Biological Forum – An International Journal **7**(2): 29-35(2015)

ISSN No. (Print): 0975-1130
ISSN No. (Online): 2249-3239

Risk of Groundwater Contamination by Commonly used Fertilizers

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(Received 12 May, 2015, Accepted 15 June, 2015)
(Published by Research Trend, Website: www.researchtrend.net)

ABSTRACT: The risk of groundwater contamination by nitrate, a representative of commonly used fertilizers, was studied. Simple lysimeter experiments were conducted using sand, loam, clay and peat representing soils with varying drainage characteristics andorganic matter contents.Nitrate was introduced on the soil surface in its pellet form (pellet method) and also in water solution (liquid method) representing the different methods of fertilizer application. Rainfall was simulated until nitrate concentration in the effluent was negligible. Results obtained show that the sorption of nitrate by the soils was in the order of peat>clay>loam>sand while the transport of nitrate through the soils was in the order of sand>loam>clay>peat. Both the sorption coefficients and retardation factor of the soils were in the order of peat (0.46 and 1.88L/kg)>clay (0.26 and 1.56L/kg)>loam (0.07 and 1.19L/kg)>sand (0.02 and 1.09L/kg) for the liquid method, and clay (0.32 and 1.70L/kg)>loam (0.19 and 1.53L/kg)>sand (0.09 and 1.38L/kg) for the pellet method. This implies that the application of fertilizer in sand could result in greater risk of groundwater contamination than in the other soils. It also implies that groundwater contamination risk would be higher with the use of fertilizer solution. Therefore, to successfully reduce the risk of groundwater contamination by nitratewhilst still enjoying the advantage of fertilizer usage, this study suggests the use of fertilizers in appropriate quantity and in grain form known as topdressing.

Keywords: Groundwater contamination; Fertilizer; Nitrate; Lysimeter experiment; Transport; Sorption.

INTRODUCTION

Groundwater contamination is one of the biggest environmental problems, and nitrate from fertilizers is among the most common and widespread contaminants in groundwater (Zhang *et al.,* 1996; Canter, 1997). Fertilizer application in soils has become a common practice due to soil infertility and increase in population. Groundwater is a major source of drinking water and when contaminated with nitrate might be unsuitable for drinking. The short term health effect of having excessive nitrate in drinking water is the occurrence of methemoglobinemia, also known as blue baby syndrome, which is a blood disorder that prevents the blood from delivering oxygen effectively to different parts of the body, especially in infants (Spalding and Exner, 1993; Canter, 1997; NECI, 2000). On the long term, excess nitrate has the potential to result in increased starchy deposits and hemorrhaging of the spleen. A potential cancer risk from nitrate in water and food has been reported (US EPA, 2001). Several epidemiologic studies have linked birth defects to exposure to nitrates in drinking water (Cedergren *et al.,* 2002; Croen *et al.,* 2001, US EPA, 1991). Furthermore, it has been suggested that there may be an increased risk of non-Hodgkin's lymphoma associated with long-term consumption of water containing nitrate concentrations greater than 4 mg/L (Ward *et al.,* 1996). More so, higher doses of nitrate have been found to have adverse reproductive effects on animals (Manassaram *et al.,* 2005). Therefore, it is important to monitor and curtail groundwater contamination by nitrate from commonly used fertilizers.

The provision of safe water and stable food supplyare essential for mankind. The increase in the world population has led to improvement in agricultural practices, including fertilizer application. Particularly, chemical fertilizers have played a major role in the increase of cereal production and their world consumption has increased as much as 7.4 times since 1961 (Brown, 1999). Fertilizer use has increased exponentially and over one-half of all fertilizer produced has been utilised since 1984 (Vitousek *et al.,* 2001). Developing nations now consume more than 63% of the nitrogen fertilizer produced globally (Vitousek *et al.,* 2001). This has allowed regions with naturally low soil fertility to be developed as productive areas of agricultural importance (Smil, 1997). A number of land-scarce countries with high population density depend on fertilizer for their very existence. As they exhaust new areas to cultivate, and as traditional agricultural practices reach their limits, people in these countries must turn to ever greater applications of fertilizer.

Currently, over one-third of the earth's land surfaces are devoted to agriculture and it is estimated that more than 90% of that land relies heavily on fertilizer application (Smil, 1997). Over 80 Tg of fertilizers are applied globally each year. Using recent rates of increase, various sources have estimated that fertilizer application will exceed 134 Tg per year by 2020 (Zhang *et al.*, 1996; World Resource Institute, 1999).

The problem with fertilizer lies not in application but in over-application (Spalding and Exner, 1993). Comparatively low cost coupled with a demand for high crop yields often encourages overuse. When fertilizer application exceeds plant demand and the denitrification capacity of the soil, fertilizer can leach to groundwater, usually as nitrate, a highly mobile form with little sorption. Conservative estimates show that between two-thirds to one-half of every metric ton of fertilizer applied is never incorporated into plant tissue (Vroomen and Taylor, 1992). Accordingly, excessive application of fertilizers was reported to cause groundwater contamination by nitrate (Vroomen and Taylor, 1992; Zhang *et al.*, 1996). Once in groundwater, nitrate can persist for decades and deteriorates the water quality inducing economic and ecological problems (Bernard *et al.*, 1998). It has been noted that fertilizer management is a factor in reducing non-point source contamination of groundwater (Gross *et al.*, 1990). Therefore, proper measures must be adopted to strike a balance in the use of fertilizer to achieve food demand while avoiding imperilling the major drinking water resource.

Nitrate is the most ubiquitous of groundwater contaminants, since its chemical composition allows it to readily travel with surface runoff and penetrate groundwater resources (Canter *et al.*, 1987). It may leach through the soil when accompanied by excess water from either irrigation or rainfall. Nitrate readily dissolves and moves with water and is not held on soil particles. Therefore, it is vulnerable to being washed out of the soil and infiltrates to groundwater. High concentrations of nitrate in groundwater are problematic due to the adverse health impacts that are caused by consumption of drinking water containing elevated concentrations of nitrate (Canter, 1997). This is primarily why the United States Environmental Protection Agency established a drinking water standard of 10 mg/L for nitrate, which is easy to exceed if enough attention is not provided when applying fertilizers (Bernard *et al.*, 1998). Physical factors such as soil type, geology and slope of land determine the rate in which the transport of nitrate into groundwater will occur. Human factors and actions that can affect transport of nitrate include irrigation, best management practices, presence of impermeable surfaces, and rates of fertilizer use (Zhang *et al.*, 1996). Nitrate transport in water also depends on geochemical conditions of the water. For instance, when dissolved oxygen is present in groundwater and organic carbon content is low, nitrate is generally stable and therefore persistent in groundwater. The recharge rate of the aquifer further influences nitrate fate in groundwater. For example, nitrate can easily be transported to shallow groundwater in well-drained areas with rapid infiltration and high permeable subsurface materials (Spalding and Exner, 1993). Nitrate concentrations in groundwater may as well fluctuate according to seasonal and annual hydrological conditions. This has prompted environmental concerns with fertilizer use.

This work aims to determine the groundwater contamination potential of nitrate from commonly used fertilizers such as NPK 15:15:15, NPK 20:10:10 and Urea. Simple lysimeter experiments were conducted using sand, loam, clay and peat with varying drainage characteristicsand soil organic matter (SOM). Nitrate was introduced on the soil surface in its pellet form and also in water solution, representing the different methods of fertilizer application. Rainfall was simulated until nitrate was not detected in the effluent sample. Results obtained show that the application of fertilizer in sand could result in greater risk of groundwater contamination than in the other soils, and that groundwater contamination risk is likely to be higher with the use of liquid method of fertilizer application than with the use of pellet method.

MATERIALS AND METHODS

A. Nitrate

Nitrate was used to represent the commonly used fertilizers in this study. This is because fertilizers will always react in the soil to give nitrate (see reaction below). The Nitrate used in this study was purchased from Analar Chemical Company, Nigeria in the form of Potassium Nitrate. Exactly 55 mg/L (0.3g pellet equivalent) of the Potassium Nitrate was prepared from the 500g bulk purchased.

Fertilizer to nitrate reaction

Reaction 1: $R-NH_2+H_2O \rightarrow NH_3+R-OH+$ *Energy (Ammonification)*

Reaction 2:$NH_3+H_2O \rightarrow NH_4^{+}+OH^{-}$ *(Ammonia hydrolysis)*

Reaction 3: $2NH_4 + 3O_2 \rightarrow 2NO_2^{-} + 2H_2O + 4H^{+}$ *(First step nitrification)*

Reaction 4:$2NO_2^{-}+O_2 \rightarrow 2NO_3$ *(Second step of nitrification)*

B. Soil description

The soils used in this study comprised sand, loam, clay and peat, representing varying soil drainage characteristics and organic matter contents. The soil samples were obtained from Port Harcourt Farmlands, within 0 - 30 cm depth which represents the top soils where fertilizer applications occur. All the soil samples were air-dried and then sieved using a 2mm sieve to obtain a uniform particle size and classification of all the soils. Table 1 summarizes the characteristics of the soils used.

Table 1: Soil type and characteristics.

Soil type	**Characteristics**			
	Particle density (g/cm^3)	Bulk density (g/cm^3)	Porosity	SOM (%)
Sand	2.77	1.68	0.40	2
Loam	2.65	1.35	0.49	15
Clay	2.57	1.18	0.54	Not required
Peat	1.44	0.82	0.43	55

C. Experimental setup

Simple lysimeter experiments were performed to investigate the sorption and transport of nitrate, a representative of the commonly used fertilizers such as NPK 20:10:10, NPK 15:15:15 and Urea, in sand, loam, clay and peat. The simple lysimeter used was as designed and reported by Ugwoha (2014) but with few modifications as follows: 11 cm internal diameter by 20 cm height, and constructed with a polyvinyl chloride pipe. A 2 cm depth layer of uncontaminated fine gravels, obtained from Port Harcourt, was placed in the bottom of the simple lysimeter and uniformly levelled. The soils were placed into the simple lysimeter in turns to a height of 15 cm, corresponding to the average depth of 32m unsaturated zone in most Port Harcourt Farmlands. The weights of the 15 cm height of the soils were 1200g, 2400g, 2100g and 1800g for peat, sand, clay and loam, respectively.

The remaining 3 cm void of the simple lysimeter prevented the overflow of accumulated rainfall-simulated water.Water was released on the soil, via the rain simulator, until it was saturated and then allowed for 2 days to attain water content equivalent to field capacity hence imitating soil in a natural environment. Thereafter, 100ml of nitrate, representing 7% volume of soil, was released on the soil as 55 mg/L solution in one experiment, and in another experiment 0.3g nitrate pellet, the equivalent of the 100 ml nitrate, was sprinkled on the soil surface. Afterward, 250 ml water was released to simulate rainfall. The release of 250 ml water continued in batches until the effluent had no trace of a measurable nitrate concentration. Finally, the soil was analysed to know the quantity of nitrate retained (sorption).

D. Sample collection

Before contamination, the soil samples andwater used were analysed for background concentrations of nitrate. After contamination and the first rainfall simulation, the first effluentwas collected. Few hours later after the effluent has stopped dropping, the second rainfall simulation and hence second effluent collection followed. This continued in the same manner until there was no trace of nitrate in the effluent. The 15 cm height of soil was divided into three layers of 5 cm each, and samples of soil collected from the three layers. The effluents and soil samples were analysed.

E. Sample analysis

The effluents and soil samples were analysed using a Genesys 10uv Sample Reader Spectrophotometer. The Genesys 10uv Spectrophotometer consists of a source of uv radiation, wavelength selector (monochromator), sample containers, detector, signal processor and result displaying screen. First, 10 ml sample was placed into a boiling tube in a cool water bath. Then, 2 ml of 30% NaCl, 10 ml of H_2SO_4 solution and 0.5 ml buccinne sulphuric acid reagent were added into the boiling tube. The tube was swirled thoroughly at each addition and allowed to cool. Thereafter, the tube was placed in a well-stirred boiling water bath at temperature of not less than 95^{o}C, and after 20 minutes immersed in a cool water bath to cool to room temperature. Absorbence was measured by the uv-visible spectrophotometer at 470nm using distilled water as blank.

F. Estimation of Water infiltration rate, absorption coefficient and retardation factor

The water infiltration rates (WIRs) in the soils were measured by releasing known volumes of water on the soil surface via the rain simulator and observing how long it took to reach the outlet. The start of drainage at the outlet indicated the time the released water arrived at the bottom of the unsaturated zone. The WIR in the soil was estimated using Eq. [1].Sorption coefficient (K_d) of nitrate was calculatedfrom the measured soil and water (effluent) concentrations using Eq. [2]. Average K_d was used in this work in order to capture the effect of nitrate sorbed between the three soil layers. The retardation factor (R) of nitrate was estimated using Equation [3] (Ugwoha and Andresen, 2014).

$$WIR = \frac{DI}{t} \quad \text{…[1]}$$

$$K_d = \frac{C_s}{C_w} \quad \text{…[2]}$$

$$R = 1 + \left(\frac{\rho}{n}\right) K_d \quad \text{…[3]}$$

Where DI is the distance infiltrated (15 cm), t is the time taken, C_S is the concentration of nitrate in soil (mg/kg), C_W is the concentration of nitrate in water (effluent) (mg/L), ρ is the bulk density of the unsaturated zone material (g/cm), and n is the porosity of the unsaturated zone (dimensionless).

RESULTS AND DISCUSSION

A. Baseline measurements

Table 2 shows the results of the baseline measurements conducted prior to contamination. The baseline concentrationsof nitrate ranged from 0.029 – 0.099 mg/kg for the four soils and 1.500 mg/L for the water, hence cannot affect the main experimental result. Although these concentrations were minimal, they were subtracted from the resultant sample concentrations after the leaching experiment to ensure accuracy. The water infiltration rates of the soils were in the order of sand>loam>clay>peat. This implies that contaminants are likely to behave differently in the different soils. Similarly, the hydraulic conductivities of the soils were in the order of sand>loam>clay>peat, which also infers that the migration of contaminants in the soils will differ.

Table 2: Baseline measurement of experimental materials.

Material	Nitrate concentration (mg/kg)	Water infiltrate rate (cm/m)	Hydraulic conductivity (cm/m)
Sand	0.096	1.5	1.1
Loam	0.029	1.0	0.73
Clay	0.099	0.6	0.44
Peat	0.096	0.5	0.37
Water	1.500 mg/L	-	-

B. Effluent sample analysis (Transport of nitrate)

The transport of nitrate in the various soils after leaching is shown in Fig. 1. Nitrate was released on the soil surface in its original form herein called pellet method and also as a prepared concentrated liquid mixture herein called liquid method.

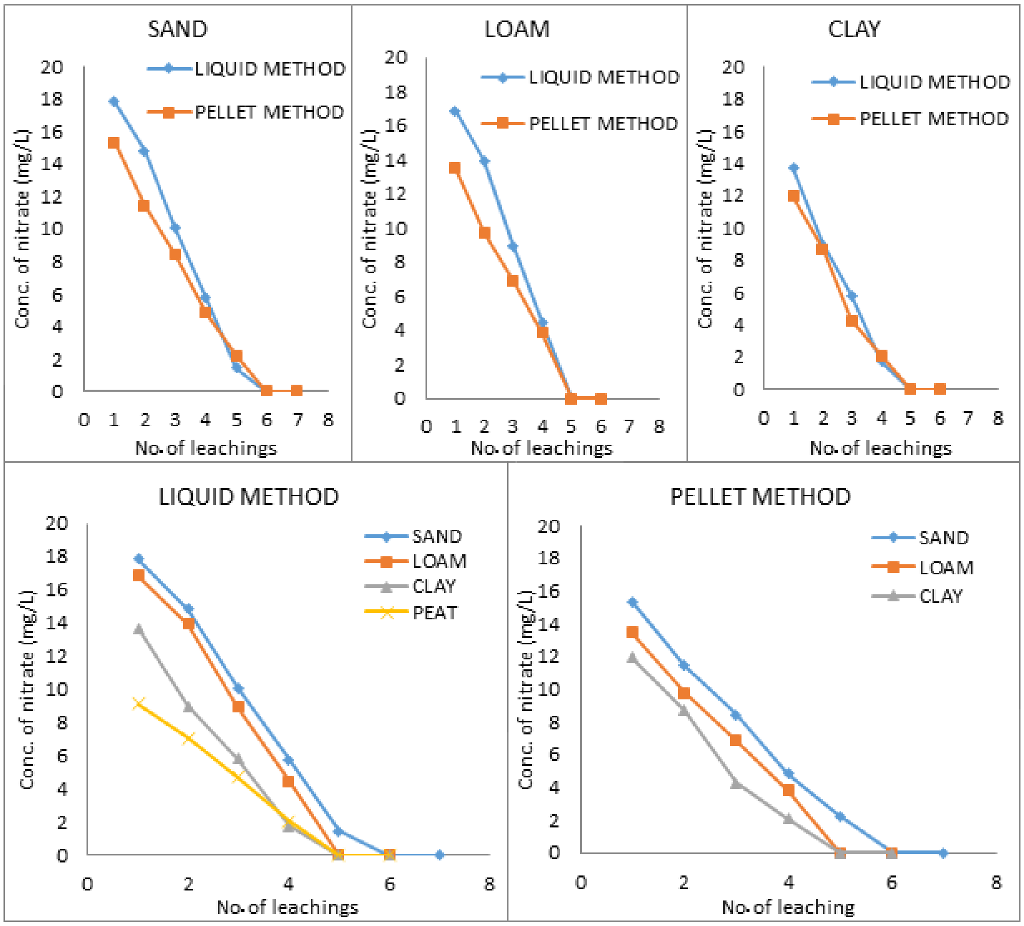

Fig. 1. Transport of nitrate in the unsaturated zone.

Pellet method was not used in peat soil as the peat soil was only used to know the effect of SOM in the transport and sorption of contaminant. Transport of nitrate was greater using liquid method than pellet method in all the soils. Using liquid method, a total of 49.99 mg/L, 44.17 mg/L, 30.24 mg/L and 22.95 mg/L of nitrate leached through sand, loam, clay and peat, respectively whereas a total of 42.32 mg/L, 33.96 mg/L and 26.99 mg/L leached through sand, loam and clay, respectively using pellet method. Soil texture and SOM affected the transport of nitrate through the soils. In both pellet and liquid methods, leaching was in the order of sand>loam>clay. Therefore, application of fertilizers on coarse-textured farmlands will result in fast transport of nitrate to the groundwater. This observation is in agreement with the report from Spalding and Exner (1993) that contamination by fertilizer occurred in the groundwater beneath a well-drained soil. In liquid methods where the effect of SOM was tested, leaching was in the order of sand>loam>clay>peat. Thus, application of fertilizers on SOM-rich farmlands will result not only in slow transport but also in least quantity of nitrate to the groundwater.

C. Soil sample analysis (Sorption of nitrate)

The result of the sorption of nitrate in the different soils is shown in Fig. 2. Sorption of nitrate was greater usingpellet method than liquid method in all the soils. Using liquid method, an average of 1.11 mg/kg, 2.97 mg/kg, 7.77 mg/kgand 10.57 mg/kg of nitrate was sorbed in sand, loam, clay and peat, respectively whereas an average of 3.81 mg/kg, 6.56 mg/kg and 8.61 mg/kg was sorbed in sand, loam and clay, respectively using pellet method. Thus, the application of fertilizers in their original form (grains) is likely to cause less groundwater contamination than when mixed with water. For both liquid and pellet methods, sorption of nitrate was in the order of clay>loam>sand.

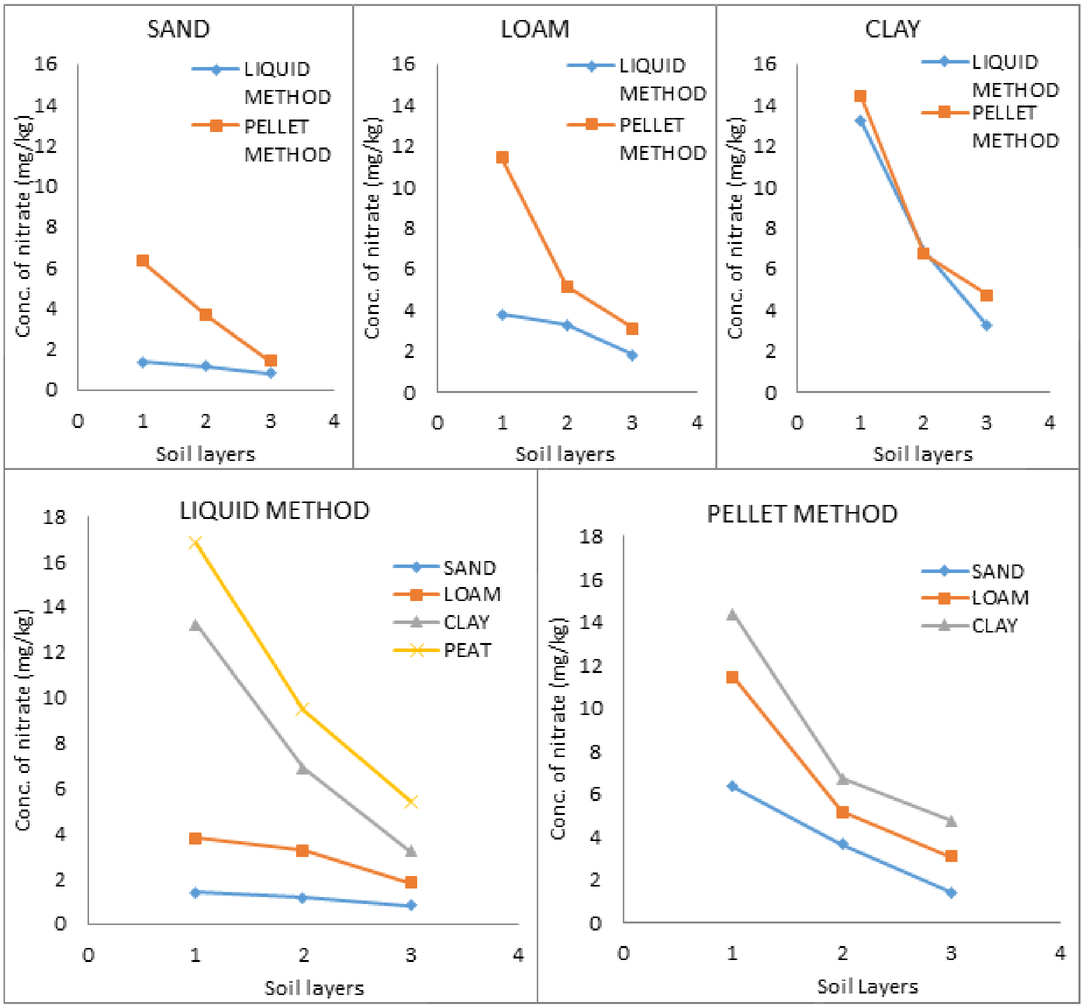

Fig. 2. Sorption of nitrate in the unsaturated zone.

The higher sorption observed in clay can be attributed to the low hydraulic conductivity of the soil. For liquid method that considered the effect of SOM, sorption of nitrate was in the order of peat>clay>loam>sand. Peat sorbed more nitrate in its soil layers than the other soils. The high SOM content of peat enables it to swell up and contain water and contaminants in its layers so they are not easily leached.

D. Sorption coefficient (K_d) of nitrate

Fig. 3 shows the K_d values of nitrate in all the soils as obtained from Equation [2]. K_d was in the order of peat>clay>loam>sand for both liquid and pellet methods. Generally, nitrate sorption in sand, loam and clay was greater using the pellet method. Sand, loam, clay and peat had a K_d of 0.02 L/kg, 0.07 L/kg, 0.26 L/kgand 0.46 L/kg, respectively using the liquid method. A K_d of 0.09 L/kg, 0.19 L/kg and 0.32 L/kg was calculated for sand, loam and clay, respectivelyusing the pellet method. Since higher K_d indicates higher concentration in soil than in water, upon application of fertilizer on farmlands, the potential for groundwater contamination by nitrate is likely to be in the order of sand>loam>clay>peat.

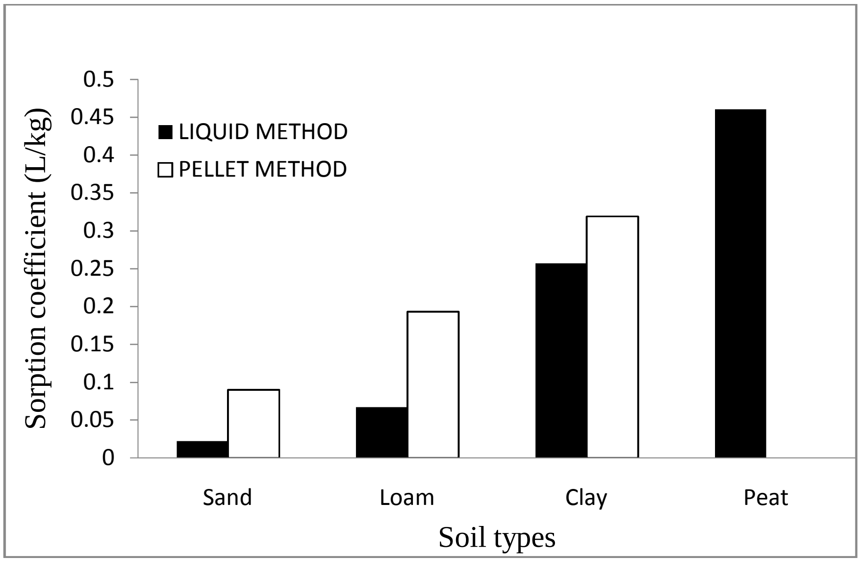

Fig. 3. Calculated sorption coefficient of soils.

E. Retardation of the migration of nitrate

Fig. 4 shows the retardation factor (R) of all the soils. R was estimated from K_d using Equation [3], and represents the degree of retardation of the migration of nitrate due to sorption. For both liquid and pellet methods, R was in the order of peat>clay>loam>sand. Sand, loam, clay and peat had R of 1.09, 1.19, 1.56 and 1.88, respectively using liquid method whereas it was 1.38, 1.53 and 1.70 for sand, loam and clay, respectivelyusing pellet method. Thus, upon fertilizer application in soil, the potential for groundwater contamination by nitrate is likely to be in the order of sand>loam>clay>peat.

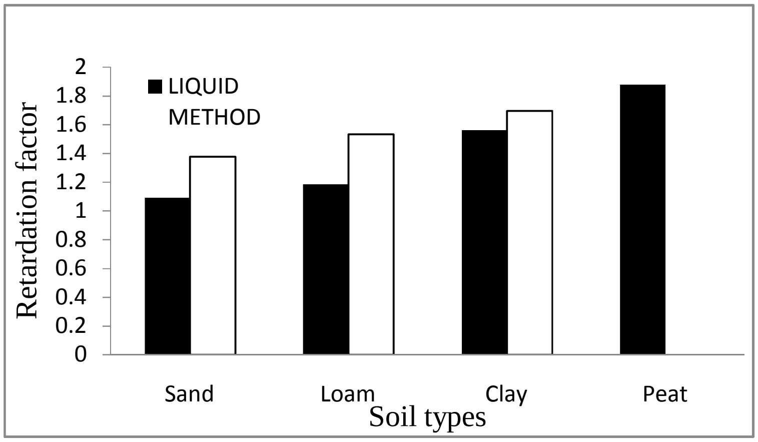

Fig. 4. Estimated retardation factors of soils.

CONCLUSIONS

Groundwater contamination by commonly used fertilizers, represented by nitrate, has been investigated. The study was necessitated by theincreasing use of fertilizers due to soil infertility and rise in population, and the health hazards and environmental risk fertilizers pose when found in drinking water. From the results obtained, it can be concluded that the risk of groundwater contamination by nitrate is likely to be in the order of sand (well-drained)> loam (fairly-drained)>clay (poorly-drained)>peat (SOM-rich) regardless the method of fertilizer application. This is because nitrate was leached as follows: sand (49.99 mg/L), loam (44.17 mg/L), clay (30.24 mg/L) and peat (22.95 mg/L) using liquid method, while it was sand (42.32 mg/L), loam (33.96 mg/L) and clay (26.99 mg/L) using pellet method. However, sorption of nitrate in the soil was in the order of peat (10.57 mg/L)>clay (7.77 mg/L)>loam (2.97 mg/L)>sand (1.11 mg/L) for liquid method and clay (8.61mg/L)>loam (6.56 mg/L)>sand (3.81 mg/L) for pellet method. Also, the sorption coefficient of nitrate was in the order of peat (0.46 L/kg)>clay (0.26 L/kg)>loam (0.07 L/kg>sand (0.02 L/kg) for liquid method, and clay (0.32 L/kg)>loam (0.19 L/kg)>sand (0.09 L/kg) for pellet method. In addition, the retardation factor of nitrate was in the order of peat (1.88)>clay (1.56)>loam (1.19)>sand (1.09) for liquid method, and clay (1.70)>loam (1.53)>s and (1.38) for pellet method. Hence, a higher concentration of nitrate is likely to be found in groundwater below farmlands with sand compared with farmlands comprising of loam, clay or peat. It can also be concluded that the pellet method of fertilizer applicationis likely to pose less threat of groundwater contamination by nitrate than the liquid method.

ACKNOWLEDGEMENT

The Authors wish to thank the University of Port Harcourt for providing the laboratory where the research was carried out.

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