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Temporal Patterns and Source Apportionment of Nitrate-Nitrogen Leaching in a Paddy Field at Kelantan, Malaysia

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Abstract: Nitrate-nitrogen leaching from agricultural areas is a major cause for groundwater pollution. Polluted groundwater with high levels of nitrate is hazardous and cause adverse health effects. Human consumption of water with elevated levels of NO_3^-N has been linked to the infant disorder methemoglobinemia and also to non-Hodgkin's disease lymphoma in adults. This research aims to study the temporal patterns and source apportionment of nitrate–nitrogen leaching in a paddy soil at Ladang Merdeka Ismail Mulong in Kelantan, Malaysia. The complex data matrix (128×16) of nitrate-nitrogen parameters was subjected to multivariate analysis mainly Principal Component Analysis (PCA) and Discriminant Analysis (DA). PCA extracted four principal components from this data set which explained 86.4% of the total variance. The most important contributors were soil physical properties confirmed using Alyuda Forecaster software (R^2 = 0.98). Discriminant analysis was used to evaluate the temporal variation in soil nitrate-nitrogen on leaching process. Discriminant analysis gave four parameters (hydraulic head, evapotranspiration, rainfall and temperature) contributing more than 98% correct assignments in temporal analysis. DA allowed reduction in dimensionality of the large data set which defines the four operating parameters most efficient and economical to be monitored for temporal variations. This knowledge is important so as to protect the precious groundwater from contamination with nitrate.

Key words: Nitrate-nitrogen, leaching, principal component analysis, discriminant analysis

INTRODUCTION

Nitrate leaching into groundwater represents an agronomical and economical direct loss of nitrogen resources. One of the sources of nitrate in groundwater is from fertilizer used in rice cultivation. Other inputs of nitrogen into paddy fields include irrigation water, precipitation and biological N_2 fixation (Campbell *et al*., 1994; Di and Cameron, 2002). Nitrogen losses are results from leaching, runoff, denitrification, ammonia volatilization as well as uptake by the rice plants. Odhiambo and Murty (1996) and Silva *et al*. (2005) relates nitrate leaching losses to various properties across soil types and land-use systems and concludes that leaching losses across land use systems can be explained by a number of parameters collectively rather than a single parameter and thus, no single parameter can be used to fully predict nitrate leaching. In Malaysia there is lack of quantitative studies on nitrate leaching in rice field under the current agricultural practices. However, the significance and prevalence of rice cultivation in Malaysia is vital and the study of its nitrate losses in the rice field is substantial. Such information is urgently required to help improve nitrogen fertilization practices and to minimize nitrogen leaching losses in the rice field.

The uses of chemometric techniques such as Principal Component Analysis (PCA) would provide a useful and promising method in tracing the contributors to nitrate leaching in paddy soils. It is a powerful pattern recognition technique to explain the variance of a large set of intercorrelated variables with a smaller set of independent variables (principal components). According to Lovchinov and Tsakovski (2006), chemometric techniques were the only way of explaining environmental

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processes, modes of pollution, factors influencing air, soil and water contamination. As emphasized by Laaksoharju *et al.* (1999), it is basically for classification and data reduction and can help to simplify and organize large data to provide meaningful insight. The result from PCA would explain how one sample is different from another, which parameters contribute the most to this difference and whether those parameters are positively or inversely correlated (Goncalves *et al*., 2006). Thus, in view of all the benefits of principal component analyses, this study aims at applying this technique to identify the parameters contributing the most to nitrate leaching in a paddy field.

Theoretically, discriminant analysis is a multicomponent statistical technique used to classify objects into mutually exclusive and exhaustive groups on the basis of a set of independent variables (Vaselli *et al.* 1997). Linear combinations of the independent will discriminate the groups in such a way that the misclassified error rates are minimized. According to Singh *et al.* (2005), Discriminant Analysis (DA) was used to determine the variables, which discriminated between two or more naturally occurring groups. DA operates on raw data and the technique constructs a discriminant function for each. It can confirm the group found by PCA. The use of multivariate techniques such as principal component analysis and discriminant analysis could provide useful and promising insights in tracing the contributors to nitrate leaching in paddy soils.

MATERIALS AND METHODS

Description of study area: The study site is known as Ladang Merdeka Ismail Mulong located in Kota Bharu, Kelantan, Malaysia. Kelantan's climate is tropical monsoon, with stable temperature within the range of 21-32°C. Dry and warm weather with consistently high humidity on the lowlands ranging from 82 to 86% occur from January to April. It has an average yearly rainfall of 2,032 to 2,540 mm, with the wettest months being from October through January. The approximate location of the study area is 668000- 671000 N and 472000-473000 E.

Nitrate-nitrogen leaching data set: The data set used in this study was generated through field and laboratory measurements. The nitrate-nitrogen concentration was measured from soil solution sampled using soil solution samplers (model 1900, Soil Moisture Equipment Co.) before cultivation, after each fertilizer applications and after harvest. The soil water were collected following the current agricultural practices of the study area at three different depths 20, 30 and 40 cm in three lysimeters located at two different paddy plots. The sampling, preservation and transportation of the water samples to the laboratory were as per standard methods (APHA, 1998). During harvest, soil samples were collected instead of soil water and the extracts measured using the cadmium reduction method (APHA, 1998). Each time the soil solution was extracted, pressure heads were also measured with tensiometers at two depths (15, 45 cm). To account for seasonal differences, soil porosity and bulk density measurement were carried out in the beginning of the rice season and again at the termination of the rice season when the soils were near wilting point. The soil porosity and bulk density was determined using specific bottle gravity method and dry oven basis method, respectively.

The soil water content was determined by gravimetric method according to the standard procedure (ASTM, 1995) on two occasions, once in the beginning of rice season and the second at the end of the season. The soil penetration resistance was measured to a depth of 40 cm near the end of the rice season using an electronically recording Eijkelkamp penetrologger fitted with a cone of 2.0 cm^{-2} diameter with 60° angle at a 2.0 cm sec^{-1} penetration speed. The water flux was calculated for each sampling occasion based on Darcy's equation. The daily rainfall, evapotranspiration and temperature readings were obtained from the Engineering Division Kemubu Agricultural Development Authority (KADA), Kota Bahru, Kelantan, Malaysia. The raw data set and their analytical methods used are presented in Table 1.

Source apportionment using principal component analysis (PCA): In Principal Component Analysis (PCA), each original observation was converted to principal component score by projecting it into the principal axes. The elements of the eigenvectors that were used to compute the scores of the observations are called principal component loadings. Since the Principal Component Scores (PCS) are usually not readily interpreted, they were rotated by varimax rotation. The varimax rotation in PCA `cleans up' the principal components by increasing the participation of the variables with higher contribution and by simultaneously reducing that of the variables with lesser contribution. The principal component technique was used in this study to filter the raw data so that only significant independent variables responsible for nitrate leaching could be determined.

Temporal variations using discriminant analysis (DA): In temporal analysis, discriminant analysis was used to

Table 1: List of parameters for analysis and their analytical methods/source

Parameters	Abbreviation	Units	Analytical methods/source
Nitrate-nitrogen concentration	NO_3-N	mg L^{-1}	Spectrophotometer
Pressure head (1)	h_1	cm	Tensiometer
Pressure head (2)	h_2	cm	Tensiometer
Hydraulic head (1)	H_1	cm	Piezometer
Hydraulic head (2)	H_2	cm	Piezometer
Percentage clay	% clay	-	Pipette method
Percentage silt	% silt	-	Pipette method
Percentage sand	% sand	-	Pipette method
Porosity	p	g cm^{-3}	Specific gravity bottle
Water flux	q	cm sec^{-1}	Darcy's equation
Dry bulk density	DBD	g cm^{-3}	Dry oven basis method
Soil water content	SWC	g	Gravimetric method
Soil penetration resistance	SPR	Mpascal	Eijkelamp penetrologger
Temperature	T	°C	Thermometer (KADA)
Evapotranspiration	ET	mm	Penman's method (KADA)
Rainfall	R	mm	Thiessen method (KADA)

*h_1, h_2: Pressure head, H_1, H_2: Hydraulic head, SPR: Soil penetration resistance, WC: Water content, ET: Evapotranspiration, Temp: Temperature, q: Water flux

determine the variables and to discriminate between two or more naturally occurring groups. In this case, two groups were selected for temporal (wet and dry seasons) evaluation. DA was performed on each raw data matrix using standard, forward stepwise and backward stepwise modes in constructing discriminant functions to evaluate the temporal variations for leaching activity. In the forward stepwise mode, variables were included step-by-step, beginning with the more significant until no significant changes were obtained; whereas, in the backward stepwise mode, variables were removed step-by-step, beginning with the less significant until no significant changes are obtained (Singh *et al*., 2005). Temporal DA was performed on raw data and it constructs a discriminate function for each group. In this study, the whole data set was divided into wet and dry seasons. The 16 parameters selected for nitrate-nitrogen leaching were the dependent variables, while the wet and dry season constituted the independent variables.

RESULTS

Source apportionment-principal component analysis (PCA): The PCA generated four principal components with eigen value greater than 1 as shown in Table 2. The four PC's with varimax rotation explained 86.4% of the total variance. Among the three PCS, PC1 explained that 39.5% of the total variance had strong negative loadings (>-0.75) on percent porosity percent silt and percent sand and strong positive loadings (>0.75) on dry bulk density, percentage clay and water content. Soil penetration resistance measurement was considered as having a moderate significant factor loading (0.652). PC1 can be said to represent soil physical properties because strong positive loadings were observed for soil dry bulk density, percentage clay and soil water content. PC2 explaining 18.49% of the total variance, had positive loadings on pressure head (0.941) and hydraulic head (0.941), representing hydrologic factors. PC3 accounting for 17.8% of the total variance, had strong positive loadings on evapotranspiration (0.904) and moderately positive loadings on pressure head (0.725), hydraulic head (0.722), rainfall (0.669) and temperature (0.661). Hence, it may be interpreted as meteorological factors. PC4 had only strong positive loading on water flux (0.771).

Table 2: Four Principal components with Eigen values, percentage total variance and cumulative percentage variance

Variables	PC1	PC2	PC3	PC4
Nitrate	-0.077	-0.295	-0.230	0.429
Pressure head (h_1)	0.043	0.941	-0.036	0.046
Pressure head (h_2)	0.079	0.610	0.725	0.100
Hydraulic head (H_1)	0.083	0.618	0.722	0.104
Hydraulic head (H_2)	0.043	0.941	-0.036	0.046
% Porosity	-0.985	-0.026	-0.034	0.166
Dry bulk density	0.985	0.026	0.034	-0.166
% Clay	0.985	0.026	0.034	-0.166
% Silt	-0.985	-0.026	-0.034	0.166
%Sand	-0.985	-0.026	-0.034	0.166
Soil penetration resistance	0.652	-0.067	0.000	-0.710
Soil water content	0.880	0.098	0.050	0.390
Rainfall	0.062	-0.506	0.669	0.158
Evapotranspiration	0.047	-0.200	0.904	0.035
Temperature	-0.028	0.049	0.661	-0.252
Water flux (q)	-0.496	0.171	0.194	0.771
Eigenvalue	6.700	3.374	2.455	1.288
% Variance	39.527	18.487	17.802	10.542
% Cumulative	39.527	58.014	75.816	86.358

To summarize the findings, the principal component generated by PCA namely PC1-PC4 was grouped under the following categories, PC1 representing soil physical properties, PC2 as hydrologic factors, PC3 attributed by meteorological factors and PC4 by water flux. The PCA results were strongly supported when generated using Forecaster, XL software. For this analysis, nitrate leaching was the independent variable and the principal component scores of PC1 to PC4 as the dependent variables. The results (Fig. 1) showed that soil physical properties contributed 53.5% to nitrate-nitrogen leaching

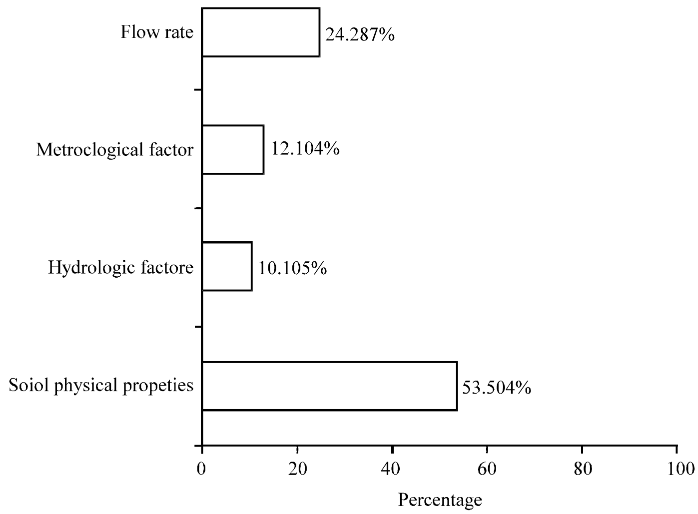

Fig. 1: Factors of nitrate-nitrogen leaching versus percentage of relative importance of each factor as generated by forecaster software

followed by water flow rate at 24.3%, hydrological factors at 10.1% and meteorological factors at 12.1%.

Temporal variation-discriminant analysis: Classification matrix (CMs) obtained from the standard; forward stepwise and backward stepwise modes of DA are shown in Table 3.

In the forward stepwise mode DA gave CMs with 98.96 and 97.67% correct classification for the dry and wet season respectively, with four significant discriminant variables. The same was observed in the backward stepwise mode. Hence, DA rendered a considerable data reduction. The four significant discriminant variables are H_2 (hydraulic head), evapotranspiration, rainfall and temperature. These are the most significant parameters to discriminate between the dry and wet seasons meaning that these four parameters account for most of the expected temporal variations observed. The trend obtained was also supported by correlation analysis which indicated evapotranspiration, rainfall and temperature as the most significant variables with season. The data of the four variables, rainfall, evapotranspiration, temperature and hydraulic head generated from DA were further processed using Forecaster XL software to forecast the most important variable. Here, the leaching rate data was used as the independent variables and the data for the four selected parameters (rainfall, temperature, evapotranspiration and hydraulic head) were the dependent variables. The result showed a good prediction with only one (2.33%) misclassified for the wet season and two (2.08%) misclassified for the dry season (Table 4).

Table 3: Classification Matrix for Discriminant Analysis of Temporal Variation

Monitoring seasons	% Correct	Season assigned by DA: Dry	Wet
Standard mode			
Dry	100.0	96	0
Wet	95.35	2	41
Total	98.56	98	41
Forward stepwise DA			
Dry	98.96	95	1
Wet	97.67	1	42
Total	98.56	96	43
Backward stepwise			
Dry	98.96	95	1
Wet	97.67	1	42
Total	98.56		

Table 4: Actual vs forecast for wet and dry season

Actual	Forecast: Wet	Dry
Wet	42	1
Dry	2	94

The relative importance of each input selected by DA was also generated from the software (Fig. 2). Among the four variables, rainfall (67.9%) exhibited the highest importance for seasonal variations of the study area followed by evapotranspiration (16.78%), hydraulic head, H_2 (8.76%) and temperature (6.56).

DISCUSSION

Abdul-Wahab *et al.* (2005) and Mandal et *al.* (2008) indicated from their study that the variable with the highest factor loading was considered as the most important contributor to the principle component. Thus,

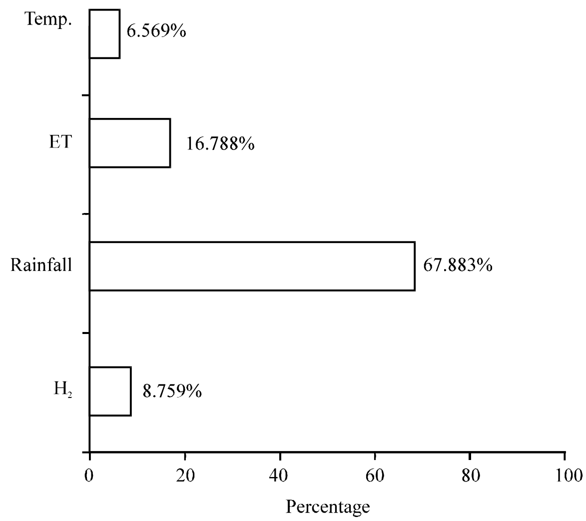

Fig. 2: Temporal contributory factors (temperature, evapotranspiration, rainfall, hydraulic head) versus percentage of relative importance of each factor forecasted from discriminant analysis (Temp: Temperature, ET: Evapotranspiration, H_2: Hydraulic head)

soil physical properties represented in PC1 are the most important factor contributing to nitrate leaching in this study area. The soil physical properties represented here are dry bulk density, percentage clay and soil water content whereas the negative strong factors are percentage silt, percentage sand and porosity. Soil penetration resistance measurement was also crucial because it represented moderate significant factor loading. Beaudoin *et al.* (2005) and Almasri and Kaluarachchi (2005) also reported that nitrate leaching was affected by the soil type which agrees well with this finding. Content of clay plays a vital role in determining vertical transport in soils as proven by Chena *et al.* (2007) in their study where they showed that flux and peak concentration of nitrate would decrease as clay content increased. Soil water content of soils would affect soil penetration resistance. As shown by Singh *et al.* (2001), the decrease in soil water content would result in an increase in soil penetration resistance and less leaching would occur. Therefore, soil water content and soil penetration resistance are interrelated. Furthermore, soil bulk density and porosity are also related to one another where bulk density of soil is inversely related to the porosity of the same soil.

Soils which have high bulk density (low soil porosity) are more compact which could restrict the plant growth and yield. Thus, this result from PCA was in agreement with other researchers (Li and Zhang, 1999; Silva *et al.*, 2005; Ajdary *et al.*, 2007) stating soil physical factors namely soil porosity, dry bulk density and soil texture as the key factors contributing to nutrient leaching into soils. Pressure heads measurements gave high positive loadings in PC2 indicating that matric potential influences water fluxes downward in this clayey soil. The more negative the matric potential, the more difficult it is to remove water from the soil. PC3 which has the strongest positive loading from evapotranspiration shows the important role of this parameter in obtaining the water mass balance in a field. Pathak *et al.* (2004) have shown the effect of evapotranspiration was utmost important in their study to determine the percolation rate of water in a paddy field in Thailand.

Rainfall had been confirmed by other studies to greatly influence nitrate migration in the soil (Rajmohan and Elango, 2005; Babiker *et al.*, 2004; Di and Cameron, 2002). Excessive rainfall would tend to leach nitrate below the root zone and ultimately to groundwater. Rainfall exceeding potential evapotranspiration over a long period of time and which occurred when the paddy field was bare without any crops in between seasons would result in nitrate leaching. This study observed that evapotranspiration had a moderate influence to nitrate-nitrogen leaching while both the hydraulic head and temperature had a weak influence. This finding agrees with Pathak *et al.* (2004), when the effect of evapotranspiration was paramount in establishing the water mass balance in their paddy field in Thailand.

Hydraulic head measurement is also significant in influencing the total energy available for water flow. The water movement carries along with it the valuable nutrient required such as nitrate into the soil layer. High temperature, on the other hand, would undoubtedly result in a dry field and hence fewer nutrients are leached down into the soil.

The temporal variation with discriminant analysis showed a potential as a tool in delineating a few parameters responsible for large variations in nitrate-nitrogen leaching. Thus, with data of rainfall, evapotranspiration, hydraulic head and temperature one could get a good prediction of the nitrate-nitrogen leaching condition in the study area irrespective to the different seasons. DA rendered an important data reduction as it uses only four variables affording more than 98% right assignments in temporal analysis. It can determine the most efficient and economical operating parameters to be monitored for temporal variations.

CONCLUSION

This study has investigated the possible factors influencing nitrate-nitrogen leaching in a paddy field. The sixteen variables used were able to explain 86.4% of the total variance of the data as generated from Principal Component Analysis. It was concluded that soil physical properties represented in PC1 contributed the most variations of nitrate leaching at this site which was confirmed through Alyuda Forecaster.

This study illustrates the usefulness of principal component analysis for the interpretation of complex data sets while identifying the important factors affecting nitrate leaching. The identification of these factors could provide an insight into effective rice cultivation management.

On the other hand, the analysis of the temporal variations suggested that hydraulic head, evapotranspiration, rainfall and temperature are the four most significant factors to discriminate between wet and dry seasons. This was confirmed from the forecaster analysis, which indicated that only one value was misclassified (2.33%) for the wet season and two values were misclassified (2.08%) for the dry season using these four parameters as the significant discriminant variables. As expected, rainfall (67.8%) was the most important factor for the seasonal variation of the study area.

Principal component analysis and discriminant analysis was able to show the similarities and differences in the data set and provided a more objective interpretation of the results. This could enhance pattern recognition in order to explain the complex interaction of nitrate-nitrogen loss in a paddy field of interest. Therefore, the multivariate (pattern recognition) approach is an assessment method for the regional paddy field and can be used as a management tool for other agricultural areas in the future.

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