

Measuring and simulating leaching of nutrients from a calcareous soil amended with sewage sludge and poultry manure

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Abstract

Leaching of nutrients due to the application of sewage sludge and poultry manure is a major problem in intensive farming. Simulating helps assess the nutrient loss and establish better methods for fertilization. This study was conducted to investigate the leaching of nutrients (NH₄-N, NO₃-N, Na, K, Ca, and Mg) from soils amended with different rates (1%, 3%, and 5%) of sewage sludge and poultry manure. The breakthrough curves of cations were also simulated by the PHREEQC program. The addition of sewage sludge and poultry manure to the soil columns increased the leaching of nutrients compared to the control soil. For all soil columns, the highest concentrations of leached nutrients were observed in the first leachate and decreased exponentially over time. Regardless of the amount of amendments applied, the percentage (the proportion of cumulative nutrient leached relative to the exchangeable one) of cumulative leaching losses of NO₃-N, Na, K, Ca and Mg were significantly higher, while NH₄-N was lower from poultry-amended soils than sewage sludge-amended soils. Based on the results, more attention should be paid to the potential risk of soil nutrient leaching especially NH₄-N, K and NO₃-N posed after applying sewage sludge and poultry manure, respectively. The simulation results indicated that predicting breakthrough curves of NH₄-N, K, and Ca (mean NRMSE < 1) by the PHREEQC program was better than Mg and Na (mean NRMSE > 1) and cation exchange was the main mechanism to control the concentrations of cations in the leachates.

Introduction

World population growth and increasing demand for food have led to excessive use of land for agriculture, a sharp decrease in soil nutrients, and consequently a diminish in the soil fertility and quality of agricultural products. The application of chemical and organic fertilizers is recommended to compensate for soil nutrients. The use of chemical fertilizers is the fastest and most reliable way to improve soil fertility and macronutrients, such as nitrogen (N) and phosphorus (P). However, chemical fertilizers contribute to the non-point source N and P losses, which increase water and soil pollution, soil acidification, and accelerate eutrophication. Leaching of nutrients from the soil to groundwater is caused by several factors, such as environmental conditions, soil physical and chemical properties, agricultural activities, and chemical and organic fertilizer application (Li et al., 2016). The application of organic fertilizers with the optimum rate of chemical fertilizers is recommended for improving soil fertility, soil structure, and activity of the organisms. Organic farming systems that rely on the use of organic matter and the lack of use of chemical fertilizers are expanding because it is environmentally friendly and improve the quality of soil and water in comparison with modern agricultural systems. Various types of organic amendments (sewage sludge, animal manures, plant residues, biochar, etc.) are used to improve the physical, chemical, and biological properties of soil. Sewage sludge is an inexpensive and nutritious organic fertilizer that is widely used in agricultural land (Opiony et al., 1998; Brady & Weil, 2012). In many countries, the banning of sewage sludge disposal by burial and the lack of suitable landfill has increased the application of sewage sludge in agricultural land. One of the advantages of using sewage sludge in agriculture is the return of essential nutrients and organic matter to soil (Brockway,

1983; Bramayard, 2002). Poultry manure, such as sewage sludge, is suggested as a source of nutrients in some research (Sharples et al., 2004) and high concentrations of macronutrients have been reported in these organic manures. But there is concern about the presence of organic and inorganic pollutants in sewage sludge and poultry manure. The nutrients and pollutants in the sewage sludge and poultry manure can be leached when they enter the soil and cause pollution of groundwater (Li et al., 2016). Agriculture is one of the primary sources of water pollution and farmers must adopt sustainable practices to maintain optimum water quality in line with international standards (Thorburn et al., 2003; Jalali, 2005; Islam et al., 2011). Water conservation, while maintaining the function of living systems, is a major challenge for the agriculture industry (Elmi et al., 2005). Leaching of nutrients is an important environmental concern because the high concentrations of some ions in drinking water are harmful to human and aquatic ecosystem health (Jalali & Martipurpour, 2008). Excessive application of organic and inorganic fertilizers in agricultural lands causes N leaching and other nutrients into surface and groundwater. Leaching of nitrate ($\text{NO}_3\text{-N}$) in soils treated with N-rich fertilizers and organic fertilizers is a serious concern that has been considered in many investigations (Shephard, 1996; Corrêa et al., 2006; Samaras et al., 2008; Shepherd and Newell-Price, 2013; Forge et al., 2016). However, ammonium ($\text{NH}_4\text{-N}$) leaching in soils amended with organic and inorganic fertilizers has received little attention in research. There is also limited knowledge about the leaching of the main nutrients in sewage sludge and poultry manure, such as sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg) (Medalie et al., 1994; McLaren et al., 2003). Although Ca, Mg, and K nutrients have low environmental and harmful effects on human and animal health, but their leaching from soil causes the loss of valuable nutrients as well as the beneficial potential of sewage sludge for agriculture. Simulation of nutrient leaching using models provides an opportunity to estimate nutrients leaching and to help to explain the changes observed during leaching while reducing or eliminating field measurement costs (Ingraham & William, 2019). The PHREEQC program is a computer program to simulate chemical reactions and transport processes in soil and has been used by many researchers (Jalali & Latifi, 2018; Mazloomi & Jalali, 2017; Embile et al., 2019). A clear understanding of the potential leaching risk of nutrients from organic amended soils is needed so that management practices can be modified to protect water quality. Therefore, this study was carried out to investigate leaching of $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, Na, K, Ca, and Mg in soil columns amended with 1%, 3%, and 5% of sewage sludge and poultry manure. The cations breakthrough curves were also simulated by the PHREEQC software.

Materials and Methods

Soil and organic amendments

The sandy loam soil used in this study was collected from 0 - 20 cm depths of the soil layers in the Azandarian area, Hamadan, western Iran (Table 1). In this area, various crops and horticultural products, including grapes, wheat, vegetables, and forage are cultivated. Two types of organic amendments (sewage sludge and poultry manure) were widely used to increase soil fertility in Iran. Sewage sludge was collected from the wastewater treatment plant, Toyserkan, Hamedan, and poultry manure were purchased from the Netherlands. Farmers in Hamedan and Iran provide a significant portion of the organic fertilizers from imported fertilizers. Both organic fertilizers were air-dried, passed through a 2 mm sieve, and kept to measure their physical and chemical properties. The total N (Kjeldahl N) was measured by the Hess method (Hess, 1971). Electrical conductivity (EC) and pH of organic amendments were measured after extraction with distilled water (1:5 w/v organic amendments to water extract). Concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in organic amendments were extracted by 1 M KCl (1:10 w/v organic amendments to water ratio) and determined colorimetrically (Mulvaney, 1996). These extracted N forms may represent the available N. Organic amendments samples were digested in nitric acid (1:20 w/v organic amendments to nitric acid ratio) for extraction of total basic cations. Total Ca and Mg were determined by the titration method and total K and Na were measured by flame photometry (Hess, 1971). Characteristics of organic sewage sludge and poultry manure are shown in Table 2. The exchangeable cations (Ca, Mg, K and Na) in sewage sludge and poultry manure were extracted using 1 N ammonium acetate (NH_4OAc). The exchangeable cations in the soil before and after the addition of different rates of sewage sludge and poultry manure are given in Table 3 (exchangeable Ca, Mg, K and Na were calculated from the sum of cation exchange capacity (CEC) of soil and organic amendments, and

exchangeable $\text{NH}_4\text{-N}$ was measured by extraction with 1 M KCl in amended soils). Soil solution properties (pH, EC, and concentrations of cations) in the control soil and sewage sludge and poultry manure-amended soils were extracted using distilled water (1:1 w/v soil to water ratio), as well as the concentration of available $\text{NO}_3\text{-N}$ by 1 M KCl was extracted (Table 3). The concentration of $\text{NO}_3\text{-N}$ was measured colorimetrically.

Leaching experiments

The collected soil was air-dried and passed through a 2 mm sieve. Different rates (1%, 3%, and 5%) of sewage sludge and poultry manure were mixed homogeneously and manually with soil. Farmers usually add a lot of organic amendments to increase their crop yield, which is more than the amount needed for the yield improvement. Therefore, different rates of sewage sludge and poultry manure were used in this experiment to compare the leaching of nutrients and the risks of groundwater pollution with real conditions. The mixtures of soil and organic amendments were placed into columns consisting of Pyrex tubes, 30 cm in length and an internal diameter of 4.9 cm. The height and bulk density of the soil inside the columns were 10 cm and 1.67 g/cm^3 , respectively. The soils were kept at the end of the column by a Whatman no. 42 filter paper, which was supported by a nylon mesh base. To prevent the dispersion of surface soil, a filter paper was placed on the soil surface of the column. Distilled water was used for leaching of nutrients from columns. Soil columns were incubated at room temperature for 20 days and irrigated daily with distilled water. The leaching experiments were carried out in two replications and a total of 14 leaching columns were set up. The leachates were collected daily and stored at 2 degC for measurement of pH, EC, $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, Na, K, Ca, and Mg parameters. The pH and EC of leachates were measured using pH and electrical-conductivity meters, respectively. Concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in leachates were determined colorimetrically (Mulvaney, 1996). The concentration of Ca and Mg were determined by the titration method and K and Na were measured by flame photometry (Hess, 1971).

Simulation of cations leaching by PHREEQC program

For the simulation of leaching of $\text{NH}_4\text{-N}$, Na, K, Ca, and Mg in the control and sewage sludge and poultry manure-amended soils, the PHREEQC program (Parkhurst & Appelo, 2013) was used. The parameters applied for simulation of cations leaching included the concentrations of cations in soil solution, the values of CEC, the values of selectivity coefficients for the exchange of different cations with exchange sites, soil column characteristics (such as length of soil columns and leaching time). The selectivity coefficients values (Table 4) applied in the leaching simulation were determined based on the change of database coefficients and the best fit to the measured data (Jalali & Latifi, 2018). The cation exchange capacity of the soil and organic amendments were measured separately and the CEC values used in the simulation were calculated based on the sum of soil and organic amendments CEC. The soil solution properties of control and amended soils were also measured in the laboratory and used for simulation. The determination coefficient (r^2), root-mean-square error (RMSE), and normalized root-mean-square error (NRMSE) were used to evaluate the performance of the cation exchange model in PHREEQC program (Xiong et al., 2006; Mazloomi and Jalali, 2019).

1. Results and Discussion

2. Electrical conductivity changes in soil leachates

Fig. 1a indicates the EC leachate for different treatments. The results showed that the application of sewage sludge and poultry manure increased leachate EC compared to the control soil. Also, increasing the rates of both amendments increased leachate EC. The leachate EC was very high on the first day in all soil columns and exponentially decreased on the second day until a steady trend on the 20th day. Values of leachate EC in soil columns amended with different rates of poultry manure were higher than sewage sludge. Poultry manure and sewage sludge contain high soluble salts and therefore their application in soil increased soil solutes and thus increased EC. When the solutes of the soil are leached and the balance between the soil solution and the exchangeable sites is achieved, the value of leachate EC reaches a constant trend (Civeira & Lavado, 2008). Many researchers have reported that the use of different organic amendments increase the concentration of soil solutes and thus increases the EC in the soil, which is consistent with the results of

the present study (Gallardo-Lara & Nogales, 1987; Selvakumari et al., 2000; Niklasch & Joergensen, 2001; Atiyeh et al., 2001; Sarwar et al., 2003; Gonzalez et al., 2010; Angelova et al., 2013).

pH changes in soil leachates

The results showed that the leachate pH in the control soil fluctuated in the range of 7.70 to 8.12 and the mean of leachate pH during the leaching period was 7.93 (Fig. 1b). The application of sewage sludge and poultry manure decreased leachate pH compared to control soil. Mean leachate pH in soil columns amended with 1%, 3%, and 5% of sewage sludge and poultry manure were 7.64, 7.56, 7.47, 7.64, 7.48, and 7.46, respectively. Adding organic matter to soil buffers soil pH changes. Soil organic matter has many negative sites that bond with hydrogen ion in acidic soils and release hydrogen ion in basic soils and this mechanism neutralizes pH in both soil types. Organic residues usually contain large amounts of ions and their decomposition initially causes a temporary increase in soil pH. The soil microorganisms during the decomposition of plant residues into $\text{NH}_4\text{-N}$ cause a temporary increase in pH. The conversion of $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$ by the nitrification process reduces pH. If the $\text{NO}_3\text{-N}$ is lost during the leaching process, the pH will show an even greater reduction. The effects of organic matter on soil pH depend on the processes of production and loss of N (leaching into the soil and uptake by the plant), the quantity and quality of soil organic matter and the initial pH (Pocknee & Sumner, 1997; Paul et al., 2003; Butterly et al., 2013). Angelova et al. (2013) indicated that organic acid (amino acids, glycine, cysteine, and humic acid) production during the process of mineralization of organic matter by heterotrophic microorganisms and nitrification by autotrophic bacteria decrease soil pH.

Leaching of $\text{NH}_4\text{-N}$

The breakthrough curves and the cumulative amount of $\text{NH}_4\text{-N}$ leached from control soil and soils amended with 1%, 3%, and 5% of sewage sludge and poultry manure are shown in Fig. 2a. The results showed that the concentration of $\text{NH}_4\text{-N}$ in the leachate from the control soil was 0.5 mg/L on the first day and decreased exponentially over time. Low $\text{NH}_4\text{-N}$ concentration in the control soil may be due to the low content of organic matter and low release of $\text{NH}_4\text{-N}$ by mineralization of organic matter. Also applied $\text{NH}_4\text{-N}$ fertilizers in light-textured soils are rapidly converted to $\text{NO}_3\text{-N}$ by nitrification process because these soils have sufficient ventilation. Therefore, low concentrations of $\text{NH}_4\text{-N}$ in control soil leachate were expected. Di and Cameron (2005) indicated that $\text{NH}_4\text{-N}$ leaching rarely occurs in soil because the concentration of $\text{NH}_4\text{-N}$ in most surface soils is low and is maintained by exchange sites. Application of sewage sludge and poultry manure increased $\text{NH}_4\text{-N}$ leaching compared to control soil. The concentration of $\text{NH}_4\text{-N}$ on the first day in soils amended with rates of 1%, 3%, and 5% of sewage sludge and poultry manure were 21.2, 72.0, 207.9, 11.1, 46.8 and 91.2 mg/L, respectively, and decreased exponentially over time. An exponential decrease in $\text{NH}_4\text{-N}$ concentration over time may be due to the reduction in $\text{NH}_4\text{-N}$ concentration in the soil solution phase, oxidation of $\text{NH}_4\text{-N}$ to $\text{NO}_3\text{-N}$, and adsorption of residual $\text{NH}_4\text{-N}$ by soil exchange sites (Qiang et al., 2004). Soil columns amended with sewage sludge had high values of $\text{NH}_4\text{-N}$ leaching on day 10 to the end of the leaching due to lower C/N ratio of sewage sludge, higher total N content and possibly greater mineralization of sewage sludge compared to poultry manure. The cumulative amounts of $\text{NH}_4\text{-N}$ leached in soil columns amended with sewage sludge were significantly higher than poultry manure (Table 5). The results also showed that in control soil and soils amended with 1%, 3%, and 5% of sewage sludge and poultry manure, the cumulative amounts of $\text{NH}_4\text{-N}$ leached was equal to 14.4%, 87.3%, 131.4%, 133.1%, 33.1%, 55.7% and 67.1% of soil exchangeable $\text{NH}_4\text{-N}$, respectively. In soil columns containing 3% and 5% sewage sludge, the amount of $\text{NH}_4\text{-N}$ leached from soil was higher than exchangeable $\text{NH}_4\text{-N}$, probably due to the decomposition of organic residues and release of $\text{NH}_4\text{-N}$ by mineralization process. Zarabi and Jalali (2012) investigated $\text{NH}_4\text{-N}$ leaching in some native calcareous soils and their results showed that the cumulative amounts of $\text{NH}_4\text{-N}$ leached were 0.8–7.4 mg/kg. They also reported that the cumulative amount of $\text{NH}_4\text{-N}$ leached was about 14.1%–143.8% of the exchangeable $\text{NH}_4\text{-N}$ in different soils. Many researchers have reported that $\text{NH}_4\text{-N}$ leaching is high in light-textured soils treated with organic residues because these soils have low CEC and high hydraulic conductivity (Deare et al., 1995; Li et al., 1997; Gundersen, 1998; Pathan et al., 2002; Zarabi & Jalali, 2012). Also when the soil exchange sites are saturated and large amounts of $\text{NH}_4\text{-N}$ fertilizers enter the soil or in adverse environmental conditions where nitrification is low

in the soil, $\text{NH}_4\text{-N}$ leaching increases (Wang & Battany, 1995; Wang & Zhang, 2004; Herrmann et al., 2005; Haynes and Judge, 2008). Oren et al. (2003) reported that high concentrations of soluble salts and high pH in the soil are the main factors preventing the oxidation of $\text{NH}_4\text{-N}$ and nitrite ($\text{NO}_2\text{-N}$), which increases $\text{NH}_4\text{-N}$ leaching in the soil. Some studies have reported that $\text{NH}_4\text{-N}$ leaching from soils treated with sewage sludge and a variety of livestock manure was negligible (Medalie et al., 1994; Cameron et al., 1995; Cameron et al., 1996; Carey et al., 1997), which is contrary to the results of the present study. The cause of the contradiction between the present study and other researches may be due to differences in soil texture, type of organic residues, amount of $\text{NH}_4\text{-N}$ in the organic residues, degree of decomposition of organic residues, and duration of leaching. There were positive correlations (Table 6) between cumulative $\text{NH}_4\text{-N}$ leaching losses and exchangeable $\text{NH}_4\text{-N}$, Ca, and Mg, while positive correlations were found with solution $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and Mg in the control and amended soil.

Leaching of $\text{NO}_3\text{-N}$

The breakthrough curve and the cumulative amount of $\text{NO}_3\text{-N}$ leached are shown in Fig. 2b. The concentration of $\text{NO}_3\text{-N}$ in the control soil in the first leachate was 14 mg/L and decreased to less than 10 mg/L over time. The rapid movement of $\text{NO}_3\text{-N}$ ions in the soil is due to the repulsive force between the $\text{NO}_3\text{-N}$ anion and the negative charge particles in the soil. Zarabi and Jalali (2012) investigated $\text{NO}_3\text{-N}$ leaching in some native calcareous soils with different textures. Their results showed that the $\text{NO}_3\text{-N}$ concentration was high in the first leachate and in the subsequent leachates the $\text{NO}_3\text{-N}$ concentration was significantly reduced, which is in agreement with the results of the present study. Razzaque and Hanafi (2004) reported that $\text{NO}_3\text{-N}$ concentration in the first leachate of peat soil was 13 mg/L and decreased abruptly. Application of sewage sludge and poultry manure amendments increased $\text{NO}_3\text{-N}$ leaching. Concentrations of $\text{NO}_3\text{-N}$ in the first leachate in columns amended with 1%, 3%, and 5% of sewage sludge and poultry manure were 32.5, 65.7, 125.1, 45.3, 150.2 and 347.6 mg/L, respectively. Nitrate concentration in poultry manure was higher than sewage sludge, so $\text{NO}_3\text{-N}$ leaching was higher in the presence of poultry manure as expected. Nitrate concentration in all soil columns reached equilibrium after about 10 days. High levels of $\text{NO}_3\text{-N}$ in leachate even after 20 days indicate the possibility of groundwater contamination with high rates of sewage sludge and poultry manure. The cumulative amount of $\text{NO}_3\text{-N}$ leached in control soil and soil columns amended with 1%, 3% and 5% of sewage sludge and poultry manure were 9.3, 25.9, 39.4, 62.5, 27.8, 75.4 and 173.9 mg/kg, respectively and significantly higher amounts of $\text{NO}_3\text{-N}$ was leached from soil amended with 5% poultry manure (Table 5). The results also showed that in the control soil and soils amended with 1%, 3% and 5 % of sewage sludge and poultry manure, the amounts of $\text{NO}_3\text{-N}$ leached was equal to 94.0%, 123.3%, 121.2%, 123.4%, 104.6%, 128.9% and 150.2% of available $\text{NO}_3\text{-N}$, respectively. Nitrate in the soil is readily transported by diffusion and mass flow process, so a large proportion of N fertilizers are exposed to leaching. Groundwater contamination by $\text{NO}_3\text{-N}$ has been reported by many researchers as a result of the overuse of organic fertilizers (Tong et al., 1997; Gonzalez et al., 2009; Masaka et al., 2013; Aronsson et al., 2014; Parvage et al., 2015). Gonzalez et al. (2009) reported a high concentration of $\text{NO}_3\text{-N}$ in leachate in a study on soil treated with poultry manure. In this study, $\text{NO}_3\text{-N}$ leaching increased significantly with increasing the application rates of sewage sludge and poultry manure. Some researchers have reported that there is a positive relationship between the applied rate of fertilizers and the leaching of $\text{NO}_3\text{-N}$ (Gondek & Konpee, 2009; Shepherd & Newell-Price, 2013). One of the reasons for high $\text{NO}_3\text{-N}$ leaching in the present study is due to the sandy texture of the soil, which caused a large amount of $\text{NO}_3\text{-N}$ in sewage sludge and poultry manure to be leached from the soil columns. Shepherd and Newell-Price (2013) indicated that $\text{NO}_3\text{-N}$ leaching in soil was affected by soil texture and was higher in sandy soils. In sandy soils, N mineralization and $\text{NO}_3\text{-N}$ leaching are high because high temperatures and sandy soil texture increase the mineralization of organic N. The effect of soil texture on N mineralization is due to the amount of clay (Breland & Hansen, 1996). In soils with high clay content, a physical shield prevents the mineralization of organic matter (Stenger et al., 1995). Sadej (2009) indicated that the amount and dominant form of N leaching in soils amended with different types of sewage sludge and sewage sludge compost depends on the application rate, application method, and type of sewage sludge.

There were positive correlations (Table 6) between cumulative $\text{NO}_3\text{-N}$ leaching losses and exchangeable Na

and EC, while positive correlations were found with solution Na, K, and Ca in the control and amended soil.

Leaching of Na and K

The breakthrough curves of Na and the cumulative amounts of Na leached are shown in Fig. 3a. The results showed that in control and amended soils maximum concentration of Na was observed in the first leachate. The high concentrations of Na in the leachate of poultry manure-amended soils are due to the higher Na content in poultry manure compared to sewage sludge (Table 2). The concentration of Na in the leachate in all soil columns decreased exponentially until day 6-14 and after this time remained constant. The results showed that significantly higher amounts of Na were leached from soil amended with 3% and 5% poultry manure (Table 5). Cumulative amounts of Na leached in control soil and soil columns containing 1%, 3% and 5% sewage sludge and poultry manure were 2.6, 9.5, 23.3, 38.9, 41.7, 125.8 and 201.1 mg/kg (Table 5), corresponding to 1.9%, 6.9%, 14.5%, 24.2%, 25.9%, 60.8% and 79.5%, respectively. There were positive correlations (Table 6) between cumulative Na leaching losses and exchangeable Na, while positive correlations were found with pH, EC, and solution Na, K, and Ca in the non-amended and amended soil.

The breakthrough curves of K and the cumulative amounts of K leached are shown in Fig. 3b. The results showed that a significant amount of K was leached from amended soils. Over time, K concentration in control and amended soils decreased exponentially and K concentration in the leachates in poultry manure amended-soils was higher than that of sewage sludge. The results showed that significantly higher amounts of K were leached from soil amended with 3% and 5% poultry manure (Table 5). The cumulative amounts of K leached in control soil and soils containing 1%, 3% and 5% of sewage sludge and poultry manure were 57.6, 68.9, 129.4, 168.5, 211.9, 746.5, 1123.4 mg/kg (Table 5), corresponding to 8.1%, 9.7%, 18.2%, 23.7%, 29.8%, 100.5% and 158.6%, of exchangeable K, respectively. The poultry manure used in the present study was enriched by K fertilizer, so in the soils amended with 3% and 5% poultry manure the amount of leached exchangeable K was higher than the soil exchangeable K. Potassium leaching in the soil depends on the concentration of K in the soil solution, the type of soil clay minerals, the dry and wet conditions of soil, and the type of cations (especially Ca, Mg, and Na) present in the solution (Evangelou & Lumbanraja, 2002). The addition of various organic residues such as poultry manure and sewage sludge increases the concentration of K in the solution phase and thus increases its leaching (Adegbedi et al., 2003; Gonzalez et al., 2009). Adding these residues also increases the concentration of Ca, Mg, and Na in the soil and thus increases the release of K from the soil exchange sites. Jones et al. (2012) reported that the application of poultry manure increased the concentration of Na and K in soil solution, and K had a higher concentration than Na in leachate, which is consistent with the results of the present study. Zhang et al. (2004) investigated the effect of animal manure on EC and solute concentration in soil leachates. Their results showed that the application of high levels of animal manure increased the concentration of nutrients such as Na and K in the leachate, and the highest concentration of Na and K were observed in the first leachate. The addition of sewage sludge to soil also increases the leaching of Na and K into the soil because sewage sludge is the source of these cations (Medali et al., 1994; McLaren et al., 2003; Ahlberg et al., 2006).

Like cumulative Na leached, there were positive correlations (Table 6) between cumulative K leaching losses and exchangeable Na, while positive correlations were found with pH, EC, and solution Na, K, and Ca in the non-amended and amended soil, indicating the similarities between these ions.

Leaching of Ca and Mg

The breakthrough curves and the cumulative amounts of Ca and Mg in control and amended soils are shown in Figs. 4. Application of amendments increased the concentration of Ca and Mg in the leachates and the leaching of both cations in all soil columns decreased exponentially over time. Increasing rates of amendments also increased the concentrations of Ca and Mg in the soil leachates. The results showed that the cumulative amounts of Ca and Mg leached in the columns treated with poultry manure were higher than the sewage sludge. The results showed that significantly higher amounts of Ca were leached from soil amended with 5% poultry manure (Table 5). The amounts of exchangeable Ca leached in the control soil and the soils amended with 1%, 3%, and 5% of sewage sludge and poultry manure were 16.2%, 18.3%, 21.5%, 23.1%,

16.4%, 23.5% and 25.7%, respectively, and the amounts of exchangeable Mg leached in these treatments were 33.5%, 37.8%, 32.9%, 48.4%, 38.3%, 59.9% and 63.5%, respectively. The trend of Mg concentration in leachate was similar to that of Ca, and the same leaching trend is due to the similar behavior of these two cations in soil (McLaren et al., 2003; Gonzalez et al., 2009). The results showed that significantly higher amounts of Mg were leached from soil amended with 3% and 5% poultry manure (Table 5). In some studies, the effects of organic residues on the leaching of Ca and Mg have been reported. Zhang et al. (2004) reported that animal manure application had a significant effect on the leaching of nutrients such as Ca and Mg, and cumulative amounts of cations leached increased with the increasing rate of manure. Haynes and Judge (2008) investigated the effect of surface application of poultry manure (0-5 cm depth) on nutrient and salinity leaching in soil columns, and measured nutrient concentrations in 4 leachate volumes on days 9, 37, 58 and 86 after the leaching. Their results showed that the addition of poultry manure increased the leaching of different nutrients such as Ca and Mg compared to control soil. Ahlberget al. (2006) investigated the leaching of various cations from surface soil treated with sewage sludge. Their results showed that soil treated with sewage sludge increased the leaching of nutrients such as Ca and Mg from the soil and the amount of Ca and Mg leached was equal.

There were positive correlations (Table 6) between cumulative Ca leaching losses and exchangeable $\text{NH}_4\text{-N}$, K, Ca, and Mg, while positive correlations were found with EC and solution $\text{NO}_3\text{-N}$, Ca, and Mg in the non-amended and amended soil. There were positive correlations (Table 6) between cumulative Mg leaching losses and exchangeable Na, while positive correlations were found with EC and solution Na, K, Ca, and Mg in the non-amended and amended soil.

In general, based on the proportion of cumulative nutrients leached relative to the exchangeable ones, the order of nutrients leached in sewage sludge-amended soils was $\text{NH}_4\text{-N} > \text{NO}_3\text{-N} > \text{Mg} > \text{Na} > \text{K} > \text{Ca}$, whereas the order for poultry-amended soils was $\text{K} > \text{NO}_3 > \text{Na} > \text{NH}_4\text{-N} > \text{Mg} > \text{Ca}$. Thus, more attention should be paid to the potential risk of soil nutrient leaching especially $\text{NH}_4\text{-N}$, and K, $\text{NO}_3\text{-N}$ posed after application of sewage sludge and poultry manure, respectively.

Simulation of cations leaching by PHREEQC program

The measured and simulated breakthrough curves of $\text{NH}_4\text{-N}$, Na, K, Ca, and Mg is shown in Figs. 5-9. The values of r^2 , RMSE, and NRMSE obtained from the cations leaching simulation are shown in Tables 7-9. The main mechanism to simulate the leaching of these cations is the cation exchange that controls the concentrations of the cations in leachates. The addition of organic amendments to soil increased CEC of soil columns, which was defined for different soil columns in the PHREEQC program. Some researchers also reported that the use of organic residues increased soil CEC (Ouedraogo et al., 2001; Walker & Bernal, 2005; Clark et al., 2007). The results showed that $\text{NH}_4\text{-N}$ leaching was well predicted (Fig. 5) in soils treated with sewage sludge and poultry manure ($r^2=0.84\text{-}0.97$, $\text{RMSE}=1.23\text{-}24.11$). But the simulation of $\text{NH}_4\text{-N}$ leaching in the control soil was not very accurate ($r^2=0.61$, $\text{RMSE}=0.14$). The $\text{NH}_4\text{-N}$ curve tailing did not match well with the measured data in soil columns treated with 3% and 5% of sewage sludge, which may be due to mineralization and ammonification of sewage sludge over time. The breakthrough curves of Na were less accurate (Fig. 6) than the other cations ($r^2=0.51\text{-}0.67$, $\text{RMSE}=1.7\text{-}93.38$), and the Na leaching was overestimated. The breakthrough curves of K (Fig. 7) and Ca (Fig. 8) indicated that K and Ca leaching in control soil and soils amended with sewage sludge and poultry manure were well predicted (High r^2 and low RMSE). Simulation of Mg (Fig. 9) leaching showed that there was no good agreement between measured and simulated data in some treatments and the simulation had low accuracy. For a better comparison of cation simulation results, the NRMSE was calculated (Table 9). The NRMSE is used to compare models with different scales or with different observation values. NRMSE values, similar to RMSE, indicate that simulation of leaching of $\text{NH}_4\text{-N}$, K, and Ca (mean $\text{NRMSE} < 1$) by cation exchange model was better than Mg and Na (mean $\text{NRMSE} > 1$). Many studies have used PHREEQC program to simulate the adsorption, transport, and leaching of different elements (Ferrell et al., 2002; Komnitsas et al., 2006; Congzhi et al., 2006; Martens et al., 2011; Mazloomi & Jalali, 2017; Jalali & Latifi, 2018). Ferrel et al. (2002) used the PHREEQC program to predict lead (Pb) transport in the clay layer of a landfill and simulated the effect of

different parameters (CEC, selectivity coefficients, diffusion coefficient, and different amounts of Pb) on Pb transport. Congzhi (2006) investigated the transport of K, Na, Ca, and Mg through soil column experiments and simulated the measured data using PHREEQC and CXTFIT programs. He reported that the simulation results were in good agreement with the measured data and PHREEQC simulated the measured data better than CXTFIT. Martens et al. (2011) measured leaching of K, Na, Ca, and Mg cations into the clay column over 2600 days (clay column was leached by different concentrations of sodium nitrate) and then simulated the measured results by PHREEQC program. They indicated that cation exchange is the predominant mechanism for control of cations leaching into the clay column.

Conclusions

Sewage sludge and poultry manure are widely used to provide nutrients for crops and improve soil quality. However, an excess application may increase the risk of nutrient loss and groundwater pollution. Since our research was performed in the laboratory, which does not exactly replicate conditions in the field, we were able to determine the relative risk of leaching among the tested organic amendments. The content of nutrients and the application rate of sewage sludge and poultry manure were influential factors on the values of leaching of nutrients. The maximum value of $\text{NH}_4\text{-N}$ leaching was observed in the soil columns amended with 5% sewage sludge and the maximum values of $\text{NO}_3\text{-N}$, Na, K, Ca and Mg leaching were observed in the columns amended with 5% poultry manure. In general, the order of nutrients leached in sewage sludge-amended soils was $\text{NH}_4\text{-N} > \text{NO}_3\text{-N} > \text{Mg} > \text{Na} > \text{K} > \text{Ca}$, whereas the order for poultry-amended soils was $\text{K} > \text{NO}_3\text{-N} > \text{Na} > \text{NH}_4\text{-N} > \text{Mg} > \text{Ca}$, indicating the potential risk of soil nutrient leaching, especially $\text{NH}_4\text{-N}$, K and $\text{NO}_3\text{-N}$ posed after application of sewage sludge and poultry manure, respectively, should be given greater attention. The output of the PHREEQC program showed that the simulated breakthrough curves, particularly for $\text{NH}_4\text{-N}$, K, and Ca were well matched to the measured data. The main mechanism to simulate the leaching of these cations was the cation exchange that controls the concentration of the cations in leachates.

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Table 1 . Some physical and chemical properties of soil.

$\text{NH}_4\text{-N}$ (mg/kg)	$\text{NO}_3\text{-N}$ (mg/kg)	Total N (%)	OM (%)	CaCO_3 equivalent (%)	EC (dS/m)	pH (H_2)
5.4	10.2	0.2	3.7	4.7	0.2	7.1

Table 2. Characteristics of organic sewage sludge and poultry manure.

Characteristics	Sewage sludge	Poultry manure
pH	6.83	7.27
EC (dS/m)	4.95	12.72
Total N (%)	3.05	1.47
C (%)	19.45	28.35
C/N	6.40	19.28
NH ₄ -N (mg/kg)	4760	780
NO ₃ -N (mg/kg)	299	595
Total Na (mg/g)	2.10	10.20
Total K (mg/g)	4.50	48.60
Total Ca (mg/g)	42.10	37.80
Total Mg (mg/g)	11.40	14.00
Exchangeable Na (cmol _c /kg)	1.12	6.90
Exchangeable K (cmol _c /kg)	0.59	0.64
Exchangeable Ca (cmol _c /kg)	42.40	34.00
Exchangeable Mg (cmol _c /kg)	12.00	6.00

Table 3. The amount of exchangeable and soil solution characteristics in control and amended soils with different rates of applied sewage sludge and poultry manure.

Parameter	Control soil	Sewage sludge 1%	Sewage sludge 3%	Sewage sludge 5%
	Exchangeable cations	Exchangeable cations	Exchangeable cations	Exchangeable cations
NH ₄ (cmol _c /kg)	0.03e	0.2d	0.6c	1.2a
Na (cmol _c /kg)	0.6c	0.6c	0.7bc	0.7bc
K (cmol _c /kg)	1.7c	1.8c	2.1ab	2.1ab
Ca (cmol _c /kg)	8.3f	8.7e	9.4c	10.2a
Mg (cmol _c /kg)	2.6d	2.7cd	2.9b	3.1a
	Soil solution	Soil solution	Soil solution	Soil solution
pH	7.42b	7.45b	7.40bc	7.30c
EC (dS/m)	1.19g	1.67f	2.10e	3.15c
NH ₄ (mM)	0.02e	0.41c	0.78b	0.95a
NO ₃ (mM)	0.07d	0.19c	0.42b	0.83a
Na (mM)	2.45f	2.75ef	2.90de	3.15cd
K (mM)	2.67f	3.05ef	3.40de	3.70d
Ca (mM)	7.80f	10.90e	13.10d	15.20c
Mg (mM)	3.20f	4.70e	7.20c	10.40a

Means followed by dissimilar letters within a row are significantly different at $p < 0.05$ according to Duncan test.

Table 4. Selectivity coefficients values used to simulate leaching of cations in control and amended soils with rates of 1%, 3% and 5% sewage sludge and poultry manure.

$Mg^{2+} + 2X^- = MgX_2$	$Ca^{2+} + 2X^- = CaX_2$	$K^+ + X^- = KX$	$Na^+ + X^- = NaX$	$AmH^+ + X^- = AmX$
1.60	2.10	2.20	2.20	2.20
1.00	1.30	1.50	1.20	0.70
0.60	0.80	0.90	0.60	0.40

$Mg^{2+} + 2X^- = MgX_2$	$Ca^{2+} + 2X^- = CaX_2$	$K^+ + X^- = KX$	$Na^+ + X^- = NaX$	$AmH^+ + X^- = Am$
0.60	0.80	0.70	0.70	0.30
0.90	1.40	0.70	0.70	0.90
0.30	0.40	0.30	0.00	0.30
0.60	0.80	0.20	0.00	0.40

Table 5. The cumulative amounts of nutrients leached from control and amended soils with rates of 1%, 3% and 5% sewage sludge and poultry manure.

nutrients	Control soil	Sewage sludge 1%	Sewage sludge 3%	Sewage sludge 5%	Poultry manure 1%
NH₄	0.27f	10.20de	46.17b	93.32a	3.87ef
NO₃	3.00d	8.40cd	12.80c	20.29b	9.04cd
Na	4.47f	15.70e	38.64d	64.85c	69.19c
K	19.25e	22.5e	42.12d	54.81cd	69.06c
Ca	87.84f	103.60e	131.10d	152.70b	91.46f
Mg	33.96b	39.84b	37.24b	58.49a	40.33b

Means followed by dissimilar letters within a row are significantly different at $p < 0.05$ according to Duncan test.

Table 6. Pearson correlation coefficients between cumulative leaching amounts of NH₄, NO₃, Na, K, Ca, and Mg and their exchangeable and solutions in control and amended soil.

		Cumulative nutrients leached		Cumulative nutri
Exchangeable cations	Exchangeable cations	NH₄	NH₄-N	NH₄-N
		Na	Na	0.92**
		K	K	0.13
		Ca	Ca	0.58
		Mg	Mg	0.92**
Soil solution properties	Soil solution properties	pH	pH	0.77*
		EC	EC	-0.44
		NH₄	NH₄	0.30
		NO₃	NO₃	0.87**
		Na	Na	0.99**
		K	K	0.46
		Ca	Ca	0.01
		Mg	Mg	0.39
				0.85**

*significant at 5 % level, ** significant at 1 % level.

Table 7. Determination coefficient (r^2) values obtained from simulation of cations leaching in in control and amended soils with rates of 1%, 3% and 5% sewage sludge and poultry manure.

Mg	Mg	Ca	Ca	K	Na	NH ₄ -N	Soil Columns
0.69	0.81	0.81	0.95	0.95	0.61	0.61	Control soil
0.30	0.72	0.72	0.79	0.79	0.64	0.84	Sewage sludge 1%

Mg	Mg	Ca	Ca	K	Na	NH ₄ -N	Soil Columns
0.54	0.83	0.83	0.81	0.81	0.51	0.91	Sewage sludge 3%
0.74	0.77	0.77	0.79	0.79	0.58	0.90	Sewage sludge 5%
0.72	0.89	0.89	0.85	0.85	0.67	0.88	Poultry manure 1%
0.74	0.88	0.88	0.94	0.94	0.57	0.97	Poultry manure 3%
0.29	0.92	0.92	0.83	0.83	0.63	0.86	Poultry manure 5%

Table 8. Root-mean-square error (RMSE) values obtained from simulation of cations leaching in in control and amended soils with rates of 1%, 3% and 5% sewage sludge and poultry manure.

Mg	Ca	K	Na	NH ₄ -N	Soil Columns
33.19	54.30	4.09	1.70	0.14	Control soil
34.08	70.52	13.71	7.73	3.77	Sewage sludge 1%
28.25	62.15	26.43	16.17	12.40	Sewage sludge 3%
26.11	71.55	39.36	28.03	24.11	Sewage sludge 5%
40.40	61.10	29.70	22.20	1.23	Poultry manure 1%
29.14	70.79	73.89	54.00	3.37	Poultry manure 3%
43.79	57.12	209.97	93.38	10.22	Poultry manure 5%

Table 9. Normalized Root Mean Square Error (NRMSE) values obtained from simulation of cations leaching in control and amended soils with rates of 1%, 3% and 5% sewage sludge and poultry manure.

Mg	Ca	K	Na	NH ₄ -N	Soil Columns
1.18	0.71	0.31	2.86	0.74	Control soil
1.27	1.01	0.90	3.70	0.54	Sewage sludge 1%
1.12	0.70	0.93	3.16	0.40	Sewage sludge 3%
0.66	0.69	1.06	3.26	0.39	Sewage sludge 5%
1.48	0.99	0.64	2.42	0.47	Poultry manure 1%
0.66	0.75	0.47	1.95	0.30	Poultry manure 3%
0.90	0.52	0.82	2.11	0.43	Poultry manure 5%
1.03	0.76	0.73	2.78	0.47	Mean

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Figure.pdf available at <https://authorea.com/users/333594/articles/459755-measuring-and-simulating-leaching-of-nutrients-from-a-calcareous-soil-amended-with-sewage-sludge-and-poultry-manure>

