DISTRIBUTION PATTERN OF NITRATE AND FLUORIDE IN SHALLOW DOMESTIC GROUNDWATER WELLS IN NORTHERN PARTS OF KELANTAN, MALAYSIA

Kishan Raj Pillai a/l Mathialagan, Mohammad Muqtada Ali Khan*,Hafzan Eva Mansor
Department of Geoscience, Faculty of Earth Science, Universiti Malaysia Kelantan, Campus Jeli,
Locked Bag No. 100, 17600 Jeli, Kelantan, Malaysia
*For correspondence; Tel. + (60) 099477155, E-mail: muqtadakhan@gmail.com

ABSTRACT: *The present study deals with the distribution of nitrate and fluoride ion concentration in shallow domestic supply of groundwater wells in parts of Kelantan, Malaysia. Groundwater consumption is essential in sustaining commercial and economic activities. Groundwater is widely regarded as one of the major sources of supply for domestic and agricultural practices. For the present investigation, twenty nine groundwater samples and three surface water samples were collected during year 2015-2016. Efforts have been made to demarcate potential origins of nitrate ion and fluoride ion in groundwater. The results were also compared with the World Health Organization (WHO) and Ministry of Health (MOH) guidelines. From the analysis, it can be inferred that the majority of groundwater samples assimilate low to moderate nitrate ion and fluoride ion concentration. Though, in one groundwater samples in location P4, the concentration of nitrate ion rises close to the permissible limit of WHO and MOH guideline. The major sources of nitrate ion in shallow domestic bores and wells are identified from zones which practice high fertilizer applications, improper sewages discharged and areas with poor management of livestock waste dumping. Increased nitrate concentrations in groundwater may indicate to several complications in a soil structues for instances, loss of fertility in the soil layers, consequently resulting in eutrophication when the groundwater discharges into surface water. Solutions for these problems include appropriate placement of groundwater wells in relation to septic tanks and piping as well as treatment of drinking water. Proper movements such as regulating contaminants or point sources with a suitable and cost-effective process such as de-nitrification method are capable in re-establishing the water quality in a particular area. Besides, strict regulation should also be brought to conserve the class of groundwater by penalizing the violators.*

Keywords: Groundwater, Nitrate, Fluoride, Assessment, Parts of Kelantan, Malaysia

1. INTRODUCTION

Availability and ease of use to a reliable and consistent source of fresh water supply such as surface water and groundwater is vital in developing a sustainable growth either commercially and other daily practices [1]. Groundwater resources in Malaysia are significant reserves that can backup and act as supplement for the growing demand of fresh water for much consumption [2,3]. Understanding the chemistry of groundwater is crucial as these resources are primarily controlled by geogenic as well as anthropogenic factors [4]. Nevertheless, groundwater is predominantly contaminated by the process of industrial development and suburbanization that has gradually advanced over time without any concern for the environmental consequences [5]. These comprise of point bases, including industrial pollutants, excess disposal amenities, wastewater management mechanism, cemeteries, and others as well [6]. Overload intake of these major ions via drinking water might possibly cause health setback on human beings in many rural areas [7]. This study is conducted with objective of evaluating the sources of physicochemical parameters including the concentration of nitrate ion and fluoride ion and their existing level in groundwater in northern parts of Kelantan state in Malaysia. The population growth rapidly rises across the nation which impacts more pressure on food sector, primarily agricultural sector to fulfill the demand of food stock and supply for the population [1,2]. Eventually the increased agricultural sector demands more resources, including a quality supply of freshwater for irrigation as well as increased land use for crop plantation [8]. Groundwater resources iareone of the alternate and major sources of fresh water supply primarily used for agricultural, drinking and irrigation purposes as well [5]. High values of nitrate and fluoride ion in drinking water possibly indicates contamination of these point sources from the well [7]. Nitrate concentrations in the subsurface aquifer system primarily depend on anthropogenic impacts such as wide spread application of fertilizers and compost near to the shallow aquifer system [9]. Nominal aspects such as placement and depth of well near to point sources, nature of underlying soil structures and chemical classification of rainwater infiltrating down into the underlying water table also influences the nitrate presence in groundwater [4,10]. High concentrations of nitrate in drinking water may impact the health system in human population as such that it can lead to various blood defects such as methaemoglobinaemia [7]. This disease leads to abnormal production of red blood cell in the blood system constraining the oxygen passage throughout the body cells. Fluoride concentrations in groundwater generally occurs from natural causes such as weathering process of fluoride bearing rocks which seeps and percolates in to the underlying aquifers body [11]. Besides, anthropogenic causes such as chemical discharges from industrial activities and regular emissions may also contribute to elevated concentrations of fluoride in groundwater [6-11]. Adequate levels of fluoride in drinking water are beneficial to health as it inhibits problem related to tooth such as preventing tooth decay particularly in children and elders. However, elevated levels of fluoride intake can also lead to several defects and most importantly conditions known as enamel fluorosis. The maximum permissible limit of fluoride in drinking water is not exceeding 1.5 mg/l. There are few standards that should be complied by this water in order to be approved and supplied to the citizens. This water must meet physicochemical parameters as well as proper amount of ion concentration and in turn supplied to citizens through a safe distribution system in adequate quantity and pressure. A proper water quality standard is standard issued by the related organization that serves as reference for the adequate concentration of ion in water so that it will be safe to be used as drinking water and other domestic purposes. The World Health Organization, (W.H.O) have emphasized on the necessity for conserving groundwater quality standards by serving guidelines for drinking water quality parameters as well as to emphasis on public health awareness [12].

2. STUDY AREA

The study area chosen for water sampling purposes is situated towards the northern part of Kelantan state in Malaysia which covers an area approximately 1400 km^2. The study area lies between latitudes 5˚ 55" and 6˚ 15” north and between longitudes of 102˚ 4” and 102˚ 25” east. The complete base map of the present-day study area with water sampling locations is presented in figure (1). The Kelantan plain is covered with Quaternary sediments with granitic bedrock underlying the plain. The sediments from the quaternary comprises of marine, fluviatile and other deposits observed in main rivers and coastal region. Most of the villagers in rural areas are using groundwater as the main source of water for domestic purposes such as for drinking water, agricultural uses as well as economic purposes. Almost all of the residential in the purported study area are fitted out with borehole and pump to benefit in groundwater withdrawal purposes as groundwater is generally consumed for domestic purposes for instance for drinking water, agricultural practices as well as commercial purposes. The typical weather of the desired study area experienced typically tropical rainforest weather conditions including wet and dry seasons during the course of the year. Equally, the northeast monsoons and southwest monsoon increases the annual rainfall activities in the study area. Heavy rains are time and again related with rainstorms and downpours, which normally take place for the period of the northeast monsoon. The landscape is greatly influenced by Kelantan River which supplies the needed water to the agricultural plantation and for domestic uses as well [13]. The topography of the study area is mostly flat and hilly surfaces but not too high. Most of the lands are used for the purpose of plantation as it provides the main economic contribution for the community there. Other than that the mountain elevation specifically in Tanah Merah are not so high. Kelantan Mountain is part of granite intrusion [14]. Geologically, the tectonic setting is embraced from Main Range, with an assortment of granitic rocks, comprising quartz, feldspars in several different proportions with hornblende and biotite minerals as the combined minerals [15].

3. MATERIALS AND METHOD

Based from this study, twenty nine representative groundwater locations were selected for sampling. The sampling location for the groundwater analysis is conducted in a manner as the locations are uniformly distributed over the entire box of study. Three surface water samples are taken from the study area. In situ parameter measurement such as electrical conductivity, temperature, total dissolved solids and pH are determined and recorded in the field using potable water analysis kit. The collected groundwater samples is then preserved at lower temperature, preferably at 4 °C.

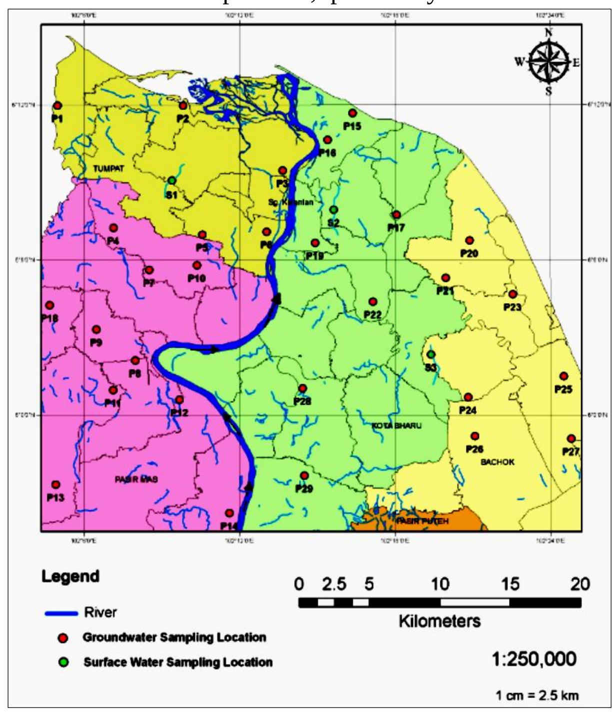

Fig (1) Sampling location in northern parts of Kelantan State, Malaysia

It is then transported into the laboratory for laboratory analysis. Chemical parameter is governed by means of the standard procedures suggested in American Public Health Association [16]. For anion concentration, nitrate ions were determined by colorimetric method using nitrate reagent while fluoride ions is determined using SPADNS reagent solutions using colorimeter DR900 respectively.

4. RESULTS AND DISCUSSION

The results obtained are tabulated in table (1) for in-situ parameter measurement and table (2) for hydro chemical parameters of nitrate and fluoride ion respectively. The data are then compared with the range of standard drinking guidelines of W.H.O and M.O.H for each anion respectively.

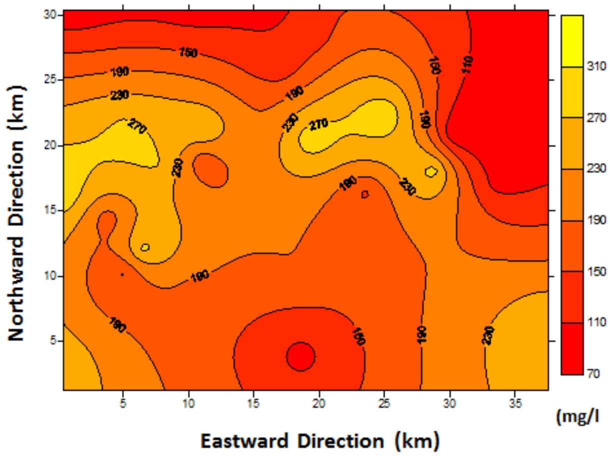

Fig (2) TDS distribution in the study area.

Tab (1) In-situ parameters of groundwater and surface water samples collected in northern parts of Kelantan State, Malaysia

No.	pH	Temperature (°C)	Electrical Conductivity (ųS cm^{-1})	TDS (mg/l)
P1	6.38	28.4	139.83	75.86
P2	6.34	27.6	149.57	87.35
P3	6.79	32.1	94.43	123.60
P4	6.93	29.1	174.69	275.98
P5	7.39	25.3	95.48	265.63
P6	7.32	29.7	79.29	196.45
P7	6.46	27.6	98.29	274.59
P8	6.23	28.9	92.70	280.43
P9	6.45	30.9	149.59	168.86
P10	6.02	26.9	194.59	163.57
P11	6.32	32.7	138.38	146.97
P12	7.29	29.5	157.58	186.65
P13	7.10	29.9	134.56	257.85
P14	5.93	30.7	147.46	157.97
P15	5.95	31.8	175.57	156.76
P16	5.91	32.2	134.78	143.76
P17	6.57	30.1	186.43	297.86
P18	6.98	31.2	249.38	304.35
P19	6.03	29.6	175.76	296.54
P20	5.83	30.9	116.60	73.34
P21	6.64	29.0	138.80	284.37
P22	5.69	26.9	198.50	143.49
P23	6.38	27.5	153.79	99.38
P24	6.63	31.2	86.97	197.75
P25	6.92	30.2	96.54	193.45
P26	6.75	31.8	85.46	214.45
P27	6.37	32.0	135.45	267.45
P28	6.28	28.9	157.87	187.87
P29	6.29	29.7	255.86	96.56
S1	6.42	31.5	294.57	74.74
S2	6.68	31.3	197.57	178.76
S3	4.61	27.8	85.59	50.39

*P=Groundwater samples
*S=Surface water samples

Tab (2) Nitrate and fluoride concentrations in the groundwater and surface water samples

No.	NO_3^- (mg/l)	F^- (mg/l)
P1	4.60	0.26
P2	3.90	0.23
P3	6.40	0.38
P4	9.60	0.37
P5	3.90	0.29
P6	3.40	0.30
P7	4.20	0.21
P8	2.30	0.39
P9	1.20	0.20
P10	3.20	0.30
P11	2.30	0.20
P12	4.20	0.20
P13	3.40	0.29
P14	5.30	0.24
P15	3.10	0.23
P16	5.20	0.31
P17	3.90	0.26
P18	4.70	0.24
P19	5.10	0.39
P20	4.80	0.25
P21	4.40	0.31
P22	3.50	0.30
P23	5.70	0.21
P24	3.40	0.23
P25	1.40	0.29
P26	3.50	0.24
P27	5.30	0.36
P28	2.70	0.38
P29	6.61	0.33
S1	5.80	0.25
S2	4.20	0.33
S3	5.20	0.23

*P=Groundwater samples
*S=Surface water samples

The TDS concentration in the study area ranges from 50.39 mg/l to 304.35 mg/l. The highest permissible limit of TDS is 1000 mg/l. The TDS distribution patterns are depicted in figure (2). From the analysis, it can be inferred that TDS concentration in groundwater is not in serious state and are low in terms of total solid content suggesting low or minor presence of suspension or impurities in the groundwater resource. The concentrations of nitrate in drinking water supply conveyed from surface water usually does not exceed 10 mg/l, though nitrate levels in groundwater time and again exceed 50 mg/l, the nitrate levels are usually lower [17]. From the result that is obtained, nitrate ion concentration in the study area ranges from 1.20 mg/l to 9.60 mg/l. Unpolluted natural water commonly comprises barely little quantities of nitrate [8-11]. Figure (3) shows the distribution patterns of nitrate ion in the study area. Based on the observed patterns, it can be inferred that majority of the area are covered by nitrate concentrations in the range from 1mg/l to 5 mg/l. Other than that, high nitrate values are observed in the north western part of the study area of up to 9 mg/l as denoted by the bright spot. Nitrate ion concentration in certain part of the study area may perhaps rise due to presence of overload fertilizer or compost which is gradually applied in agrarian activities [4,5]. High nitrate concentration may attribute to consequence of lower temperatures, conceivably owing to augmented evapotranspiration for the period of post monsoon [18]. From the study area, it can be observed that the temperature is high with maximum temperature recorded of 32.7˚C. Thus, based on the previous explanation, the high temperatures recorded in the study area can be attributed with lower concentrations of nitrate possibly due to prominent process of evapotranspiration in the groundwater system. Nitrate absorptions in groundwater can be a thoughtful concern as it might characterize a loss of potency from overlying topsoil, consequential in eutrophication [1,7]. Shallow water table or unconfined aquifers are more prone to contamination from chemical effluents or discharges and seepages attributed from agricultural practices such as chemical fertilizers, nitrogenous based compounds and toxic pesticides, improper placement and passage of on-site sanitation and sewerage and chemical industrial effluents [8-11]. The acceptance level of nitrate in drinking water supply is shown in table (3).

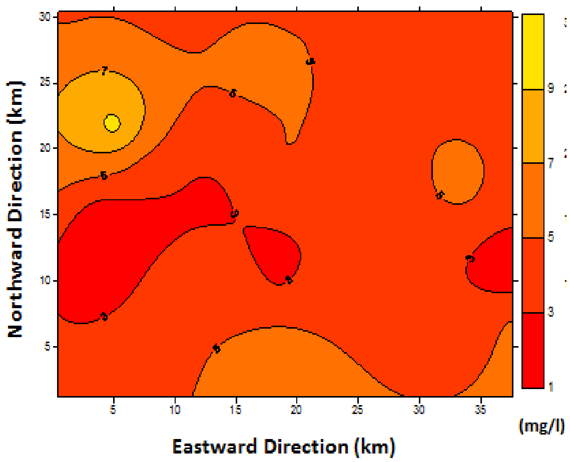

Fig (3) Nitrate, NO_3^- ion distribution in the study area.

Tab (3) Classification of nitrate ion in groundwater based on the W.H.O. and M.O.H suitability for drinking purpose [12,13]

Ion	Rank	Criteria (mg/l)	Remarks
Nitrate, NO_3^-	1	<10	Acceptable by WHO & MOH
	2	10-50	Only acceptable by WHO
	3	50-100	Rejected
	4	100-500	Rejected
	5	>500	Rejected

The primary source of fluoride ion in drinking water supply is often attributed from naturally occurring basis. A fluoride rich mineral comprises of fluorite, apatite, mica, amphiboles, as well as clay [20]. Fluoride ions can also be released into the surrounding environment from assorted minerals such as phosphate-containing rock which is widely exploited to produce phosphate based fertilizers and other related chemicals [16]. Figure (4) illustrates the concentration of fluoride ion in the study area ranges from 0.20 mg/l to 0.39 mg/l. The permissible limit of fluoride ion in drinking water is 1.5 mg/L by W.H.O as shown in table (4). The fluoride concentrations in the study area are rather low compared to the permissible limit. Thus it can be inferred that groundwater in the preferred study area is not contaminated from elevated concentrations of fluoride. Higher concentrations of fluoride may leads to several conditions including dental effects such as enamel fluorosis and also impact the bone structures through skeletal fluorosis. Based on the distribution plot, it can be noticed that high fluoride concentrations are observed in the middle sector of the study area.

Tab (4) Classification of fluoride ion in groundwater based on the W.H.O. and M.O.H suitability for drinking purpose [12,13]

Ion	Rank	Criteria (mg/l)	Remarks
Fluoride, F^-	1	<1	Acceptable by WHO & MOH
	2	1.01-1.5	Acceptable by WHO & MOH
	3	1.51-2.00	Rejected
	4	2.01-3.00	Rejected
	5	3.00>	Rejected

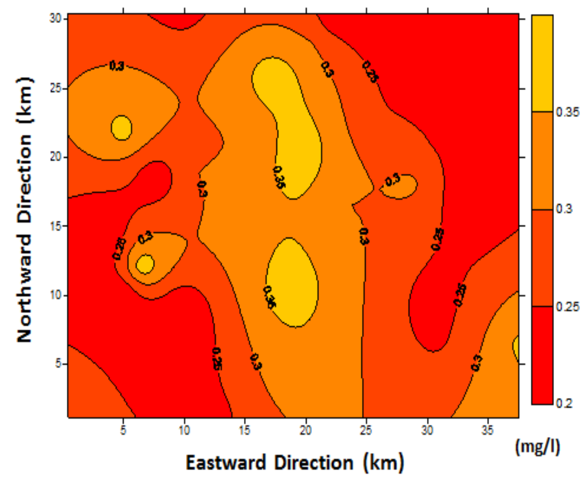

Fig (4) Fluoride, F^- ion distribution in the study area.

5. CONCLUSIONS

The concentration of the nitrate and fluoride ions in the water samples in the northern part of Kelantan state are assessed to be lower the permitted limit established by the World Health Organization (WHO) and Ministry of Health (MOH). Nonetheless, few districts covering domestic shallow wells is considerably approaching the standard limit of drinking water guidelines set by the local authorities and given these wells could become polluted, given few years' time. Subsequently, these shallow domestic wells may perhaps results in health complications if the groundwater extracted from the aquifer in that particular region is used for domestic purposes such as for drinking purposes and other domestic purposes as well. The application of groundwater as one of the main domestic water supply in Kelantan is crucial. Thus an improved understanding of the influence of bacteriological and biochemical impurities in water source are very much needed for the inclusion of comprehensive Water Quality Index (WQI), inclusive Water Safety Plan (WSP) and Quantitative Microbial Risk Assessment (QMRA) approaches [21]. Proper placement of groundwater wells near to residential area could prevent the groundwater from being polluted. The wells for example, should be located a specified distance from agricultural area such as paddy field or in these research case, rubber plantation to avoid the aquifer from being polluted by pesticides and other chemical substances used in agricultural field [18-21]. Avoiding pesticide pollution of groundwater is fairly simple. Regions where recharge areas are recognized and identified should not be contaminated with the application of pesticides. Thus, the key principals to approach and address these impending problems are mainly attributed to prevention of contaminants from reaching the recharge mechanism of an aquifer is by practicing a proper and safe routine of groundwater maintenance and its development. Related organizations and other quality departments should also constantly update the risk assessment of fluoride such as incorporating key information and related data to better estimate the level of exposure of certain levels of fluoride in health system. This information should be made available to the public as it can develop an understanding among the communities regarding the fluoride benefits as well as its impacts in elevated levels. Other than that, a profound research and investigation of groundwater quality assessment integrating systematic tools including stable isotope of water analysis and subsurface modeling of underlying aquifers should also be conducted by the responsible authorities so as to monitor the level of contamination of groundwater in the aquifer.

6. ACKNOWLEDGEMENT

The financial assistance received from Fundamental research Grant (R/FRGS/A08.00/00644A/002/2015/000228) is highly acknowledged. The authors are also grateful to faculty of Earth Science, Universiti Malaysia Kelantan, Campus Jeli, for endowing with basic facilities to carry out the present investigation.

7. REFERENCES

[1] Mishima, Y., Takada, M. and Kitagawa, R., “Evaluation of intrinsic vulnerability to nitrate contamination of groundwater: Appropriate fertilizer application management” *Environmental Earth Sciences*, **63**: 571-580(2011).

[2] Arumugam, K. and Elangovan, K., “Hydro chemical characteristics and groundwater quality assessment in Tirupur Region, Coimbatore District, Tamil Nadu, India” *Environmental Geology*, **58**: 509-1520(2009).

[3] Mohammed, A. F., Yaacob, W. Z. W., Taha, M. R. and Samsudin, A. R., “Groundwater and soil vulnerability in the Langat Basin Malaysia” *European Journal of Scientific Research*, **27**(4): 628-635(2009).

[4] Cheong, J., Hamm, S., Lee, J., Lee, K. and Woo, N., “Groundwater nitrate contamination and risk assessment in an agricultural area, South Korea” *Environmental Earth Sciences*, **66**(4): 1127-1136(2011).

[5] Longe, E. O. and Balogun, M. R., “groundwater quality assessments near a municipal landfill, Lagos, Nigeria” *Research Journal of Applied Sciences, Engineering and Technology*, **2**(1): 39-44(2010).

[6] Amoako, J., Karikari, A. Y. and Ansa-Asare O. D., “Physico-chemical quality of boreholes in Densu Basin of Ghana” *Applied Water Science*, **1**: 41-48(2011).

[7] Mondal, N. C., Saxena, V. K. and Singh, V. S., “Occurrence of elevated nitrate in groundwaters of Krishna delta, India” *Afr J Environ Sci Technol*, **2**(9): 265-271(2008).

[8] Chen, S., Wu, W., Hu, K. and Li, W., “The effects of land use change and irrigation water resource on nitrate contamination in shallow groundwater at county scale” *Ecological Complexity*, **7**(2): 131-138(2010).

[9] Agarwal, R., “Nitrate contamination in ground water samples of Gangapur city town (Sawai Madhopur District) Rajasthan” *Journal of Chemical, Biological and Physical Sciences*, **2**(1): 511-513(2012).

[10] Igbinosa, E. O. and Okoh, A. I., “Impact of discharge wastewater effluents on the physic-chemical qualities of a receiving watershed in a typical rural community” *International Journal of Environmental Science and Technology*, **6**(2): 1735-1742(2009).

[11] Elango, L., Kannan, R. and Kumar, M. S., “Major ion chemistry and identification of hydro geochemical processes of groundwater in a part of Kancheepuram district, Tamil Nadu, India” *Environmental. Geosciences*, **10**(4): 157-166(2003).

[12] World Health Organization (WHO), “Drinking Water Quality: Third Edition incorporating the First and Second Agenda, Recommendations. Geneva, **1**(2008).

[13] Ministry of Health Malaysia (MOH). “National standard for drinking water quality: First Edition” *Malaysia’s Health*. Kuala Lumpur, Malaysia, 89-96(2008).

[14] Jasir, B. and Ali, C. A., “Lower Permian radiolarian from the Pos Blau area, Ulu Kelantan, Malaysia” *Journal of Asian Earth Sciences*, **15**(4): 327-339(1997).

[15] Tjia, H. D. and Almashoor, S. S., “The Bentong suture in southwest Kelantan, Peninsular Malaysia” *Bulletin of Geological Society of Malaysia*, **39**: 195-211(1996).

[16] Rajmohan, N. and Elango, L., “Identification and evolution of hydro geochemical processes in the groundwater environment in an area of the Palar and Cheyyar River Basins, Southern India” *Environmental Geology*, **46**: 47-61(2004).

[17] APHA., “Standard methods for estimation of water and waste water” *American Public Health Association*, Washington, DC, **19**(1995).

[18] Nolan, B. T., “Relating nitrogen sources and aquifer susceptibility of nitrate in shallow ground waters of the United States” *Ground Water*, **39**: 290-299(2001).

[19] Wick, K., Heumesser, C. and Schmid, E., “Groundwater nitrate contamination: Factors and indicators” *Journal of Environmental Management*, **111**(30): 178-186(2012).

[20] Kumar, P. J. S., "Assessment of fluoride contamination in groundwater as precursor for electro coagulation" *Bulletin of Environmental Contamination and Toxicology*, **1**(2): 8-12(2012).

[21] Asadi, A., Huat, B. B. K., Hanafi, M. M., Mohamed, T. A. and Shariatmadari, N., "Physicochemical sensitivities of tropical peat to electro kinetic environment" *Geosciences Journal*, **14**(1): 67-75(2010).

*For correspondence; Tel. + (60) 099477155,
E-mail:muqtadakhan@gmail.com