Application of pig slurry to soils. Effect of air stripping treatment on nitrogen and TOC leaching

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ABSTRACT

The effect of physical–chemical slurry treatment on the mobility and transformation of nitrogen and organic matter from pig slurry after soil application is evaluated. Two different pig slurries (one treated by stripping with air at $pH = 9$ and another non-treated) were applied at the top of a soil column, containing approximately 100 kg of soil. Effluents were monitored measuring concentration values of ammonia, nitrites, nitrates and total organic carbon (TOC). The breakthrough curves were modelled using STANMOD and HYDRUS 1D codes. Low concentrations of ammonia were detected in the effluent recovered at the bottom of the soil profile for both types of slurry. Nitrate concentration in effluent was lower and more homogenous over time when applying stripping treated pig slurry. In N modelling, adsorption of ammonia by soil proved an important process, nitrite and nitrate adsorption being less significant, although not negligible. Transformation from ammonia to nitrite controls the kinetics of the nitrification process. Total organic carbon in the column effluent was higher in the experiment using treated pig slurry, which can be attributed to organic matter solubilisation in the stripping treatment process.

1. Introduction

Pig slurry and manure from farms have traditionally been used as fertilizers in agricultural applications. However, livestock specialization and intensification as well as a gradual decrease in crop areas in recent decades make proper use of these by-products without causing environmental pollution difficult, especially in pig farming. Pig slurry contains a high quantity of nitrogen that can be leached to groundwater; possibly generate a high nitrate concentration that on occasions makes water harmful for human consumption (e.g., Ongley, 1997). This may lead to serious environmental and health problems in areas where uncontrolled discharge of pig slurry takes place.

The main risk factor of pig slurry application is its high ammonia content. During the nitrification process, ammonia (NH_4^+) is first transformed into nitrite (NO_2^-), and then into nitrate (NO_3^-) by means of soil aerobic bacteria action (Cavagnaro et al., 2008). Under adequate moisture and temperature conditions, nitrification rate can reach 10–70 kg/ha per day. This nitrate intake, which is higher than crop needs, is leached in-depth and poured into groundwater. Processes to reduce ammonia content in pig slurry before soil application are thus of great interest for environmental research.

Air stripping is a widely applied physical-chemical process for removing ammonia from wastewaters. The stripping process involves the mass transfer of ammonia from the liquid phase to the gas phase. Transfer is accomplished by contacting the high concentration liquid ammonia with a gas (usually air) that does not initially contain ammonia (Metcalf and Eddy, Inc, 2003).

To evaluate the efficiency of this particular pig slurry treatment, it is necessary to study the behaviour of the treated slurry once it has been applied to the soil. In particular, it is important to take into account the transformations among the different nitrogen forms and the hydrodynamic conditions during the solute transport process.

Experimentation with large soil columns constitutes an interesting tool to study transport of different pig slurries under controlled and comparable experimental conditions. Miscible displacement experiments are perhaps the most important among the available methodological approaches for characterizing solute transport. Soil column lysimeters provide a fundamental understanding of solute transport processes by combining the ability to imitate a natural environment and the boundary conditions control (Álvarez-Benedí et al., 2005a).

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The purpose of this work was to study the effect of an air stripping treatment of pig slurry on the transport and transformation of the main solutes (i.e., ammonia, nitrite, nitrate and total organic carbon) in soil. The results of this study will prove relevant for gaining an insight into leaching differences when treated or non-treated pig slurries are applied to the soil and for preventing possible environmental impact.

2. Materials and methods

2.1. Soil

The soil was a Typic Xerofluvent collected from Zamadueñas (Valladolid, Spain), a loamy sand (56% sand, 28% lime, 16% clay), with a pH = 7.9; organic matter OM = 1.6%; cation exchange capacity CEC = 8.24 meq/100 g, and bulk density $\rho = 1.2$ g/cm^3.

2.2. Pig slurries

The pig slurry used came from a pig farm situated in the province of Valladolid (Spain). A fraction of the pig slurry was packed inside closed containers and a second fraction was treated by ammonia stripping in air presence (Del Álamo et al., 2004), with a previous alkalinisation step. It is important to note the difference between fresh pig slurry (recently collected, all nitrogen is present as ammonia), non-treated pig slurry (just before land application, some ammonia has been transformed into nitrates), and treated pig slurry (after the stripping process, in which most of the ammonia has been removed and some ammonia has been transformed into nitrate).

Characterization of the different pig slurries was carried out according to the Standard Methods for the examination of water and wastewater (APHA, AWWA, WEF, 2005). Total nitrogen was analyzed by the Macro-Kjeldahl method, titrimetric method using a preliminary distillation step was employed for ammonia nitrogen, nitrite and nitrate concentrations were determined by ion chromatography with chemical suppression of eluent conductivity. Total organic carbon was analyzed by the high-temperature combustion method using a Shimadzu TOC-5050 with a solid sample module SSM 5000A. The characteristics of the different pig slurry types used in this work are shown in Table 1.

2.3. Description of the column experiments

The experimental device is based on a 0.25 m diameter and 1 m deep PVC column filled with 100 kg of disturbed soil using the procedure described by Corwin (2000). The column was connected to an automatic effluent collector system, which controlled the lower boundary condition by means of suction. At the top of the column a homogenous water distribution system, comprising a needle matrix, was installed.

Two experiments were carried out in the described soil column under steady flow conditions. To determine the hydrodynamic conditions of the column, the conservative tracer pentafluorobenzoic

acid (PFB) was added in both experiments. At the beginning of the experiments, steady soil moisture saturation conditions were imposed. Soil humidity was registered continuously during the experiments at five different depths using TDR devices. As expected due to the steady water flows in the column, no significant changes in soil humidity were detected during the experiments. Almost identical soil humidity values were registered in both experiments.

In the first experiment, a volume of 0.70 L of the treated pig slurry and 0.5 g of PFB were applied. In the second experiment, 0.80 L of non-treated pig slurry and 0.5 g of PFB were applied. After these initial applications, a constant flow of 1.4 mL/min of a 0.02 M CaCl$_2$ solution was applied at the top of the column with a standard pump used in chromatography, as this equipment produces a very stable flow.

In both cases, 9 mL samples were recovered every two hours for analysis. HPLC chromatography with an ultraviolet-visible detector was used to analyze PFB (Haws et al., 2004). Ammonia concentration was measured using the titrimetric method. Ion chromatography with chemical suppression of eluent conductivity was applied to analyze nitrite and nitrate concentrations. The high-temperature combustion method using a Shimadzu TOC-5050 instrument was employed for total organic carbon determination. APHA, AWWA, WEF (2005) methods were employed for the ammonia, nitrite, nitrate and TOC analysis.

Once all the concentrations were negligible, the experiments were concluded. The final times were 675 h and 479.5 h, for experiments 1 and 2, respectively.

2.4. Numeric modelling

STANMOD (STudio of ANalytical MODels, Simunek et al., 1999a) software, including the CXTFIT 2.1 algorithms (Toride et al., 1999) was employed to estimate the transport parameters in the soil column from the experimental PFB tracer data and the TOC transport parameters. Reverse simulation using Levenberg–Marquardt non-linear least squares was applied to fit the experimental tracer and TOC breakthrough results to the mathematical resolution of the theoretical transport model. The model, based on the convection–dispersion equation, considers two non-equilibrium soil regions (mobile and stagnant water fraction) (Van Genutchen and Wierenga, 1977) and linear isotherm adsorption equilibrium. The solute adsorption is modelled through the retardation factor R:

$$R = 1 + \frac{\rho}{\theta} \cdot K_D$$

ρ being the soil density [M L^{-3}], θ the soil humidity [L^3 L^{-3}] and K_D [L^3 M^{-1}] the solute adsorption linear equilibrium coefficient.

The HYDRUS 1D code was used (Simunek et al., 1999b) to model the more complex multisolute transport in soils (ammonia, nitrite and nitrate). The program solves the flow and transport equations applying a Galerkin type finite difference method (Gray and Pinder, 1976). HYDRUS also provides reverse simulation using a Levenberg–Marquardt algorithm. Solute adsorption is, again, modelled through the retardation factor R considering linear isotherm equilibrium adsorption. This software allows solute chain reaction simulation using first order kinetic reactions. HYDRUS thus proves highly suitable to represent the transformation of ammonia into nitrite and nitrate using a model widely tested (Persicani, 1996; Tebes-Stevens and Valocchi, 2000).

A multisolute transport simulation with HYDRUS 1D was thus carried out, using hydrodynamic values obtained for the tracer, and simulating simultaneous transport of nitrates, nitrites, ammonia, and TOC (Álvarez-Benedí et al., 2005a,b).

Table 1
Pig slurry composition.

	Fresh	Treated	Non-treated
Total N (mg/L)	2350	1790	2350
Ammonia N (mg/L)	1810	310	750
N-NO$_3^-$ (mg/L)	106	1302	1150
N-NO$_2^-$ (mg/L)	Nd[a]	95	Nd[a]
TOC (mg/L)	4442	4389	4442

[a] Nd.: Non detected.