were administered to rats, 50%–60% of perchlorate transfer through milk was observed (Clewell et al., 2003a). They also reported that perchlorate-induced iodide deficiency during gestation will result in developmental effects. However, the extent of inhibition in fetal thyroid remains unknown. Histological examination of the thyroid gland in rats showed colloid depletion and hypertrophy of follicular epithelial cells when high doses of ammonium perchlorate were administered (Khan et al., 2005). On administration of 1000 ppm perchlorate in drinking water, adult rats showed decreased T_3 and T_4 concentrations and reductions in inhibitory function (Gilbert and Sui, 2008). At doses of 10 mg/kg/day, with 14 and 90 days of exposure, rats developed significant increase in thyroid weights and thyroid histopathology consisting primarily of follicular cell hypertrophy with microfollicle formation and colloid depletion (Siglin et al., 2000). Thyroid changes are reversible if a non-treatment recovery period is given (Siglin et al., 2000).

Perchlorate acts as a thyroid hormone inhibitor in ground dwelling birds (Chen et al., 2009; Rainwater et al., 2008). Perchlorate exposure at 2000 mg/L in drinking water for 7.5 weeks, beginning on day 5 post-hatch, caused hypothyroidism in young Japanese quail and affected the expression of thyroid-responsive genes during early post-hatch development (Chen et al., 2009). Birds with 1000 μg perchlorate/g body mass exhibited a greater begging intensity, decreased motivation for spontaneous movement (e.g., attempts to fly), and reduced capacity to wean themselves from parental care (Rainwater et al., 2008). Administration of ammonium perchlorate (12.5 μg/L to 4000 mg/L) via drinking water in bobwhite quail chicks, for 8 weeks, resulted in decreased plasma thyroid-stimulating hormone (TSH), hypertrophied thyroid glands and decreased thyroid hormone (TH) (McNabb et al., 2004).

Thyroid status variation was noted in rhesus monkeys by the administration of ammonium perchlorate through food at doses of 0.006, 0.34, and 12.8 mg/kg/day (Ozpinar et al., 2011). Fatty acid acts as an energy source for infant mammals and is involved in some other biological processes (German and Dillard, 2006). Changes in fatty acid composition were observed in milk fat from goats (*Capra aegagrus hircus*), dosed with perchlorate (0.1 and 1 mg/kg body weight/day) for 31 days (Cheng et al., 2007). In contrast to other animal toxicity studies, ammonium perchlorate was found to be catalyzing the increased production of thyroid hormone production in developing deer mice (*Peromyscus maniculatus)*, resulting in increased total T_4 concentrations (Thuett et al., 2002).

Impacts in Humans

Perchlorate is one of the most potential inhibitor of T_4 release (Hornung et al., 2010). It inhibits uptake of iodide at the cellular level (Soldin et al., 2001; Kirk, 2006). The Na^+/I^- symporter (sodium-iodide symporter [NIS]) is a key plasma membrane protein that mediates active iodide uptake in the thyroid (for the production of thyroxine (T_4) and triiodothyronine (T_3)), lactating breast etc. (Dohan et al., 2007; Groef et al., 2006; Wolff, 1998). The human sodium/iodide symporter has a 30-fold higher affinity for perchlorate than for iodide (Tran et al., 2008). Perchlorate ion has size similar to that of the iodide ion (Urbansky, 2002). At high concentrations, perchlorate competes with iodide for NIS and can reduce or block the iodide uptake by thyroid cells, thereby impairing the thyroid functions (Ting et al., 2006). Iodine uptake inhibition and adverse effects by perchlorate also depends on the presence of other NIS inhibitors such as nitrate and thiocyanate (Groef et al., 2006). Perchlorate was used to treat overactive thyroid glands (Snyder et al., 2006), Graves disease and hypothyroid conditions (Orgiassi and Mornex, 1990), until reports came out on the development of agranulocytosis and aplastic anemia with fatalities (Larsen and Ingbar, 1992).

Perchlorate is a health threat to developing infants and children (Dyke et al., 2007). The risk depends on factors like thyroid status of mother during gestation, thyroid status of the fetus, maternal and infant iodine intake, exposure of each to other thyroid hormone-disrupting chemicals (Kirk, 2006). Perchlorate also inhibits the transport of iodine into milk (Dasgupta et al., 2008). As neural development of fetus is TH-dependent, perchlorate can result in a permanent adverse effect (Kirk, 2006). Neonates are more susceptible to endocrine disruption by perchlorate as it inhibits the iodide uptake in the mammary gland thereby increasing the perchlorate concentration in milk (Clewell et al., 2003b). While little of the maternal iodine finds its way into milk, bulk of the perchlorate intake ends up in milk (Dasgupta et al., 2008). Infants and children have the highest estimated intakes of perchlorate on a body weight basis (Murray et al., 2008). Fetus is predicted to receive the greatest dose (per kg body weight), because of dependence on the factors like placental sodium-iodide symporter activity and reduced maternal urinary clearance of perchlorate (Clewell et al., 2007). Higher levels of urinary perchlorate were found in children compared with adolescents and adults (Blount et al., 2007). Environmental exposure to perchlorate has no effect on the neonatal blood TSH levels (Li et al., 2000)— environmental exposure to perchlorate up to 15 μg/L showed no effect on neonatal TSH levels for the first month of life. Children from areas with perchlorate in drinking water (up to 24 μg/L) showed no evidence of increase in pediatric neurobehavioral disease or a decrease in fourth-grade academic performance (Chang et al., 2003).

Various reports indicate that perchlorate does not accumulate in human tissues (Eichler, 1929; Stanbury and Wyngaarden, 1952). Perchlorate was even detected in breast milk samples, urine samples and infant formula samples (Pearce et al., 2007; Kirk et al., 2007). It was detected from urine samples of all 2820 U.S. residents analyzed by Blount et al. (2007), indicating the widespread human exposure to perchlorate. A 6-month exposure to perchlorate at doses up to 3 mg/day had no effect on thyroid function, including inhibition of thyroid iodide uptake as well as serum levels of thyroid hormones, TSH and serum thyroglobulin (Tg) (Braverman et al., 2006). Perchlorate was detected in blood samples of adults in China, where it was found to be at levels 10 times higher than that in the U.S. population (Zhang et al., 2010). 34 mg/kg absorption of occupational airborne perchlorate had no-observed adverse effects on human health (Lamm et al., 1999).

Perchlorate exposure may have effects in pregnancy that are not reflected in maternal thyroid function (Brent, 2010). Low-level perchlorate exposure did not affect thyroid function in iodine-deficient pregnant women (Pearce et al., 2010). As there are many issues, it must be ensured that women of reproductive age are best served by adequate iodine intake that can take the form of vitamin containing iodine (Brent, 2010).

There is no federal drinking water standard for perchlorate. EPA has established an official reference dose (RfD) of 0.0007 mg/kg/day of perchlorate (a reference dose is defined by the EPA as a scientific estimate of a daily exposure level that is not expected to cause adverse health effects in humans) (Groef et al., 2006; Tikkanen, 2006). Some suggest that US EPA reference dose (RfD) for perchlorate is conservatively health protective (Charnley, 2008). The reference dose, 0.0007 mg/kg/day (24 μg/L drinking water), is intended to protect the most sensitive life stage: the fetus (Anderson et al., 2006). But some others are of the opinion that a groundwater preliminary remedial goal of 24.5 μg/L can lead to a 7-fold increase in breast milk concentration, causing nursing infants to exceed the reference dose (average exceedence, 2.8 fold) (Ginsberg et al., 2007). They suggest that drinking water perchlorate level should be $<$6.9 μg/L, to keep the nursing infants' exposure below the RfD. Zewdie et al. (2010) suggest 2 μg/L drinking water standard for perchlorate. A public health goal of 6 ppb (0.0037 mg/kg/day) was found to be adequately protective of sensitive subpopulations, including pregnant women, their fetuses, infants and people with hypothyroidism (Ting et al., 2006).

Perchlorate does not inhibit cell proliferation in humans (Tran et al., 2008). Chronic exposure to perchlorate may result in human health risks like hypothyroidism, goiter and mental retardation (if exposure occurs during critical periods in neurodevelopment) (Merrill et al., 2003). Many physiologically based pharmacokinetic models were developed to describe the effects of perchlorate on human health (Merrill et al., 2005).

Remediation

Possible technologies for perchlorate reduction include physical separation (precipitation, anion exchange or membrane filtration, reverse osmosis and electro dialysis), chemical and electrochemical reduction, and biological or biochemical reduction (Srinivasan and Viraraghavan, 2009; Urbansky, 1998) (Table 2). But it is difficult to remove perchlorate using typical physical-chemical water treatment technologies (Logan, 1998).

Biological approaches are gaining attention for the treatment of perchlorate (Hatzinger, 2005). Biodegradation of perchlorate was identified as one of the most effective techniques from the 1950's onwards, but its importance was noticed only when perchlorate contamination emerged as a threat. Perchlorate can be effectively attenuated by microaerophilic or anaerobic microorganisms (Coates and Achenbach, 2004; Logan, 1998; Rikken et al., 1996; Wu et al., 2001; Holdren et al., 2008). Dechloromonas, Azospira and Dechlorospirillum genera showed reliable degradation of perchlorate (Achenbach et al., 2001; Zhang et al., 2002; Coates et al., 1999; Coates and Achenbach, 2004). Later about 40 phylogenetically and metabolically diverse microbial species including members of the Proteobacteria, Firmicutes, *Moorella perchloratireducens* and Sporomusa sp. were found to be capable of perchlorate reduction (Coates and Achenbach, 2004). Novel dissimilatory perchlorate-reducing bacteria *Dechloromonas hydrogenophilus* and *Propionivibrio militaris* were isolated from enrichments (Thrash et al., 2010).

Perchlorate reduction produces chloride and oxygen as degradation products by the following pathway (Rikken et al., 1996):

$$ClO_4^- \Longrightarrow ClO_3^- \Longrightarrow ClO_2^- \Longrightarrow Cl^- + O_2$$

This is a two-enzyme catalyzed reaction. Perchlorate is reduced to chlorate and chlorite by reductase enzyme (Kengen et al., 1999) and chlorite dismutase disproportionate the chlorite into chloride and oxygen (Coates and Achenbach, 2004; van Glinkel et al., 1996).

Microbial respiration of perchlorate is influenced by environmental conditions, and reduction of perchlorate is directly dependent on bioavailable molybdenum and presence or absence of competing electron acceptors (Chaudhuri et al., 2002; Kim and Logan, 2001; Logan, 2001; Rikken et al., 1996; Coates et al., 1999). In some strains molybdenum is essential and in some strains presence of oxygen and nitrate can inhibit the process (Coates and Achenbach, 2004; Song and Logan, 2004; Chauduri et al., 2002; Rikken et al., 1996; van Glinkel et al., 1996; Xu et al., 2003). The bacterial species found to reduce perchlorate (*Dechloromonas aromatica*, *Azospira suillum* and *Dechloromonas agitate*), are inhibited by oxygen (Sun et al., 2009). Perchlorate ion acts as an electron acceptor aiding successful bacterial reduction of perchlorate (Sellers et al., 2007).

Perchlorate reducer *Dechlorosoma suillum*, reduces perchlorate only under anaerobic conditions and is dependent on the presence of molybdenum. Dissolved oxygen concentrations less than 2 mg/L too inhibited perchlorate reduction by D. *suillum*. Nitrate had inhibitory effects on perchlorate reduction with D. *suillum*, whereas nitrate had no inhibitory effects on perchlorate reduction with *Dechloromonas agitata* (Chaudhuri et al., 2002). Lag time for microbial reduction of perchlorate is inversely proportional to nitrate reduction (Gal et al., 2008). Information is available on the aerobic perchlorate reducers that are independent of molybdenum (Shete et al., 2008) Three isolates of microbes - *Pseudomonas stulzeri* (Proteobacteria) and the other two belonging to *Arthrobacter* (Actinobacteria)) were found to be capable of perchlorate reduction under aerobic condition, and independent of molybdenum (Shete et al., 2008). But these showed some inhibition of perchlorate reduction at perchlorate concentrations higher than 17 mM (Shete et al., 2008). Most of the perchlorate-contaminated sites have perchlorate reducing bacteria and can be used in perchlorate degradation through the addition of different electron donors, such as acetate and lactate (Wu et al., 2001).

Bioreactors are engineered systems that maintain high densities of pollutant-metabolizing organisms in contact with groundwater or wastewater (Hatzinger, 2005; Rittman and McCarty, 2001). Bioreactors are used to treat perchlorate in high-strength wastewater treatment, groundwater treatment and drinking water treatment. In the case of drinking water treatment various designs of hydrogen-based reactors have been tested in laboratory, to reduce perchlorate (Logan and LaPoint, 2002; Miller and Logan, 2000; Nerenberg et al., 2002; Chung et al., 2007). The main drawback is that hydrogen is only sparingly soluble in water; this can result in an

Table 2. *Summary of remediation methods*

Method	Reference
Physical separation	Srinivasan and Viraraghavan, 2009
Chemical and electrochemical reduction	Urbansky, 1998
Biodegradation	Hatzinger, 2005; Coates and Achenbach, 2004; Wu et al., 2001; Thrash et al., 2010; Rikken et al., 1996
Bioreactors	Hatzinger, 2005; Rittman and McCarty, 2001
Hydrogen-based reactor	Logan and Lapoint, 2002; Miller and Logan, 2000; Nerenberg et al., 2002; Chung et al., 2007
In-situ groundwater remediation	Giblin et al., 2000; Hunter, 2002; Logan and Lapoint, 2002; Leeson et al., 2006
Graphene	Lakshmi and Vasudevan, 2013
Phyto-remediation	Tan et al., 2004; Cope et al., 1967; van Aken and Schnoor, 2002

insufficient supply being available to completely bioreduce perchlorate, particularly in waters containing appreciable quantities of competing electron acceptors such as nitrate and oxygen (Logan and LaPoint, 2002; Miller and Logan, 2000). For drinking water treatment (Kim and Logan, 2001; Xu et al., 2003) and in-situ groundwater remediation (Giblin et al., 2000; Hunter, 2002; Logan and LaPoint, 2002; Leeson et al., 2006) biological processes are effective.

Microbial reduction is a cost-effective, in-situ bioremediation technique for perchlorate-contaminated water (Sturchio et al., 2003). Salt-tolerant bacterial isolates—*Haloferax denitrificans*, *Paracoccus halodenitrificans* and *Citrobacter* sp.—were found to be very effective in the removal of perchlorate from the spent regenerant brine used in ion-exchange technology (Okeke et al., 2002). Biological perchlorate reduction can be achieved using a hydrogen-oxidizing hollow-fiber membrane-biofilm reactor system. Here, the optimal pH is 8 and no specialized inoculation is required. Perchlorate reduction occurs simultaneously with nitrate reduction (Nerenberg et al., 2002). Perchlorate-degrading fed-batch reactors were also tested (Anupama et al., 2013) to study the kinetics of chlorite dismutase, the enzyme involved in perchlorate degradation and the result indicated that the compounds such as ammonia, nitrite and metal-chelating chemicals can retard the activity of the enzyme. Graphene, prepared by a facile liquid-phase reactor exfoliation is an excellent perchlorate adsorbent, and removes perchlorate from water, making it potable (Lakshmi and Vasudevan, 2013).

Phyto-remediation is another method for the removal of perchlorate from soil and groundwater. Trees such as ash, chinaberry, elm, willow, mulberry and hackberry have been proved to be perchlorate accumulators (Tan et al., 2004). Wheat stem and head, alfalfa, smart weed, water cress etc. also accumulate perchlorate (Cope et al., 1967). Phyto-remediation of perchlorate was observed inside poplar trees (*Populus deltoid* × *nigra*) and the perchlorate undergoes reduction to chlorate, chlorite and chloride (van Aken and Schnoor, 2002). Perchlorate uptake by plants is largely affected by nitrate and pH. Increased nitrate concentration and pH reduces perchlorate uptake, thereby considerably slowing down the phyto-remediation process (Seyfferth et al., 2008a).

Conclusion

Perchlorate is fast becoming a threat to the environment. In almost all areas of science, viz., environment, food, agriculture, chemistry, health etc. widespread research on various aspects of perchlorate like pollution, bioaccumulation, toxicity, remediation etc is going on. Still the problem persists, and prescribing a permissible limit of perchlorate in drinking water to avoid health problems remains a distant reality. Further work in this area is also very much essential to provide clear data on perchlorate sources, its ecotoxicity, fate, and impacts.

Acknowledgment

The authors are grateful to the anonymous reviewers for their valuable suggestions and guidance in shaping this article.

Funding

The financial support from DST-FIST, Government of India is gratefully acknowledged. First author also acknowledges the Junior Research Fellowship from UGC, Government of India.

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Energy, Ecology and Environment

ISSN 2363-7692
Volume 5
Number 4

Energ. Ecol. Environ. (2020) 5:286-293
DOI 10.1007/s40974-020-00163-5

Springer

Energ. Ecol. Environ. (2020) 5(4):286–293
https://doi.org/10.1007/s40974-020-00163-5

ORIGINAL ARTICLE

Perchlorate contamination of drinking water sources in Kerala, South India, and its degradation using advanced chemical treatment

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Received: 4 February 2019 / Revised: 15 April 2020 / Accepted: 17 April 2020 / Published online: 28 April 2020

Abstract Perchlorate is an inorganic chemical reported to be resulting in widespread contamination of water bodies and even drinking water systems. The presence of perchlorate was identified in various drinking water sources (well, tap, borewell and bottled water) using liquid chromatography–mass spectrometry technique. The concentration of perchlorate in these samples is found in the order of bottled water ≫ well water > tap water > bore well water. Since most of the people in the study area depend upon this contaminated water for drinking purpose without any treatment, another important goal of this study was to propose suitable methods to remove or minimize the perchlorate concentration. This has been accomplished by advanced reduction processes (ARPs). Screening experiments including advanced oxidation processes such as UV photolysis, sonolysis, Fenton's reaction in combination with reducing agents like sulfite, persulfate, ferrous iron at different pH and various concentrations were done. The experiments with ARPs are found to be degrading the perchlorate up to 32% in 5 h in Fenton-type reaction, and further experiments with modifications in the activation methods and reducing agents may give promising results for perchlorate degradation. Therefore, ARP technique offered more prominent results in terms of perchlorate removal, which can be easily extended in large-scale applications.

Keywords Sonolysis · UV photolysis · Distillation · Fenton reaction · ARP

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1 Introduction

Water contaminated by emerging contaminants becomes a critical issue these days. Perchlorate is an important emerging inorganic contaminant, which is reported in various water resources and in soil all over the world. Perchlorate is a negatively charged, highly oxidized ion of chlorine and is highly soluble in water (Wolff 1998;Urbansky 2002). The ammonium, sodium and potassium salts of perchlorate are widely used as oxidizers in rocket propellants, fireworks, ammunitions, etc. (ITRC 2005; Srinivasan and Viraraghavan 2009; Sijimol and Mohan 2014). The presence of perchlorate was reported in ground water, tap water, rain water and surface water from different parts of the world (Tikkanen 2006; Quinones et al. 2007; Wagner et al. 2007; Kannan et al. 2009; McLaughlin et al. 2011; Anupama et al. 2012). The consumption of water polluted with perchlorate anion may cause increased thyroid disorders (Wolff 1998; Urbansky 2002). All these reports showed the importance of implementing a suitable treatment protocol for perchlorate ions. In fact, these ions are hydrophilic, nonvolatile and kinetically inert in nature and therefore hard to remove from aqueous environment by conventional methods. The conventional water treatment methods failed to remediate perchlorate, and at the same time, techniques like carbon adsorption and ion exchange techniques are very expensive (Evans et al. 2002). Moreover, techniques like anion exchange, precipitation processes, chemical and electrochemical reduction reactions, biological and biochemical processes can be employed for perchlorate remediation (Urbansky 1998; Srinivasan and Viraraghavan 2009; Sijimol et al. 2015). Reduction processes are the one of the easy ways to

degrade these ions and are represented by the half reaction given in Eq. 1

$$ClO_4^- + 8e^- + 8H^+ \rightarrow Cl^- + 4H_2O \; E = +1.388V \quad (1)$$

Bioremediation is considered as an advantageous option for perchlorate removal (Lv et al. 2020). Bioreactors are proved to be effective for the remediation of perchlorate (Miller and Logan 2000; Kim and Logan 2001; Logan and LaPoint 2002; Nerenberg et al. 2002; Xu et al. 2003,Chung et al. 2007; Ucar et al. 2019). However, the drawback is that anaerobic environment is necessary for the microbes to act upon perchlorate; hence, it is time-consuming. Microbial reduction of perchlorate produces chloride and oxygen as degradation products by a two-enzyme catalyzed reaction (Rikken et al. 1996) (Eq. 2):

$$ClO_4^- \rightarrow ClO_3^- \rightarrow ClO_2^- \rightarrow Cl^- + O_2 \quad (2)$$

Reductase enzyme reduces perchlorate to chlorate and chlorite (Kengen et al. 1999), and chlorite dismutase disproportionates the chlorite into chloride and oxygen (Coates and Achenbach 2004; van Ginkel et al. 1996).

Advanced oxidation processes (AOPs) and advanced reduction processes (ARPs) are other unutilized options for perchlorate remediation. AOPs are widely used for the degradation of organic compounds (Pang et al. 2011), where the hydroxyl radical destructs most of the organic components. Based on the generation of hydroxyl radical, it can be classified into UV/H_2O_2 photolysis, photocatalysis, sonolysis (Rayaroth et al. 2016), electrochemical methods (Oturan et al. 2008), etc. In sonolysis, ultrasound irradiation of aqueous solution creates smaller cavities, which grows during each acoustic cycle and finally undergoes violent collapse to release extreme conditions of high temperature and pressure (Petrier and Francony, 1997). Under this condition, the water molecule cleaves to release hydroxyl radical and hydrogen atom (Eq. 3). The degradation rate in sonolysis is really compound specific. In sonolysis, hydrophobic and volatile compounds undergo faster degradation compared to other AOPs due to their affinity toward the highly reactive interface region of the cavitating bubble and inside the bubble (Lim et al. 2011; Barik and Gogate 2016). Hydrophilic compounds are relatively stable in sonolysis.

In Fenton's reaction, the cleavage of oxidizing agents (H_2O_2 or $S_2O_8{}^{2-}$) is activated by transition metal ions (mainly Fe^{2+}) (Eqs. 4–5). Persulfate-based Fenton process generates sulfate radical ions which is also a strong reactive species.

$$H_2O))) \rightarrow {}^{\cdot}OH + {}^{\cdot}H \quad (3)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^- \quad (4)$$

$$Fe^{2+}_{(aq)} + S_2O^{2-}_{8(aq)} \rightarrow Fe^{3+}_{(aq)} + SO^{\cdot-}_{4(aq)} + SO^{2-}_{4(aq)} \quad (5)$$

Advanced reduction processes (ARPs) are used for reducing oxidized contaminants (Zhaokun et al. 2019). When properly activated, chemicals like dithionite, sulfite, sulfide and ferrous iron may yield highly reactive species (Liu et al. 2013). UV irradiation in combination with reducing agents also results in the production of highly reactive reducing free radicals (Liu et al. 2013). Preliminary studies were conducted on the usage of ARPs for the degradation of inorganic compounds like perchlorate (Vellanki et al. 2013). However, no reports on the activation of sulfite ions by ultrasound and sulfate radical-based method for the removal of perchlorate ions are available.

The present study focused on the perchlorate contamination of drinking water in Kerala, its seasonal behavior around industrial areas and extent of perchlorate contamination around firework display sites. Based on the extent of pollution, the present study also assessed the effectiveness of ARPs on the laboratory-scale degradation of perchlorate in drinking water.

2 Materials and methods

2.1 Materials

Sodium perchlorate and methylamine (Sigma-Aldrich),Ferrous sulfate heptahydrate (Emplura), sodium sulfite (Merck) and persulfate (from potassium persulfate, Sisco Research Laboratories) were used as received. Deionised water obtained from CascadaTM Labwater system with a specific resistivity of > 18 MΩ cm was used to prepare the aqueous solution.

2.2 Sampling and analysis

Drinking water samples (well $n = 225$, bore well $n = 13$, tap water $n = 19$, bottled water $n = 68$) were collected from selected regions of various districts of Kerala. Samples were filtered using 0.2-µm filter paper and stored under 4° C. Seasonal sampling (post-monsoon $n = 35$, pre-monsoon $n = 35$ and monsoon $n = 35$) was done around rocket propellant manufacturing site, rocket testing facility and firework manufacturing units. Soil ($n = 42$) and water ($n = 42$) samples from and around five major firework display sites before and after the fireworks were tested. Various sampling locations are shown in Fig. 1.

Perchlorate in the samples was analyzed using liquid chromatography–mass spectrometry (Shimadzu LCMS-2020) (EPA Method 331.0). Dionex AS-21 column was used with methylamine as solvent. Selective ion monitoring technique was employed for the analysis. The instrumental parameters used for the analysis of perchlorate are

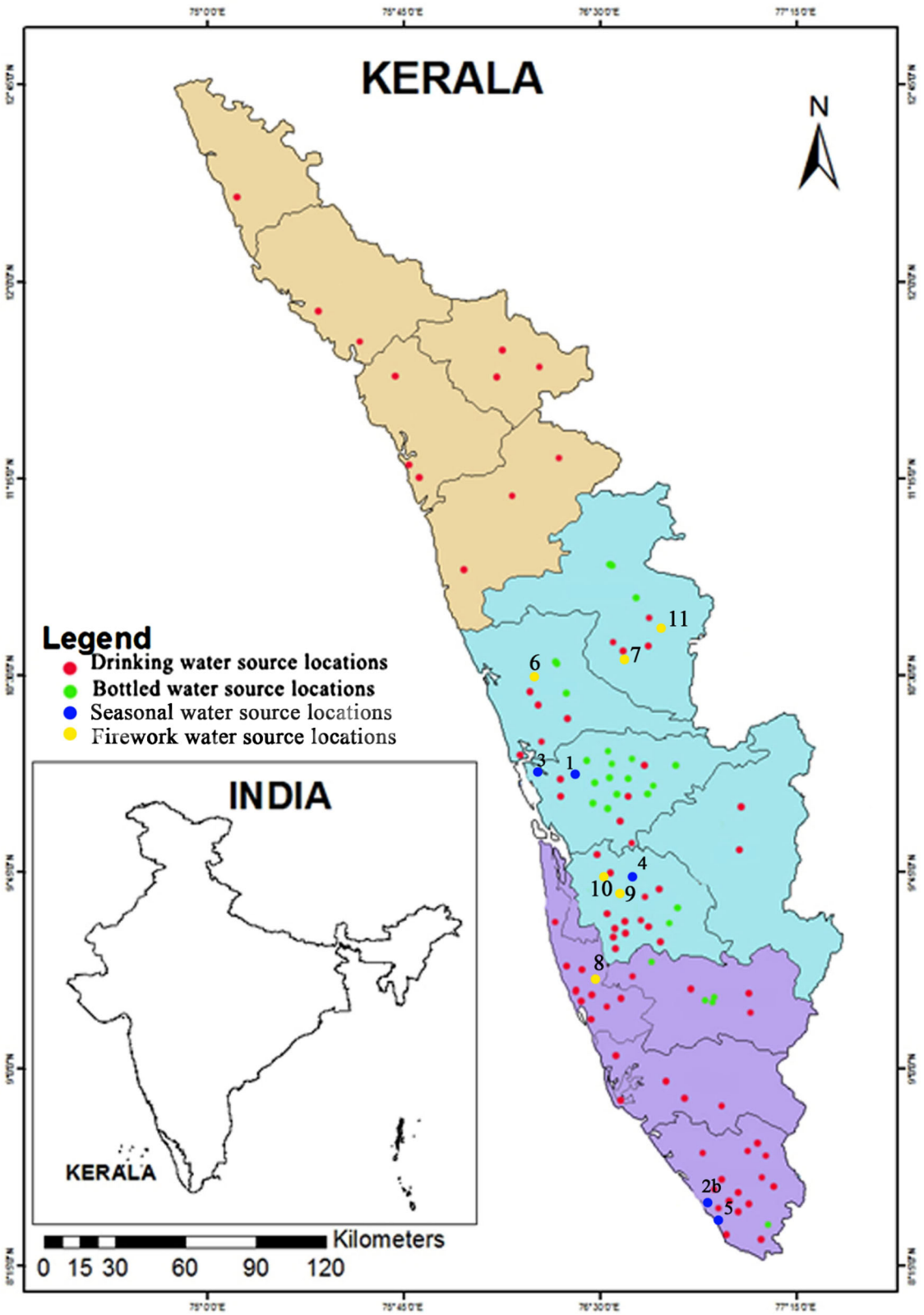

Fig. 1 Map showing sampling locations

given as follows: autosampler—SIL-30 AC Nexera X2; MS—single quadrupole; flow rate—0.35 ml/min; solvent system—isocratic 100% methylamine (2%); injection volume—50 ml. Total run time for each sample is 15 min. Method detection limit for perchlorate is 2 ppb, and limit of quantification is 4 ppb.

2.3 Sonochemical degradation

The sonochemical degradation was carried out in a 500-ml reaction vessel; the ultrasound was introduced at the bottom of the vessel using an L3 ELAC Nautik ultrasound generator powered by an Allied Signal R/F generator (T & C power conversion, Model AG 1006). The degradation was carried out at 350 kHz and 80 W power at varying pH using perchlorate and sulfite. Experiments were done for 6 h, and samples were collected every 1 h.

2.4 UV photolysis

UV irradiation experiments were carried out on a photoreactor with 125-W medium pressure deuterium lamp inserted on the quartz vessel as the light source supplied by Scientific Aids & Instruments Corporation (SAIC, Chennai). For each experiment, about 150 ml of the sample solution was placed on the immersion well reactor, made up of borosilicate glass. The samples were removed from the immersion well reactor after different irradiation times by using a micropipette/syringe and were used for further analysis. Samples were taken at an interval of 1 h, and the whole experiments were carried out for 5 h.

2.5 Fenton-type reaction

Perchlorate standards were stirred using magnetic stirrer (Rotek RMS 5H) in different pH conditions (acidic, neutral and basic). Three major experiments were done using this method. Perchlorate alone in different pH was initially done and a positive result observed in acidic pH. Hence, experiments were continued in acidic conditions. Perchlorate was added with iron (II) sulfate, and it was stirred. Finally, perchlorate standards were mixed with iron (II) sulfate and persulfate and then stirred. The duration of each experiment was 5 h, and samples were collected at an interval of 1 h.

3 Results and discussion

3.1 Drinking water

Perchlorate was detected in well water samples of almost all districts of Kerala (Table 1). Mean perchlorate in well water samples was 58.82 ppb, and it exceeds the permissible limit of 24.5 ppb. A few bore well samples also showed perchlorate contamination with an average of 6.22 ppb, whereas in tap water it is 3.54 ppb. The results showed that bore well and tap water are comparatively safe than well water. In Kerala, majority of people depend on well water for drinking purposes. Bottled water was also contaminated with perchlorate with an average of 84.71 ppb which is three times higher than the permissible limit.

3.2 Seasonal monitoring

Perchlorate was detected in drinking water samples of areas around the perchlorate-handling industries irrespective of seasons (Table 2). Perchlorate was found to be maximum during post-monsoon and pre-monsoon seasons. During this time, rainfall is minimum and the pollutant get concentrated. Minimum perchlorate is noticed during monsoon season due to dilution. However, widespread contamination was noticed during monsoon, and it is because of this dilution.

3.3 Firework study

Soil and water samples before fireworks in all the sites were below detectable levels only. After fireworks, almost all the soils were heavily contaminated with perchlorate. Perchlorate in soil ranged from 16.62 ± 42.83 to 20451.14 ± 17767.34 μg/kg, and in water, it ranged from 1.89 ± 3.75 to 7.23 ± 8.55 μg/L. Water samples of wells situated near to the site were also contaminated. Perchlorate in the soil might have leached into the ground water during the rain fall, and this might have caused the widespread contamination in the area.

The results show that drinking water of Kerala is heavily perchlorate-contaminated. Various industries and firework displays play a major role for the same. Degradation of perchlorate at the handling sites or the minimum usage of perchlorate at the handling sites or the minimum usage of perchlorate in fireworks is the only way to prevent further contamination.

3.4 Perchlorate remediation using advanced reduction and oxidation processes

As the drinking water samples were found to be heavily contaminated with perchlorate, it is important to find out some remedial options. In this objective, 5 ppm of perchlorate was used to study the degradation pattern. Perchlorate reduction was noticed in all the reactions (sonolysis, Fenton-type reaction, UV photolysis) ranging from 4.68 to 32.25%. None of the reactions have shown

Table 1 Average perchlorate in different types of drinking water samples

Type of water	No. of samples analyzed	No. of samples in which perchlorate was detected	Mean perchlorate (ppb)
Well water	225	73	58.82 ± 183.65
Bore well water	13	5	6.22 ± 7.49
Tap water	19	6	3.54 ± 4.99
Bottled water	68	32	84.71 ± 223.72

Table 2 Seasonal variation of average perchlorate in drinking water

Site	Post-monsoon (ppb)	Pre-monsoon (ppb)	Monsoon (ppb)
Site 1 (perchlorate manufacturing site)	3760.16 ± 9007.53	5094.87 ± 12159.55	601.28 ± 1360.64
Site 2 (rocket testing site)	640.4 ± 1172.04	468.57 ± 1174.97	80.61 ± 146.04
Site 3 (firework manufacturing site 1)	61.56 ± 150.79	25.42 ± 13.44	13.99 ± 16.90
Site 4 (firework manufacturing site 2)	1.03 ± 2.72	BDL	20.72 ± 14.25
Site 5 (control site)	BDL	BDL	BDL

complete removal in the given conditions. In order to check the degradation via oxidative process, initial experiment has been carried out with direct UV photolysis method, where the main species is hydroxyl radical. Only 5% to 10% reduction of perchlorate was observed at varying conditions, which is seems to be insignificant. The experiments involving UV did not show any significant degradation, and it seems perchlorate was stable toward UV light and oxidation process by ·OH alone.

3.5 Sonochemical degradation

Sonolysis was carried out for a period of 6 h. Nearly 25% of the initial concentration of perchlorate was removed from the aqueous medium. pH is a critical parameter in water treatment processes, and therefore, degradation was carried out under varying pH. When the degradation was monitored under acidic pH, no significant variation in the removal efficiency was noted. However, at alkaline pH, this method becomes less effective. Similar experiments were carried out with the addition of sulfite ion. It is found that removal efficiency was almost similar to control experiment under neutral pH condition. A higher degradation efficiency of 29% was observed under acidic pH. Highly significant variation of perchlorate degradation is shown ($p = 0.01$) when reaction was carried out in the presence of sulfite under varying pH. The observed results are also similar to the previous reports for the organic contaminants (Nejumal et al. 2014).

The pH-dependent degradation of pollutants in sonolysis could be explained mainly based on their capacity to move toward the highly reactive liquid–gas interface of the cavitating bubble. Since the pKa value of perchloric acid is highly negative, most of the pollutants lie in the liquid region of the bubble, where only OH radical persists as the major species. Due to the strong acidic nature of perchlorate, the above condition will not be changed by varying the initial pH. Therefore, the difference in the degradation could not be explained based on structural changes. However, this could be explained based on the surface charge on the interface of the bubble. It is reported that acidic pH results in the formation of more protonium ions (H_3O^+) in the solution. These charged ions were enriched in the liquid–gas interface of the cavitating bubble. This generates more positive bubbles as reported earlier (Pegram and Record 2006). Perchlorate ions are more negatively charge and will have more affinity toward the positively charged region (Pegram and Record 2006). This region is more susceptible for thermal degradation. This is therefore reflected in the degradation efficiency. On the other hand, at alkaline pH, the bubbles become negatively charged and therefore perchlorate is fully detached and lies far away from the interface region, where only hydroxyl radical is present. Also, the negatively charged bubbles repel from each other and cannot grow by bubble coalescence. This makes an inefficient cavitation process. This might cause lower removal efficiency at higher pH.

The synergistic effect of ultrasound and sulfite ions will generate other reactive species such as sulfur dioxide radical, sulfite radicals and hydrated electrons in the medium. These species can easily react with perchlorate than usual hydroxyl radical.

3.6 Fenton-type ($Fe^{2+}/S_2O_8^{2-}$) reaction

$Fe^{2+}/S_2O_8^{2-}$ is an alternative to the Fe2 +/H_2O_2 process, because of the stability of persulfate. This process generates sulfate radical anion by the reaction 4, which is a strong one electron oxidant. In order to check the removal efficiency of this process, experiment has been performed

with different PS and Fe concentrations (2, 3 and 5 ppm) and also by varying the initial pH (3, 7 and 11). All the observed results are presented in Table 3. It is found that only 10% of the perchlorate removal was observed at neutral pH of 7 when the Fe^{2+} and PS concentrations were 1 ppm and 3 ppm, respectively. However, it gets enhanced when the Fe^{2+} concentration was increased to 2 ppm, but further changes in the oxidant concentration decreased the removal efficiency to 9%. The degradation rate shows highly significant variation ($p = 0.01$) when perchlorate was reacted with persulfate and iron at different pH. In this case, a maximum removal efficiency of 35% was observed at acidic pH of 3.

For the effective generation of radical, our system requires more persulfate ion (Eq. 6). At lower concentration of PS, the reaction will generate fewer amounts of reactive species. This is clear from the lower removal efficiency at lower persulfate concentration. However, when the PS concentration is increased, the reaction produces abundant of reactive species for the removal of perchlorate. Moreover, beyond the optimized oxidant concentration level self-scavenging of the ROS by sulfate radical is possible. This might cause a reduction in the removal efficiency.

$$ClO_4^- + SO_4^{\cdot -} \rightarrow ClO_4 \quad (6)$$

As in the case of other Fenton reaction, the generation of radicals is more prominent under acidic condition. At acidic pH, the dissociation of persulfate is feasible and it can easily react with Fe^{2+} for the generation of sulfate radicals. When the pH is increased from acidic to neutral pH value, hydrolysis of Fe^{2+} may reduce their reactivity toward the persulfate. At alkaline pH, the precipitation of hydroxides occurs and results in the deactivation of persulfate ion (Eqs. 7–9). Thus, the generation of reactive species is limited. In addition, the generated sulfate radical could be converted into hydroxyl radical (which is not much affecting the degradation of perchlorate) by Eq. 10.

Table 3 Experimental conditions and perchlorate reduction percentage using Fenton-type reaction: [(experimental condition ClO_4^-] = 5 ppm, and total time; 5 h)

$[Fe^{2+}]$, ppm	$[S_2O_8^{2-}]$, ppm	pH	Perchlorate reduction (%)
1	3	3	25.5
1	3	7	9.9
1	3	11	14.6
2	3	3	32.2
2	3	7	19.0
2	3	11	4.6
3	5		

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3(s)} + 3H^+ \quad (7)$$

$$Fe(OH)_{3(s)} \rightarrow FeOOH_{(s)} + H_2O \quad (8)$$

$$FeOOH_{(s)} + SO_4^{2-} + 2H_2O \rightarrow FeSO_4 + 2OH^- + 1/2\ H_2 + 1/2\ O_2 \quad (9)$$

$$SO_4^{\cdot -} + -OH \rightarrow {}^{\cdot}OH + SO_4^{2-} \quad (10)$$

Screening experiments using ARPs for perchlorate remediation have been reported recently (Vellanki et al. 2013). Negligible removal (0–10%) of perchlorate was observed using UV and sonolysis involving sulfite and ferrous as reducing agents. The present study also confirmed the fact that UV removal of perchlorate is only negligible (maximum 10.7%). However, combination of ultrasound and sulfite gave 28.8% removal. Fenton-type reaction has shown maximum degradation (32.2%) when ferrous and persulfate combinations were used as reducing agents. It is a well-known factor that the production of hydroxyl radicals is higher in acidic conditions. However, in alkaline condition the sulfate radicals react easily with the hydroxyl radicals produced in the system. This phenomenon reduced its lifetime in the system. Therefore, the degradation also gets reduced. In addition, it was found that the oxidation potential of hydroxyl radical is more in acidic medium compared to the alkaline conditions (Nejumal et al. 2014).

Pilot-scale bioreactors were able to remove perchlorate to a quantity below 4 ppb levels after 106 days(Evans et al. 2002). It requires reduction of dissolved oxygen, nitrate and addition of acetic acid and ammonium phosphate (anaerobic biological perchlorate reduction). Perchlorate and chlorate in raw waste water and creek water were completely reduced using microbes in 4–7 days and 8–29 days. But substrates like acetate, lactate, citric acid or molasses need to be added (Wu et al. 2001). Aerobic conditions reduce the effectiveness of ARPs (Vellanki et al. 2013). Also, at room temperature perchlorate degrades very slowly. This may be one of the reasons for the low removal of perchlorate. The use of strong reducing agents that do not contaminate drinking water and their best suiting degradation techniques at various conditions (pH, concentration etc.) need to be found out for complete degradation of perchlorate.

4 Conclusion

Perchlorate contamination is widespread in the drinking water systems. Perchlorate in drinking water exceeded in many sites, more than the permissible limits. Continuous usage of this contaminated water, without proper treatment,

can result in thyroid disorders. Suitable and efficient remediation techniques are need of the hour. Screening experiments using ARPs for perchlorate remediation point out that there is a possibility of complete degradation of perchlorate from environmental matrices. Further research is needed to find out the apt method of AOP and its corresponding best suitable reducing agents. Compared with other methods employed, ARPs are not time-consuming; the present study also confirms the fact. The present study indicated that the combination of ARPs and AOPs with other conventional methods could be a better option for the removal of perchlorate from water.

Acknowledgements Authors acknowledge the financial support from Department of Environment and Climate Change, Govt. of Kerala through a major project. The financial support from DST-FIST and DST-PURSE, Government of India, for developing instrumental facility is gratefully acknowledged. First author also acknowledges the Junior and Senior Research Fellowship from UGC, Govt. of India.

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