Estimating impacts of land use on groundwater quality using trilinear analysis

Ying Ouyang, Jia En Zhang & Lihua Cui

Environmental Monitoring and Assessment

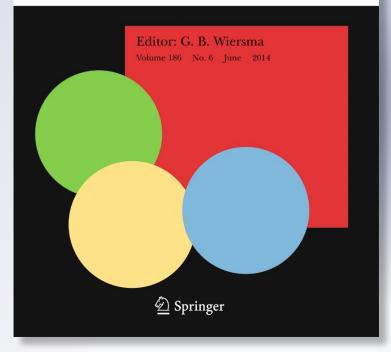
An International Journal Devoted to Progress in the Use of Monitoring Data in Assessing Environmental Risks to Man and the Environment

ISSN 0167-6369

Environ Monit Assess DOI 10.1007/s10661-014-3784-8



An International Journal devoted to progress in the use of monitoring data in assessing environmental risks to Man and the environment.





Your article is protected by copyright and all rights are held exclusively by Springer International Publishing Switzerland (outside the USA). This e-offprint is for personal use only and shall not be self-archived in electronic repositories. If you wish to self-archive your article, please use the accepted manuscript version for posting on your own website. You may further deposit the accepted manuscript version in any repository, provided it is only made publicly available 12 months after official publication or later and provided acknowledgement is given to the original source of publication and a link is inserted to the published article on Springer's website. The link must be accompanied by the following text: "The final publication is available at link.springer.com".



Estimating impacts of land use on groundwater quality using trilinear analysis

Ying Ouyang · Jia En Zhang · Lihua Cui

Received: 22 May 2013 / Accepted: 27 April 2014 © Springer International Publishing Switzerland (outside the USA) 2014

Abstract Groundwater is connected to the landscape above and is thus affected by the overlaying land uses. This study evaluated the impacts of land uses upon groundwater quality using trilinear analysis. Trilinear analysis is a display of experimental data in a triangular graph. Groundwater quality data collected from agricultural, septic tank, forest, and wastewater land uses for a 6-year period were used for the analysis. Results showed that among the three nitrogen species (i.e., nitrate and nitrite (NO_x), dissolved organic nitrogen (DON), and total organic nitrogen (TON)), NOx had a high percentage and was a dominant species in the groundwater beneath the septic tank lands, whereas TON was a major species in groundwater beneath the forest lands. Among the three phosphorus species, namely the particulate phosphorus (PP), dissolved *ortho* phosphorus (PO_4^{3-}) and dissolved organic phosphorus (DOP), there was a high percentage of PP in the groundwater beneath the septic tank, forest, and agricultural lands. In general, Ca was a dominant cation in the groundwater beneath the septic tank lands, whereas Na was a dominant cation in

Y. Ouyang (🖂)

USDA Forest Service, Center for Bottomland Hardwoods Research, 100 Stone Blvd., Thompson Hall, Room 309, Mississippi State, MS 39762, USA e-mail: youyang@fs.fed.us

J. E. Zhang

Department of Ecology, South China Agricultural University, Wushan Road, Tianhe, Guangzhou, China

L. Cui

College of Natural Resource and Environment, South China Agricultural University, Guangzhou 510642, China the groundwater beneath the forest lands. For the three major anions (i.e., F^- , CI^- , and SO_4^{2-}), F^- accounted for <1 % of the total anions in the groundwater beneath the forest, wastewater, and agricultural lands. Impacts of land uses on groundwater Cd and Cr distributions were not profound. This study suggests that trilinear analysis is a useful technique to characterize the relationship between land use and groundwater quality.

Keywords Land use · Groundwater quality · Trilinear analysis

Introduction

Groundwater is a valuable and major resource for human and terrestrial life consumption in addition to provide baseflow for keeping most rivers flowing all year long and wetland healthy as well as to maintain good water quality by diluting sewage and other effluent (Lerner and Harris 2009). Contamination of groundwater resources with toxic chemicals and excess nutrients is a serious environmental concern (Ouyang 2012). With increased recognition of the importance of groundwater resources for human consumption and terrestrial life, a greater need exists to assess groundwater quality.

Groundwater quality variations result from natural conditions and anthropogenic activities. Natural conditions alter groundwater quality by means of recharge and discharge, mineral dissolution, flow paths, residence times, and mixing fresh groundwater with residential water or intruded seawater. Anthropogenic activities affect groundwater quality through the vadose zone leaching of contaminants due to accidental Author's personal copy

spillage, leakage, and inappropriate application of chemicals at the land surface; the intrusion of water with high dissolved solids due to groundwater withdrawals; and the introduction of irrigation water from deep aquifers to surficial aquifers (Boniol 1996).

Groundwater is connected to the landscape above and is thus affected by land uses through the changes in recharge and flow path, the demands for groundwater supply, and the increases in pollutant generation. Inappropriate land use, particularly poor land management, could cause chronic groundwater quality degradation. The severity of groundwater contamination is directly related to human activities, which can be quantified in terms of the intensity and type of land uses. A simple way to assess the impacts of land use on groundwater quality is to compare the contents of contaminants in groundwater among different land uses. In the last decades, numerous studies have been performed to examine the relationship between land use and groundwater contamination (Eckhardt and Stackelberg 1995; Gardner and Vogel 2005; Scanlon et al. 2005; Lerner and Harris 2009; Sarukkalige 2011). Eckhardt and Stackelberg (1995) investigated the relation of groundwater quality to land use in Nassau and Suffolk Counties, Long Island, NY. Their study areas (22 to 44 square miles) include four land uses, namely suburban land sewered more than 22 years, suburban land sewered less than 8 years, suburban land without a regional sewer system, agricultural land, and undeveloped (forested) land. Comparing groundwater quality data from 90 wells, these authors found that the contents of nitrate, alkalinity, boron, synthetic solvents, and pesticides in the groundwater samples are lowest from the undeveloped area and are intermediate to high from the suburban and agricultural areas. Sarukkalige (2011) assessed the spatial variation of groundwater quality and its relationship to land use in Perth Metropolitan, Western Australia. This author showed that groundwater beneath agricultural land is particularly susceptible to nutrient loading due to the application of fertilizers. By studying the relationship between groundwater contamination and land use, the sustainability of groundwater resources can be addressed and integrated with better land use practices and water protection strategies.

Multivariate statistical tools have been widely used to analyze water quality variations in streams and aquifers (Ouyang et al. 2006; Skeppstrom and Olofsson 2006; Andrade et al. 2008). Andrade et al. (2008) applied cluster analysis, factor analysis, and principal component analysis to estimate the effects of land use on groundwater composition in an alluvial aquifer in Trussu River, Brazil. Based on their cluster analysis, two zones of groundwater quality constituent distribution are differentiated: the upland zone is mainly for irrigation and livestock activities, and the lowland zone is occupied by human settlements. Gardner and Vogel (2005) predicted groundwater nitrate concentration from land use with maximum likelihood and logistic regression techniques. These authors demonstrate that nitrate concentrations down gradient from agricultural land are significantly higher than that of elsewhere, and the number of septic tanks and the percentages of forest, undeveloped, and high-density residential land within a 1,000-ft radius of a well are reliable predictors of nitrate concentration in groundwater. All of these studies have provided invaluable insights into the applications of multivariate statistical techniques to assess relationship between groundwater quality and land use. However, few efforts have been devoted to evaluating the impacts of land uses upon groundwater quality compositions using trilinear analysis.

Trilinear analysis (or plot) is a display of experimental data in a triangular graph. These data should contain three components, each of which is typically expressed as a percentage of the total of the three, and the sum of the three components should be equal to 100 % (USDA 1951; Piper 1953; Holm 1988; Shikazel and Crowe 2007). For instance, the total nitrogen (TN) in groundwater is the sum of the following three compositions: total organic nitrogen (TON), nitro oxides (NO_x), and ammonium (NH_4^+) . A trilinear analysis can be used to plot the relative percentages of the three nitrogen compositions in a triangular diagram. Lipson and Siegel (2000) applied the trilinear analysis to investigate the fate and transport of the aromatic hydrocarbon compounds of benzene, toluene, and xylene. These authors demonstrated how to apply trilinear analysis to characterize the physiochemical controls governing the fate and transport of the aromatic hydrocarbon compounds in groundwater. Trilinear analysis is also used to plot sediment textures such as percentages of sand, silt, and clay (Shikazel and Crowe 2007). The goal of this study was to evaluate the relationship between groundwater quality and land use using the trilinear analysis. More specifically, our objective was to estimate impacts of four different land uses (i.e., agricultural, septic tank, forest, and wastewater land uses) upon groundwater quality compositions, including nitrogen, phosphorus,

cations, anions, and heavy metals. Groundwater quality data collected from the Lower St. Johns River Basin (LSJRB), FL, for a 6-year period were used for the analysis.

Methods and materials

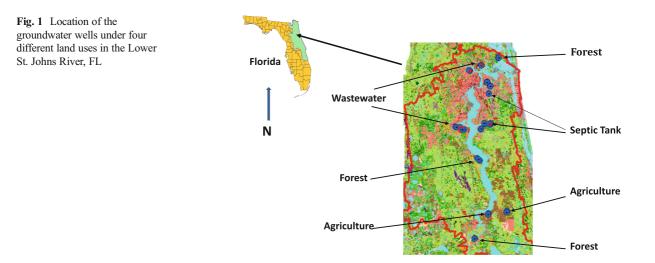
Study site

Water quality data used in this study were collected from a shallow groundwater system of the LSJRB from March 2003 to March 2009. The LSJRB is situated in northeast Florida, between 29° and 30°N and between 81.13° and 82.13°W (Fig. 1) with an area of about 7,192 km². Land covers in this basin largely consist of residential, commercial, industrial, agriculture, forest, and surface water. This area is contaminated with point and nonpoint source pollutants, including nutrients, hydrocarbons, pesticides, and heavy metals (Durell et al. 2001).

Fifty-nine shallow groundwater wells (Fig. 1) were installed or activated by the St. Johns River Water Management District of Florida and its contractor (LBG, Inc. 2004) in 2003 for the purpose of monitoring groundwater quality in the LSJRB. These wells were placed in four different land uses, including the septic tank (residential) area, forestry, agriculture, and wastewater (spray field). Each land use had two different sites, and each site had at least 3 and up to 15 wells, depending on the size of land use in that location. Well casing depths ranged from 4 to 7 m, which are considered shallow groundwater wells in Florida. Sampling activities included the collection of groundwater samples, the in situ measurement of water level, and the slug test of hydraulic conductivity. The groundwater sampling and water level measurement were conducted seasonally for a 6-year period (2003–2009). All sampling activities were conducted in accordance with the SJRWMD standard operating procedures for the collection and analysis of water quality samples and field data (SJRWMD 2010). These standard operating procedures are in compliance with the US EPA's standard methods for groundwater sampling and analysis. Statistical analysis was performed with SAS 9.0, and all of the experimental data were statistically evaluated using *F*-test at α =0.05.

Data format and trilinear analysis

An Excel Macro for generating trilinear plots (Shikazel and Crowe 2007) was used for trilinear analysis in this study. This Excel Macro (free of charge) requires input data in a specific format. As stated in the "Introduction" section, these data should contain three compositions with the same unit (i.e., mg/L or μ m/L for this study), each of which is typically expressed as a percentage of the total of the three, and the sum of the three components should be equal to 100 %. In this study, five groups of groundwater quality compositions were used, namely the nitrogen, phosphorus, major cations, major anions, and major heavy metals. The nitrogen group was divided into three compositions as follows: total organic nitrogen (TON), nitro oxides (NO_x), and ammonium (NH⁴₄), and the sum of the three compositions is the total



nitrogen (TN) or TN=TON+ NO_x + NH_4^+ . The phosphorus group was divided into three compositions as follows: particulate phosphorus (PP), dissolved ortho phosphorus (PO_4^{3-}) , and dissolved organic phosphorus (DOP), and the sum of the three compositions is the total phosphorus (TP) or TP=PP+ PO_4^{3-} +DOP. The major cations were made of Ca²⁺, Mg²⁺, and Na⁺, and the sum of the three cations is the total major cations (TMC) or TMC= $Ca^{2+}+Mg^{2+}+Na^+$. The major anions were made of Cl^- , SO_4^{2-} , and F^- , and the sum of the three anions is the total major anions (TMA) or TMA= $Cl^{-}+SO_{4}^{2-}+F^{-}$. The major heavy metals were made of As, Cd, and Cr, and the sum of the three heavy metals is the total major heavy metals (TMHM) or TMHM=As+ Cd+Cr. Data for each group were then expressed as percentage for each composition related to the four different land uses (see Table 1 for nitrogen group as an example). Once the data were formatted and organized, the Excel Macro, developed by Shikazel and Crowe (2007), was employed to perform trilinear analysis.

As mentioned above, trilinear analysis is an interpolation of experimental data using a triangular graph. These data should contain three components, each of which is expressed as a percentage of the total of the three, and the sum of the three components should be equal to 100 %. The data from the three percentage components are converted to X-Y coordinates using the following equations (Shikazel and Crowe 2007):

$$X = A + B\cos(60^{\circ}) \tag{1}$$

$$Y = A\sin(60^{\circ}) \tag{2}$$

where A is the first of the three percentage components and B is the second of the three percentage components. For detailed procedures on how to format the data and run the Excel Macro, please consult the computer note by Shikazel and Crowe (2007).

Results and discussion

Nutrient vs. land use

species in the shallow groundwater beneath the septic tank areas was mainly presented in the form of NO_x. This finding was further confirmed by our descriptive statistical analysis (Table 2). For example, the mean and maximum concentrations of NO_x were, respectively, 7.37 and 43.70 mg L^{-1} in the groundwater beneath the septic tank areas and were, respectively, 0.51 and 1.65 mg L^{-1} in the groundwater beneath the agricultural lands. The former mean and maximum concentrations of NOx were, respectively, about 14 and 26 times higher than those of the latter. This occurred because septic systems discharge the greatest total volume of wastewater directly into soils overlaying groundwater and are the second largest source of groundwater NOx contamination in Florida and USA (Canter 1996; Spalding and Exner 1993). For the undeveloped forest lands, there were a high percentage of TON (80-100 %) and the low percentages of NO_x (0–30 %) and NH₄ (0–20 %) in the groundwater (Fig. 2). The high percentage of TON was a result of the decomposition of organic matter, which is enriched in forest lands. Large percentage ranges were found for TON (40-90 %), NO_x (30-80 %), and NH₄ (30-90 %) in the wastewater (spray field) land use areas although an increase in percentage for one nitrogen species resulted in a decrease in percentages of the other two nitrogen species. Very low percentage of NO_x (0-10 %) in the groundwater was observed in agricultural lands, which was in compliance with the statistical analysis (Table 2). Result indicated that leaching of NO_x into the underlying groundwater from the agricultural lands was much less than those of the septic tank and wastewater land use areas. This could happen because of the uptake of NO_x by crop roots in agricultural lands before leaching into the groundwater.

Figure 2 further revealed that a percentage increase in NO_x would result in a percentage decrease in NH_4 in the groundwater system. For example, when the percentage of NO_x ranged from 80 to 100 % for the septic tank area, the percentage of NH_4 was reduced to 0–10 % (see the bottom angle on the right). In contrast, when the percentage of NH_4 ranged from 80 to 100 %, the percentage of NO_x was 0–5 % for the same land use (see the top angle). This occurred because NO_x is the product of NH_4 during its oxidation process under aerobic conditions.

Changes in percentage for the three phosphorus species under four different land uses are shown in Fig. 3. There were no data clusters for different land uses except for the septic tank areas, where all data points were crowded at the bottom left angle. In these septic

| Table 1 Percentages of nitrogen species in a specific | centages of | nitrogen s | species in a | | t used for r | unning the | Excel Mac | format used for running the Excel Macro program | | | | | | | |
|---|------------------|--------------------|--------------|------------------|---------------------------------------|------------------|------------|---|---------------|------------------|-------|-------------|---------------|------------------|-----------------|
| Septic tank | %NO _x | $\% \mathrm{NH}_4$ | %TON | Forestry | $%ONO_{\rm x}$ | %NH ₄ | %TON | Wastewater | $%OO_{\rm x}$ | %NH ₄ | NOT% | Agriculture | $%OO_{\rm x}$ | %NH ₄ | Monit . NOL% |
| AM-MW-1 | 0.40 | 88.68 | 10.92 | BP-MW-1 | 6.06 | 0.00 | 93.94 | EH-MW-1 | 1.93 | 63.66 | 34.41 | EP-MW-1 | 7.05 | 52.87 | 40.09 |
| AM-MW-1 | 0.46 | 81.30 | 18.24 | BP-MW-1 | 5.71 | 8.10 | 86.19 | EH-MW-1 | 1.38 | 63.75 | 34.86 | EP-MW-1 | 7.32 | 49.37 | 43.30 |
| AM-MW-1 | 0.58 | 82.50 | 16.92 | BP-MW-1 | 3.97 | 14.06 | 81.97 | EH-MW-1 | 2.44 | 40.60 | 56.96 | EP-MW-1 | 6.47 | 29.41 | 64.12 |
| AM-MW-1 | 0.26 | 82.50 | 17.24 | BP-MW-1 | 10.48 | 13.00 | 76.52 | EH-MW-1 | 2.60 | 51.54 | 45.86 | EP-MW-1 | 2.88 | 66.68 | 30.44 |
| AM-MW-1 | 0.50 | 85.07 | 14.42 | BP-MW-1 | 11.31 | 17.87 | 70.83 | EH-MW-1 | 5.64 | 53.93 | 40.43 | EP-MW-2 | 1.70 | 31.37 | 66.92 |
| AM-MW-1 | 0.29 | 79.77 | 19.94 | BP-MW-2 | 12.24 | 0.00 | 87.76 | EH-MW-2 | 1.54 | 25.65 | 72.81 | EP-MW-2 | 2.38 | 32.01 | 65.61 |
| AM-MW-1 | 0.28 | 88.16 | 11.56 | BP-MW-2 | 3.50 | 5.68 | 90.82 | EH-MW-2 | 1.76 | 21.68 | 76.56 | EP-MW-2 | 5.11 | 32.21 | 62.68 |
| AM-MW-1 | 0.30 | 94.63 | 5.08 | BP-MW-2 | 21.25 | 20.81 | 57.94 | EH-MW-2 | 1.70 | 12.16 | 86.14 | EP-MW-2 | 1.83 | 35.86 | 62.31 |
| AM-MW-1 | 0.15 | 92.66 | 7.19 | BP-MW-2 | 6.26 | 7.26 | 86.48 | EH-MW-2 | 2.22 | 22.13 | 75.65 | EP-MW-2 | 1.14 | 41.43 | 57.43 |
| AM-MW-1 | 0.24 | 93.32 | 6.44 | BP-MW-2 | 2.74 | 16.07 | 81.19 | EH-MW-2 | 3.75 | 26.82 | 69.43 | EP-MW-3 | 1.70 | 49.69 | 48.60 |
| AM-MW-1 | 0.63 | 96.23 | 3.13 | BP-MW-3 | 1.53 | 43.05 | 55.43 | EH-MW-3 | 2.73 | 29.38 | 67.89 | EP-MW-3 | 1.09 | 61.84 | 37.07 |
| AM-MW-1 | 1.57 | 97.60 | 0.84 | BP-MW-3 | 25.50 | 29.55 | 44.94 | EH-MW-3 | 3.12 | 41.46 | 55.42 | EP-MW-3 | 6.28 | 6.28 | 87.43 |
| AM-MW-1 | 0.47 | 99.53 | 0.00 | BP-MW-3 | 1.93 | 8.34 | 89.72 | EH-MW-3 | 7.26 | 17.91 | 74.83 | EP-MW-3 | 9.51 | 63.87 | 26.63 |
| AM-MW-1 | 0.24 | 99.76 | 0.00 | BP-MW-3 | 14.19 | 10.94 | 74.86 | EH-MW-3 | 34.40 | 13.15 | 52.45 | YP-MW-1 | 8.36 | 48.24 | 43.40 |
| AM-MW-1 | 0.48 | 94.79 | 4.73 | BP-MW-3 | 29.59 | 5.22 | 65.18 | EH-MW-3 | 3.42 | 43.64 | 52.94 | YP-MW-1 | 5.07 | 33.06 | 61.88 |
| AM-MW-1 | 2.13 | 85.29 | 12.58 | MC-MW-1 | 2.78 | 0.00 | 97.22 | JC-MW-1 | 1.52 | 17.14 | 81.35 | YP-MW-1 | 2.47 | 38.04 | 59.49 |
| AM-MW-1 | 2.48 | 0.24 | 97.28 | MC-MW-1 | 7.88 | 7.09 | 85.03 | JC-MW-1 | 6.50 | 7.33 | 86.17 | YP-MW-1 | 12.54 | 31.47 | 55.99 |
| AM-MW-1 | 0.00 | 86.69 | 13.31 | MC-MW-1 | 3.70 | 8.85 | 87.46 | JC-MW-1 | 1.12 | 5.55 | 93.33 | YP-MW-1 | 6.63 | 44.33 | 49.03 |
| AM-MW-1 | 0.26 | 91.24 | 8.50 | MC-MW-1 | 8.22 | 22.23 | 69.55 | JC-MW-1 | 1.43 | 67.04 | 31.53 | YP-MW-2 | 0.72 | 60.00 | 39.27 |
| AM-MW-1 | 0.54 | 88.19 | 11.27 | MC-MW-1 | 2.36 | 4.44 | 93.19 | JC-MW-1 | 2.68 | 18.45 | 78.87 | YP-MW-2 | 0.43 | 25.39 | 74.18 |
| AM-MW-1 | 0.24 | 99.76 | 0.00 | MC-MW-2 | 24.40 | 0.00 | 75.60 | JC-MW-2 | 0.70 | 33.97 | 65.33 | YP-MW-2 | 0.33 | 47.86 | 51.81 |
| AM-MW-1 | 0.53 | 87.76 | 11.71 | MC-MW-2 | 80.27 | 19.73 | 0.00 | JC-MW-2 | 4.45 | 13.27 | 82.28 | YP-MW-2 | 0.53 | 55.92 | 43.55 |
| AM-MW-1 | 0.05 | 77.35 | 22.60 | MC-MW-2 | 57.70 | 1.25 | 41.05 | JC-MW-2 | 14.57 | 17.47 | 67.96 | YP-MW-2 | 8.66 | 12.97 | 78.37 |
| AM-MW-1 | 0.22 | 93.90 | 5.88 | MC-MW-2 | 9.24 | 29.16 | 61.60 | JC-MW-2 | 2.60 | 31.58 | 65.82 | YP-MW-3 | 3.58 | 60.66 | 35.76 |
| AM-MW-1 | 1.26 | 87.81 | 10.93 | MC-MW-2 | 32.17 | 0.00 | 67.83 | JC-MW-2 | 2.23 | 14.10 | 83.67 | YP-MW-3 | 4.20 | 65.39 | 30.41 |
| AM-MW-2 | 99.37 | 0.00 | 0.63 | MC-MW-3 | 7.27 | 0.00 | 92.73 | JC-MW-3 | 0.66 | 49.79 | 49.55 | YP-MW-3 | 3.69 | 42.32 | 53.99 |
| AM-MW-2 | 99.08 | 0.00 | 0.92 | MC-MW-3 | 43.52 | 56.48 | 0.00 | JC-MW-3 | 5.84 | 49.27 | 44.89 | YP-MW-3 | 9.58 | 31.86 | 58.57 |
| AM-MW-2 | 98.98 | 0.00 | 1.02 | MC-MW-3 | 8.91 | 0.00 | 91.09 | JC-MW-3 | 15.17 | 31.04 | 53.79 | YP-MW-3 | 10.30 | 83.57 | 6.13 |
| = | ÷ | = | F | = | = | ÷ | = | ÷ | = | ÷ | = | ÷ | ÷ | = | E |
| : | = | = | ÷ | = | ÷ | ÷ | = | = | ÷ | ÷ | ÷ | Ŧ | = | = | F |
| ÷ | = | = | ÷ | = | ÷ | = | ÷ | = | = | = | ÷ | = | = | ÷ | = |
| The quotation marks in the table denote more availabl | ז marks in | the table d | lenote more | e available obse | e observed data have not been omitted | lave not be | en omitted | | | | | | | | |

Environ Monit Assess

Author's personal copy

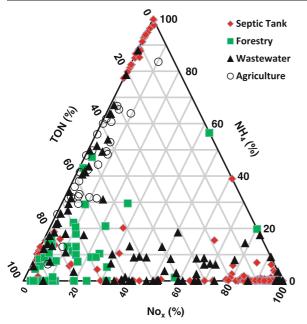


Fig. 2 Distribution of $\% NO_x, \,\% NH_4,$ and % TON in the ground-water under four different land uses

tank areas, there were very low DOP (0-5 %) and PO₄³⁻ (0-10 %) but high PP (85–100 %) in the groundwater. The low percentages of DOP and PO₄³⁻ in the groundwater occurred because these dissolved phase P species were absorbed by soil particles and precipitated through chemical reactions with ions such as iron, aluminum, and calcium before leaching into the underlying groundwater. Although the reasons for the high percentage of PP in the groundwater remain to be investigated, a possible explanation would be more PP leaching into groundwater due to less absorption of the PP. Uusitalo et al. (2003) estimated the contribution of PP runoff in four study sites in southern Finland. These authors found that the loss of PP in surface runoff is 3- to 5-folds higher than those of dissolved phosphorus.

Analogous to the case of the septic tank areas, most of the P data from the undeveloped forest lands were situated around the bottom left angle. There was a high percentage of PP (80–100 %) but low percentages of DOP (0–10 %) and PO_4^{3-} (0–20 %) in the groundwater (Fig. 3). These occurred due to the same reasons as for the case of the septic tank areas. In contrast, most of the P data from the agricultural lands were scattering in the triangle. Such wide ranges in percentage of the P species indicate that no discernible impacts of agricultural lands on groundwater P species distributions although the exact reasons remain to be investigated. The percentage ranges for P species in the groundwater beneath the wastewater (spray field) land use areas were 0–30 % for DOP, 0–90 % for PP, and 0– 100 % for PO₄³⁻, which was consistent with their average concentrations (DOP=0.024 mg L⁻¹, PP= 0.109 mg L⁻¹, and PO₄³⁻=0.198 mg L⁻¹) shown in Table 1. Result indicated that leaching of PO₄³⁻ into the underlying groundwater from the spray field was larger than those of the DOP and PP. This could happen because there was more PO₄³⁻ in the wastewater (http:// www.lenntech.com/phosphorous-removal.htm).

Ion vs. land use

There were several data clusters for the major cations under four different land uses (Fig. 4). For the septic tank land use areas, the data were concentrated at the bottom of the triangle. Among the three major cations, Ca, Na, and Mg accounted, respectively, for 45–65, 20– 50, and 5-15 %. It is apparent that Ca was a dominant cation in the groundwater beneath the septic tank land uses. In contrast, Na was a dominant cation (accounting for 50-90 %) in the groundwater beneath the undeveloped forest land, while Ca and Mg accounted for only 5-30 %. There was a data cluster for agricultural land, where Na accounted for 50-70 %, Ca accounted for 20-30 %, and Mg accounted for 10–20 %. Analogous to the case of agricultural lands, a somewhat similar data cluster was found for wastewater (spray field) land uses. The higher percentages of Na in the groundwater beneath the forest, agricultural, and wastewater land uses indicated that the impact of these land uses on Na was minimal.

Among the three major anions used in this study, F^- accounted for <1 % of the total anions in the groundwater beneath the forest, wastewater, and agricultural lands (Fig. 5). This was so because the mean concentrations of Cl⁻ and SO₄²⁻ in the groundwater for these land uses were three orders of magnitude higher than that of F (Table 2). In contrast, the Cl⁻ and SO₄²⁻ accounted, respectively, for 15–100 and 0–85 % for wastewater and forest land uses. These wide percentage ranges indicated the uneven distributions of Cl⁻ and SO₄²⁻ in the groundwater aquifer for these land uses. A similar but somewhat narrow percentage range for Cl⁻ and SO₄²⁻ was found in the groundwater beneath the agricultural lands.

Unlike the cases of forest, wastewater, and agricultural land uses, there was a data cluster at the bottom of the triangle (Fig. 5) for the septic tank land use. For this

| | Septic tank | | | Forestry | | | Wastewater | | | Agriculture | | |
|--------------------|---------------------------|---------------|-------------|---------------------------|------------------------|-------------|---------------------------|---------------|-------------|---------------------------|------------|-------------|
| | NO _x (mg/L) | NH4 (mg/L) | TON (mg/L) | NO _x (mg/L) | NH4 (mg/L) | TON (mg/L) | NO _x (mg/L) | NH4 (mg/L) | TON (mg/L) | NO _x (mg/L) | NH4 (mg/L) | TON (mg/L) |
| Mean | 7.3768 | 0.1111 | 0.2352 | 0.0159 | 0.0268 | 0.2000 | 1.9224 | 0.1948 | 0.2765 | 0.0407 | 0.5069 | 0.5643 |
| Standard error | 0.2757 | 0.0198 | 0.0101 | 0.0022 | 0.0064 | 0.0463 | 0.3476 | 0.0508 | 0.0444 | 0.0069 | 0.0760 | 0.0920 |
| Median | 6.6462 | 0.0010 | 0.1708 | 0.0114 | 0.0069 | 0.0748 | 0.0319 | 0.0037 | 0.0954 | 0.0276 | 0.3589 | 0.4957 |
| Standard deviation | 6.2451 | 0.4493 | 0.2300 | 0.0147 | 0.0436 | 0.3138 | 3.4586 | 0.5051 | 0.4413 | 0.0367 | 0.4021 | 0.4868 |
| Minimum | 0.0000 | 0.0000 | 0.000 | 0.0027 | 0.0000 | 0.0000 | 0.0036 | 0.0000 | 0.000 | 0.0079 | 0.0397 | 0.0526 |
| Maximum | 43.7001 | 3.4704 | 1.9600 | 0.0793 | 0.2064 | 1.3422 | 10.5512 | 3.3131 | 2.3880 | 0.1779 | 1.6537 | 2.6905 |
| | PO ₄ -D (mg/L) | DOP (mg/L) | TP-P (mg/L) | PO ₄ -D (mg/L) | DOP (mg/L) | TP-P (mg/L) | PO ₄ -D (mg/L) | DOP (mg/L) | TP-P (mg/L) | PO ₄ -D (mg/L) | DOP (mg/L) | TP-P (mg/L) |
| Mean | 0.0051 | 0.0002 | 0.1065 | 0.0187 | 0.0057 | 0.0541 | 0.1981 | 0.0244 | 0.1094 | 0.0678 | 0.1248 | 0.0549 |
| Standard error | 0.0003 | 0.0001 | 0.0250 | 0.0046 | 0.0026 | 0.0086 | 0.0511 | 0.0067 | 0.0294 | 0.0177 | 0.0734 | 0.0121 |
| Median | 0.0052 | 0.0000 | 0.0542 | 0.0069 | 0.0009 | 0.0479 | 0.0177 | 0.0059 | 0.0366 | 0.0216 | 0.0406 | 0.0362 |
| Standard deviation | 0.0017 | 0.0004 | 0.1300 | 0.0239 | 0.0134 | 0.0447 | 0.3110 | 0.0405 | 0.1786 | 0.0922 | 0.3816 | 0.0627 |
| Minimum | 0.0008 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0084 | 0.0000 | 0.0000 | 0.0015 | 0.0058 | 0.0000 |
| Maximum | 0.0080 | 0.0014 | 0.5557 | 0.0755 | 0.0664 | 0.1606 | 1.3872 | 0.1387 | 0.7149 | 0.3228 | 2.0241 | 0.2285 |
| | Ca (mg/L) | Mg (mg/L) | Na (mg/L) | Ca (mg/L) | Mg (mg/L) | Na (mg/L) | Ca (mg/L) | Mg (mg/L) | Na (mg/L) | Ca (mg/L) | Mg (mg/L) | Na (mg/L) |
| Mean | 34.4602 | 3.6327 | 23.1910 | 6.4091 | 1.4933 | 6.3671 | 27.6628 | 11.6787 | 52.8741 | 85.8738 | 40.7408 | 148.7827 |
| Standard error | 6.6074 | 0.5389 | 4.7257 | 2.9842 | 0.1788 | 0.5605 | 3.7750 | 1.5668 | 7.5656 | 14.2195 | 8.2818 | 23.4963 |
| Median | 26.3362 | 2.7570 | 20.7690 | 0.8565 | 1.2771 | 5.5190 | 34.1320 | 11.2590 | 32.6910 | 60.4380 | 18.4980 | 74.3750 |
| Standard deviation | 21.9141 | 1.7873 | 15.6735 | 17.9053 | 1.0726 | 3.3630 | 22.9623 | 9.5305 | 46.0197 | 73.8868 | 43.0335 | 122.0902 |
| Minimum | 7.9918 | 1.7383 | 7.8179 | 0.3890 | 0.3470 | 1.8460 | 0.7406 | 1.2050 | 6.3620 | 23.6488 | 7.4020 | 36.1580 |
| Maximum | 67.6880 | 6.8063 | 47.2990 | 74.5460 | 4.7340 | 14.7690 | 65.3340 | 31.3230 | 132.0350 | 263.1010 | 154.7610 | 456.3350 |
| | Cl (mg/L) | $SO_4 (mg/L)$ | F (mg/L) | Cl (mg/L) | SO ₄ (mg/L) | F (mg/L) | Cl (mg/L) | $SO_4 (mg/L)$ | F (mg/L) | Cl (mg/L) | SO4 (mg/L) | F (mg/L) |
| Mean | 36.50588 | 58.775 | 0.054057 | 11.585951 | 6.40566 | 0.047471 | 84.0961504 | 65.106865 | 0.138721 | 318.79048 | 233.1193 | 0.473566 |
| Standard error | 7.379285 | 8.9104 | 0.006706 | 0.8453215 | 0.96809 | 0.005077 | 11.8645546 | 10.849681 | 0.027644 | 57.772531 | 40.00683 | 0.140326 |
| Median | 30.17323 | 46.933 | 0.048722 | 11.089421 | 4.38271 | 0.038845 | 52.850314 | 41.948858 | 0.0491 | 245.537 | 146 | 0.1648 |
| Standard deviation | 27.61076 | 33.34 | 0.025091 | 5.3462825 | 6.12272 | 0.032111 | 72.1692682 | 65.996036 | 0.168153 | 300.19487 | 207.8816 | 0.729153 |
| Minimum | 7.871853 | 19.95 | 0.0153 | 2.7082484 | 0 | 0.005 | 1.19 | 0 | 0.005 | 44.428352 | 19.4 | 0.091904 |
| Maximum | 94.4 | 108.7 | 0.1122 | 21.156 | 27.3 | 0.1511 | 199.996 | 235.0668 | 0.537489 | 1022.6265 | 808.2459 | 2.6316 |
| | As (µg/L) | Cd (µg/L) | Cr (µg/L) | As (µg/L) | Cd (µg/L) | Cr (µg/L) | As (µg/L) | Cd (µg/L) | Cr (µg/L) | As (µg/L) | Cd (µg/L) | Cr (µg/L) |
| Mean | 1.312422 | 0.0523 | 0.234084 | 0.6375107 | 0.04602 | 0.72186 | 5.55551493 | 0.0314812 | 1.212952 | 4.269674 | 0.09817 | 2.955282 |
| Standard error | 0.181514 | 0.0043 | 0.022516 | 0.0997753 | 0.00825 | 0.128238 | 0.91991564 | 0.0052012 | 0.080103 | 0.6273352 | 0.013842 | 0.921919 |
| Median | 0.354161 | 0.0288 | 0.115604 | 0.2164859 | 0.02009 | 0.3333 | 1.541787 | 0.0009699 | 1.134055 | 2.99488 | 0.061255 | 1.7695 |
| Standard deviation | 2.926826 | 0.069 | 0.363057 | 0.8868224 | 0.07332 | 1.1398 | 8.17638906 | 0.0462294 | 0.711973 | 5.5404748 | 0.122248 | 8.14217 |
| Minimum | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Maximum | 74 20 | 0 5371 | 210 C | 102 | | | | | | | | |

Environ Monit Assess

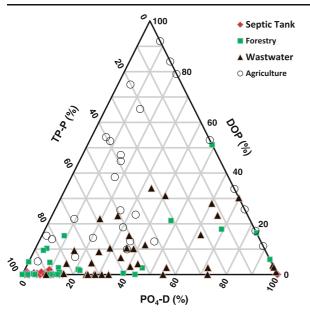


Fig. 3 Distribution of %PO₄-D, %DOP, and %PP in the ground-water under four different land uses

land use, F^- accounted for 20–50 %, Cl⁻ accounted for 45–65 %, and SO₄²⁻ accounted for 5–15 %. A relatively high percentage range of F^- in the groundwater beneath the septic tank land use occurred because of the high F^- content in the tap water.

Table 2 showed that the mean concentration of Cl^- was higher than that of SO_4^{2-} for the agricultural, wastewater, and forest lands but was lower than that of SO_4^{2-}

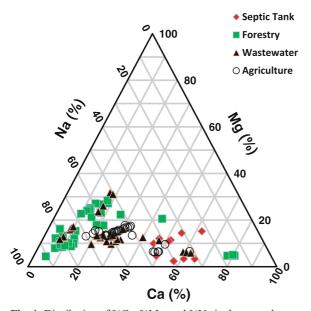


Fig. 4 Distribution of %Ca, %Mg, and %Na in the groundwater under four different land uses

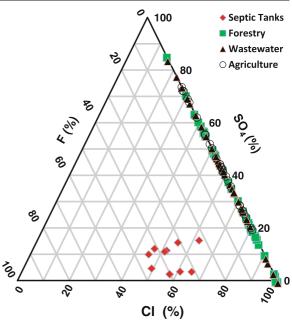


Fig. 5 Distribution of %Cl, %SO4, and %F in the groundwater under four different land uses

for the septic tank lands. A higher Cl^- content in groundwater could be the result of natural characteristics in the study areas, which are very close to the estuarine environment. Overall, the mean Cl^- and SO_4^{2-} concentrations were about two to three order of magnitudes higher than that of the F⁻. Fluoride in the groundwater aquifer was not a concern as its maximum concentration did not exceed 1.5 mg/L, which is a drinking water standard (WHO 1984).

Heavy metal vs. land use

Variations in percentage for the three major heavy metals under four different land uses are shown in Fig. 6. There were data clusters at the bottom angle on the right for the wastewater and agricultural lands, showing that As accounted for about 50–100 % of the total major heavy metals used this study. This finding could be confirmed by the mean concentrations of As from the same land uses (Table 2). That is, the mean concentrations of As were 5.56 and 4.23 mg/L, respectively, for wastewater and agricultural lands, which were much higher than those of forest and septic tank land uses. Results indicated agricultural practices such as fertilizer and pesticide applications and wastewater usages could be a source of As contamination. For the septic tank and forest lands, there were data scattering around

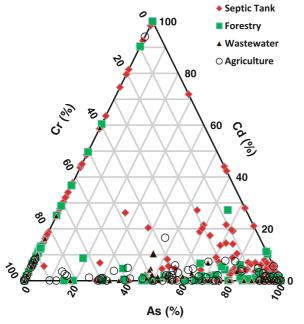


Fig. 6 Distribution of %As, %Cd, and %Cr in the groundwater under four different land uses

the triangle. Results indicated that impact of septic tank and forest lands on groundwater As distribution was not profound. There were very low mean As contents in the groundwater beneath these land uses (Table 2). Figure 6 further revealed that there was a very low percentage of Cd (0–10 %) for the wastewater and agricultural land uses. This finding postulated that agricultural and wastewater land uses were not a major source of Cd contamination. In contrast, Cr had a wide range in percentage change among all four different land uses. Therefore, the impact of land uses on groundwater Cr was trivial.

Conclusions

This study was undertaken to evaluate the relationships between groundwater quality and land use using trilinear analysis. The outcome showed that the nitrogen in the shallow groundwater beneath the septic tank land use areas was mainly present in the form of NO_x . This occurred because septic systems discharge the greatest total volume of wastewater directly into soils overlaying the groundwater. In contrast, the nitrogen in the shallow groundwater beneath the undeveloped forest lands was mainly presented in the form of TON. This happened as a result of the decomposition of organic matter, which is enriched in forest lands. There were very low percentages of DOP and PO_4^{3-} but high percentage of PP in the groundwater beneath the septic tank land use areas. The low percentages of DOP and PO_4^{3-} in the groundwater occurred because these dissolved phase P species were absorbed by soil particles and precipitated through chemical reactions with ions such as iron, aluminum, and calcium before leaching into the underlying groundwater. Although the reasons for the high percentage of PP in the groundwater remain to be investigated, a possible explanation would be more PP leaching into groundwater due to less absorption of the PP.

Unlike the case of septic tank lands, most of the P data from the agricultural lands were scattering in the triangle. Such wide ranges in percentage of the P species indicated that no discernible impacts of agricultural lands on groundwater P species distributions although the exact reasons remain to be investigated. In general, leaching of $PO_4^{3^-}$ into the underlying groundwater from the spray field (wastewater land use) was larger than those of the DOP and PP. This could happen because there was more $PO_4^{3^-}$ in the wastewater.

Ca was a dominant cation in the groundwater beneath the septic tank land uses, whereas Na was a dominant cation in the groundwater beneath the forest, agricultural, and wastewater land uses. Among the three major anions used in this study, F^- accounted for <1 % of the total anions in the groundwater beneath the forest, wastewater, and agricultural lands. These were wide percentage ranges in Cl⁻ and SO₄²⁻ for forest, wastewater, and agricultural lands, indicating the uneven distributions of these anions in the groundwater aquifer. Unlike the cases of forest, wastewater, and agricultural land uses, there was a relatively high percentage of F⁻ in the groundwater beneath the septic tank land use due to the high F⁻ content in the tap water.

Arsenic had high percentages among the three major heavy metals from the wastewater and agricultural lands. Impact of septic tank and forest lands on groundwater As distribution was minimal. Furthermore, impact of the four land uses on groundwater Cr was trivial. This study revealed that trilinear analysis is a useful technique to characterize the relationship between land use and groundwater quality.

Trilinear plot is a useful tool to characterize water quality constituents in surface and groundwater systems. It can also be used for soil grain size and chemistry analysis. However, if the water bodies with different total concentrations show identical percentage on the diagram, it is difficult to distinguish various mechanisms that may cause similar change in water chemistry by trilinear plot. For these situations, other alternatives such as cluster analysis, principal component analysis, maximum likelihood, and conventional statistics should be used for further estimations. For an elaborate description of the limitations on trilinear analysis, the interested readers should consult the excellent report published by Cheng (1988).

References

- Andrade, E. M. D., Palácio, H. A. Q., et al. (2008). Land use effects in groundwater composition of an alluvial aquifer (Trussu River, Brazil) by multivariate techniques. *Environmental Research*, 106, 70–177.
- Boniol, D. (1996). Summary of groundwater quality in the St. Johns River Water Management District. Palatka: Special Publication SJ96-SP13. St. Johns River Water Management District.
- Canter, L. W. (1996). *Nitrates in groundwater* (p. 263). New York: Lewis Publishers.
- Cheng, S. L. (1988). Trilinear diagram revisited: application, limitation, and an electronic spreadsheet program. *Groundwater*, 26, 505–510.
- Durell, G. S., Seavey, J. A., & Higman, J. (2001). Sediment quality in the lower St. Johns River and Cedar-Ortega River Basin: chemical contaminant characteristics. Duxbury: Battelle.
- Eckhardt, D. V. A., & Stackelberg, P. E. (1995). Relation of ground-water quality to land use on Long Island, New York. *Ground Water*, 33, 1019–1031.
- Gardner, K. K., & Vogel, R. M. (2005). Predicting groundwater nitrate concentration from land use. *Ground Water*, 43, 343–352.
- Holm, P. E. (1988). Triangular plots and spreadsheet software. Journal Geoscience Education, 36, 157–159.
- LBG (Legget, Brashears & Graham, Inc.). (2004). Quantification of the role of shallow groundwater nutrient enrichment on exporting nutrient into the Lower St. Johns River Basin. Palatka: St. Johns River Water Management District.

- Lerner, D. N., & Harris, B. (2009). The relationship between land use and groundwater resources and quality. *Land Use Policy*, 26S, S265–S273.
- Lipson, D., & Siegel, D. I. (2000). Using ternary diagrams to characterize transport and attenuation of BTX. *Ground Water*, 38, 106–113.
- Ouyang, Y. (2012). Estimation of shallow groundwater discharge and nutrient load into a river. *Ecological Engineering*, *38*, 101–104.
- Ouyang, Y., Nkedi-Kizza, P., Wu, Q. T., Shinde, D., & Huang, C. H. (2006). Assessment of seasonal variations in surface water quality. *Water Research*, 40, 3800–3810.
- Piper, A. M. (1953). A graphic procedure in the geochemical interpretation of water analysis. Washington DC: United States Geological Survey. ASIN: B0007HRZ36.
- Sarukkalige, P. R. (2011). Assessment of spatial variation of groundwater quality and its relationship with land use in Perth metropolitan. *Journal of Water Resource and Protection*, 3, 311–317.
- Scanlon, B. R., Reedy, R. C., Stonestrom, D. A., Prudicz, D. E., & Dennehy, K. F. (2005). Impact of land use and land cover change on groundwater recharge and quality in the southwestern US. *Global Change Biology*, 11, 1577–1593.
- Shikazel, S. G., & Crowe, A. S. (2007). An excel macro for generating trilinear plots. *Groundwater*, 45, 106–109.
- SJRWMD (St. Johns River Water Management District). (2010). Field standard operating procedures for surface water sampling. Palatka FL: St. Johns River Water Management District. 32177 386-329-4500.
- Skeppstrom, K., & Olofsson, B. (2006). A prediction method for radon in groundwater using GIS and multivariate statistics. *Science of the Total Environment*, 367, 666–680.
- Spalding, R. F., & Exner, M. E. (1993). Occurrence of nitrate in groundwater—a review. *Journal of Environmental Quality*, 22, 392–402.
- USDA. (1951). Soil survey manual. USDA handbook no. 18. Washington DC: United States Government Printing Office.
- Uusitalo, R., Turtola, E., Puustinen, K., Paasonen-Kiveka, M., & Uusi-Kamppa, J. (2003). Contribution of particulate phosphorus to runoff phosphorus bioavailability. *Journal of Environmental Quality*, 32, 2007–2016.
- WHO. (1984). Guidelines for drinking water quality. In *Health criteria and other supporting information* (2nd ed., Vol. 2). Geneva: World Health Organization.