



SOILS AS NATURAL REACTORS FOR SWINE WASTEWATER TREATMENT

[LOS SUELOS COMO REACTORES NATURALES PARA EL TRATAMIENTO DEL AGUA RESIDUAL PORCINA]

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SUMMARY

The ability of soils as natural reactors depends of soil properties such as organic matter content (OM), cation exchange capacity (CEC) and percentage of clay (PC) as well as the properties waste in question, in this case, swine wastewater (SWW) Pedotransfer functions (PTF) enable certain processes to be determined from easily measured soil properties. The aims of this study were i) to generate PTF to estimate the retention and mineralisation of dissolved organic matter (DOM) present in swine wastewater (SWW) based on measurements of OM, CEC and PC and ii) to identify the soils most suited to acting as natural reactors for treating SWW, using multicriteria analysis. Samples were taken from ten soils (epipedons or superficial samples) to measure the retention of dissolved organic matter (RDOM) in 30 cm high soil columns, making three applications of SWW. In addition, an experiment was carried out in pots to measure the effect of SWW on soil carbon evolution (SCE) and the potential anaerobic nitrogen mineralisation (PANM). Multiple regressions were made using soil OM (%), CEC ($\text{cmol}^+ \text{kg}^{-1}$) and PC (%) as independent variables and RDOM (measured as chemical oxygen demand), SCE and PANM as dependent variables. The PFT found were: $\text{RDOM} = 41.5 + (2.8*\text{CEC}) - (0.81*\text{PC}) - (3.5*\text{OM})$ $r = 0.81$; $\text{SCE} = 542.3 + (20.1*\text{OM}) + (4.6*\text{CEC}) - (2.7*\text{PC})$ $r = 0.96$; $\text{PANM} = -8.4 + (3.45*\text{OM}) + (1.12*\text{PC}) - (2.20*\text{CEC})$ $r = 0.88$. The most suitable soils for acting as natural reactors of SWW were the Luvisol (LVct) and an unclassified EPI-1.

Keywords: mineralisation; pedotransfer functions; soil carbon evolution; dissolved organic matter.

RESUMEN

La capacidad de los suelos como reactores naturales, depende de cada suelo y sus propiedades edáficas,

tales como el contenido de materia orgánica (MO), la capacidad de intercambio catiónico (CIC) y el porcentaje de arcilla (ARC), así como de las propiedades del residuo en cuestión, en este caso, las aguas residuales porcinas. Las funciones de pedotransferencia (FPT) permiten estimar un determinado proceso a partir de propiedades de los suelos de fácil medición. Los objetivos de este trabajo fueron: a) Generar FPT para estimar la retención y mineralización de materia orgánica disuelta (MOD) de aguas residuales porcinas (ARP) utilizando propiedades edáficas como la MO, la CIC y ARC; y b) identificar los suelos con mayor aptitud para su uso como reactores naturales para el tratamiento de las ARP por medio de un análisis multicriterio. Se tomaron muestras de 10 epipedones. Para medir la retención de MOD, se construyeron columnas de suelo de 30 cm y se realizaron tres aplicaciones de ARP. Se realizó un experimento en macetas para medir el efecto de las ARP en la evolución de carbono (Evol-C) y la mineralización potencial anaeróbica de nitrógeno (MPAN). Se efectuaron las regresiones múltiples utilizando MO (%), la CIC ($\text{cmol}^+ \text{kg}^{-1}$) y la arcilla (%), de los suelos, como variables independientes y la retención de MOD (medida como demanda química de oxígeno), Evol-C y MPAN, como variables dependientes. Las FPT encontradas fueron: Retención de MOD = $41.5 + (2.8*\text{CIC}) - (0.81*\text{ARC}) - (3.5*\text{MO})$ $r = 0.81$ Evol-C = $542.3 + (20.1*\text{MO}) + (4.6*\text{CIC}) - (2.7*\text{ARC})$ $r = 0.96$ MPAN = $-8.4 + (3.45*\text{MO}) + (1.12*\text{ARC}) - (2.20*\text{CIC})$ $r = 0.88$ Los suelos con mayor aptitud como reactor natural de las ARP fue el Luvisol (LVct) y uno no clasificado, EPI-1.

Palabras clave: mineralización; funciones de pedotransferencia; evolución de carbono en suelos; materia orgánica disuelta.

INTRODUCTION

Soils can act as filters, since they have a natural capacity for depurating wastewaters with a high organic load, making them potential natural reactors for treating wastes (McBride, 1989; Bautista *et al.*, 2000; Bouma, 2006; 2009). However the intensity of such processes depends on the particular characteristics of the soil and residue in question. The quantity and type of mineral in the clay fraction and the organic matter (OM) content are the soil components that most influence the retention and mineralisation of organic compounds because of the quantity and type of electrical charges, the water holding capacity and extracellular enzyme adsorption capacity. For example, in Vertisols, smectite may adsorb the extracellular enzymes secreted by saprophytic organisms and reduce mineralisation, while Fe and Al oxides in Ferrasols and Acrisols may catalyse OM mineralisation by fomenting chemical oxidation, but not protect the OM of the extracellular enzymes (Bautista *et al.*, 2000); in Andosols the amorphous oxides of Fe and Al (allophane and imogolite) reduce OM mineralisation (Parfitt *et al.*, 1999, 2002).

In the state of Yucatan, Mexico, 6 095 500 m³ of swine wastewater (SWW) are produced each year, of which 37% remain untreated (Drucker *et al.*, 2003) and are dumped directly on soils or deposited in underground caves close to the pig farms, representing an important threat to groundwater. SWW are potentially beneficial for agricultural soils because of their OM content, especially in tropical areas in which organic materials are essential for maintaining soil fertility and crop production. Indeed, several studies have pointed to the beneficial effects of using sewage sludges and wastewaters for this purpose (Beltrán *et al.*, 2005; Vaca Paulín *et al.*, 2006; Ferreras *et al.*, 2006), although possible changes in soil processes and short, medium and long term consequences for the environment as regards possible contamination problems should always be born in mind (Bautista *et al.*, 2000). The wastewaters from pig farms contain dissolved organic matter (DOM), along with a large variety of compounds and organic molecules of low molecular weight, which are labile and rapidly mineralised. One cubic meter of slurry may contain up to 7.6 kg total nitrogen, 6.5 kg phosphates and 7.2 kg potassium, with a chemical oxygen demand (COD) of 47 kg (Coma and Bonet, 2004). In Yucatan the wastewaters (9428.37 m³ day⁻¹) from 670174 pigs contained an organic load of 443133.39 kg day⁻¹ in the form of COD (Méndez *et al.*, 2009).

Mathematical models, denominated pedotransfer functions (PTF), have been generated in recent years, based on soil properties assessed from samples or standardized laboratory analyses which are used to

estimate processes, particularly those concerned with the soil's hydraulic properties and moisture holding capacity (Wösten *et al.*, 2001; Rawls *et al.*, 2003; Pachepsky *et al.*, 2006). PTF are used in agronomy to calculate the periodicity of irrigation water and chemical applications (Pachepsky *et al.*, 2006). PTF of this kind are a straightforward way of helping farmers to organise their inputs and to diminish any negative impact on the environment.

Given that the OM and clay content of soils, together with the CEC, are the properties that most influence the retention and mineralisation of the soil OM, it was thought opportune to explore the use of these properties to elaborate PTF that can be used to estimate these processes. In addition, if the soils of the same soilscape are considered, PTF might be useful for evaluating soils for use as reactors for the treatment of high organic load wastewaters.

The aim of this work was to i) generate PTF to estimate the retention and mineralisation of dissolved organic matter (DOM) in swine wastewater (SWW) based on measurements of OM, CEC and PC and, ii) identify the soils most suited to acting as natural reactors for treating SWW by means of a multicriteria analysis.

MATERIAL AND METHODS

Study site

The state of Yucatan is located in the north of the Yucatan Peninsula, southeast Mexico. The geological formations in the state of Yucatan are made up of Tertiary limestones, which are sequentially distributed from earlier in the north (Pliocene-Miocene) to older in the south (Eocene). The main soil groups in the southern part of the state of Yucatan are Leptosols, Cambisols, Luvisols, and Vertisols, overlaid by sediments of the Pliocene epoch that constitute karstic plains and hills, made up mainly of Leptosols and Cambisols. The coastal zone is made up of plains of sediments from the Quaternary period, mainly consisting of Arenosols, Solonchaks, Gleysols and Histosols (from the Pleistocene and Holocene epochs) (Lugo and García, 1999). The climate in Yucatan has the following subtypes: BS₀wh, the driest of the semiarid climates, with summer rains; BS₁x'(w)h, the least dry of warm semiarid climates, with no a definite rainy season (irregular); Aw₀, the driest of subhumid, warm and very warm climates, with summer rains; and Aw₁, with an intermediate humidity level among the warm subhumid climates with summer rains (García, 2004). The types of vegetation present in Yucatan are coastal dune scrub, mangrove swamp, thorn forest, deciduous seasonal forest (most common type), savannah, semi-evergreen seasonal forest and, less

commonly, evergreen seasonal forest (Flores and Espejel, 1994).

Swine wastewater and soil determinations

Samples of swine wastewater were characterised by filtering through Whatman No. 5 filter papers, five repetitions per sample and measuring the following: pH, electrical conductivity (EC), biochemical oxygen demand (BOD), chemical oxygen demand (COD), phosphates, carbonates, chlorides and sulphates (APHA, AWWA, WPCF, 1992). Microbiological analyses were made to determine the presence of pathogens, but, since these data were negative, they are not presented.

Ten representative soils of Yucatan State were chosen for the experiment. Seven were identified according to the World Reference Base for Soil Resources (IUSS working group WRB, 2006): Haplic Gleysol (calcaric, arenic) (GLha[ca-ar]), Calcaric Arenosol (ARca), Lithic Leptosol (LPli), Cutanic Luvisol (LVct), Mollic Gleyic Vertisol (VRgl-mo), Haplic Luvisol (LVha) and Leptic Cambisol (CMle). Another three soils were not classified since samples were taken from the corresponding epipedons (0 to 20 cm) only; these were denominated EPI-1, EPI-2 and EPI-3.

To measure the soil characteristics the following methods were used: texture by Bouyoucos hydrometer, OM with potassium dichromate, CEC and exchangeable cations displaced by ammonium acetate and measured by atomic absorption spectroscopy, pH by potentiometry in a 1:2.5 soil:water ratio and EC by conductimeter in a 1:2.5 soil:water ratio (Okalebo *et al.*, 1993).

Moisture and dissolved organic matter retention

The use of soil columns to measure DOM is common (Williams *et al.*, 2000; McCracken *et al.*, 2002). In our case, to measure moisture retention and the DOM of the SWW the soil columns were contained in PVC tubes of 30 cm height and 10.5 cm diameter. The first 20 cm consisted of dry soil sieved to 2 mm. Three consecutive additions of SWW (5, 10 and 15 cm, corresponding to volumes of 395, 785 and 1180 mL, respectively) were made to these columns. These quantities of SWW were chosen to simulate two extreme cases of rainfall (5 and 15 cm) and an intermediate level (10 cm), a gradient that reflects the rainfall regime of Yucatan. In this way, the accumulated quantities were 5, 15 and 30 cm after the first, second and third addition, respectively. To collect the lixiviates funnels and suitable recipients were placed below the columns.

The experimental design was completely random with four repetitions. The COD of the residual water was considered a measure of the DOM content of the SWW. To characterise the SWW, the COD was measured before and after passing through the soil columns. The quantity of RDOM in the soils was estimated as follows:

$$\text{RDOM} = [\text{COD}_i - \text{COD}_f]$$

where RDOM = retention of dissolved organic matter (%); COD_i = initial chemical oxygen demand in the water applied (mg kg^{-1}); COD_f = chemical oxygen demand in the filtered water (mg kg^{-1}).

The quantity of water retained was estimated according to the following formula:

$$\text{WR} = [\text{VW}_a] - [\text{VW}_f]$$

where: WR = water retained (%); VW_a = volume of water applied (ml); VW_f = volume of filtered water (mL).

The time the SWW was applied to the soil columns was noted, as was the time the last filtered drop fell, the difference being taken as the hydraulic residence time (HRT) in minutes.

To observe the differences between the soils a variance analysis was made. A multiple regression analysis was made using the soil PC, OM and CEC as independent variables and RDOM of the soil columns as dependent variable (Lind *et al.*, 2004).

$$\text{RDOM} = Y_0 + (b_1 * \text{CEC}) + (b_2 * \text{PC}) + (b_3 * \text{OM})$$

where: RDOM = retention of dissolved organic matter; Y_0 = ordinate of the origin

CEC = cation exchange capacity in $\text{cmol}(+) \text{kg}^{-1}$; PC = clay (%); OM = organic matter (%); b_1 , b_2 and b_3 = partial regression coefficients.

Mineralisation of nitrogen, soil carbon evolution and changes in soil salinity

To measure the changes in N mineralisation, soil carbon evolution and electrical conductivity, a pot experiment was carried out as follows (Bautista *et al.*, 2000). In a completely randomised experiment with four repetitions, one application of SWW (250 ml) was made to pots containing 500 g of dry soil sieved to 2 mm.

Potential anaerobic nitrogen mineralisation (PANM) was measured in the fourth week after SWW application (Anderson and Ingram, 1993):

$$\text{PANM} (\text{mg kg}^{-1}) = [\text{mg NH}_4^+]_7 - [\text{mg NH}_4^+]_0$$

where: PANM (mg kg^{-1}) = potential anaerobic mineralisation of nitrogen; $[\text{mg NH}_4^+]_7$ = mineralisation of ammonium in seven days; $[\text{mg NH}_4^+]_0$ = mineralization of ammonium at day 0.

The soil carbon evolution was measured every week for four weeks following the application of SWW, using an NaOH trap (Anderson and Ingram, 1993):

$$\text{SCE} = (C - V) * N * 6$$

where: SCE= soil carbon evolution in mg kg^{-1} ; C= volume of HCl used in control (ml); V= volume of HCl used in titration; N= normal concentration of HCl; 6= equivalent weight of carbon.

Soil salinity was measured in the third week of the experiment as EC in a 1:2.5 soil:water ratio (Okalebo *et al.*, 1993).

Statistical analysis

With the results obtained, an ANOVA was made at levels of significance of 0.1 or confidence of 90%, using the STATISTICA program. For RDOM, comparisons were made between soils for each layer of SWW applied. In the case of SCE, weekly comparisons were made between soils. As regards PANM, the comparison was between soils at day 0 (no incubation) and day 7 (after incubation). When the ANOVA results were significant, a Tukey multiple comparison analysis was made at the same level of significance. Multiple regressions were made with the STATGRAPHICS Plus 4.1 program, using the soil clay %, OM and CEC as independent variables and RDOM, SCE and PANM as dependent variables, in order to find the degree of association between them (Lind *et al.*, 2004).

$$\text{RDOM} = Y_0 + (b_1 * \text{CEC}) + (b_2 * \text{PC}) + (b_3 * \text{OM})$$

$$\text{PANM} = Y_0 + (b_1 * \text{CEC}) + (b_2 * \text{PC}) + (b_3 * \text{OM})$$

$$\text{SCE} = Y_0 + (b_1 * \text{CEC}) + (b_2 * \text{PC}) + (b_3 * \text{OM})$$

Where RDOM= retention of dissolved organic matter; SCE= soil carbon evolution; PANM= potential anaerobic nitrogen mineralisation; Y_0 = ordinate of the origin; CEC= cationic exchange capacity in $\text{cmol}(+) \text{kg}^{-1}$; PC= clay (%); OM= organic matter (%); b_1 , b_2 and b_3 = partial regression coefficients.

Cross-validation (Geisser, 1974) is one of several statistical resampling techniques used to test the strength of a model prediction. It is used as a warning signal in testing for goodness-of-fit and thus for judging acceptability. For this purpose, Excel was used.

Multicriteria analysis

Multicriteria analysis is a useful tool for taking decisions, especially for questions involving a multiplicity of factors, criteria or variables. For an overall evaluation of the effects of SWW on the soils an analysis was made, considering RDOM (deputation) and SCE (decomposition) as environmental properties; PANM (fertilisation) as fertility criterion and EC (salinity) as degradation criterion. In addition, the total soil profile depth was considered as a related physical property and protection factor. The multicriteria index (MI) was calculated as follows:

$$\text{MI} = [(\text{RDOM} * 0.20) + (\text{SCE} * 0.20) + (\text{PANM} * 0.20) + (\text{EC} * 0.20) + (\text{TD} * 0.20)] / 5$$

where: RDOM= retention of dissolved organic matter; SCE= soil carbon evolution; PANM= potential anaerobic nitrogen mineralisation; EC= electrical conductivity; TD= total depth of soil profile.

The components of the MI were transformed into relative values (0 to 1). Equal weight (0.2) was assigned to the criteria analysed since the level of importance was not differentiated between the variables. The index aims to identify the soils in which SWW would have the lowest negative effects and the greatest beneficial effects for agriculture (Auxiliadora and Manera, 2003)

RESULTS AND DISCUSSION

Characterisation of SWW and soils

The SWW samples could be considered potentially harmful for both soils and underground water due to their EC, BOD and COD (Table 1) Although Mexican legislation NOM-001 concerning discharges into water bodies does not consider COD, the BOD levels of the samples exceeded the 150 mg L^{-1} established for agricultural use (SEMARNAT, 1996).

Some soils have a high percentage of sand (e.g. AR and GL), some can be considered clayey (e.g. VR and LV) and others have intermediate values (Table 2). All soils studied are karstic in origin, which is reflected in the high Ca and Mg concentration and in the pH values, which are mostly in excess of 7.

Water holding capacity of soils evaluated

The 5 cm addition of SWW was totally retained in all the soil columns except GLha, in which retention only reached 60% and the mean HRT was 23 minutes. For the 10 cm addition of SWW, retention fell in all the soils, ranging from 35% in GLha to 64% in LPli. The

residence times were 20 minutes in most of the soils, about 50 minutes in GLha, about one hour in CMle and 2 hours 40 minutes in VRgl-mo. This slow filtration rate observed in the Vertisols was expected given the quantity and type of clays they contain. However, for the last of the layers applied (15 cm), the HRT for this soil fell substantially (to one hour) as did water retention, probably as a result of the clay becoming saturated. In general, the moisture retention of the soils in the last addition fell to less than 30% in the columns, reaching 3% in LVha and CMle. The results show that this dose represents a high risk for underground waters (Table 3 and 4). It is important to emphasise that no preferential flows were observed between the walls of the PVC columns and the soils since: 1) HRT values were high in all cases; 2) the soils of the study zone have a karstic origin with high levels of CaCO_3 , a characteristic that probably influenced the DOM, even in those soils with a high percentage of sands, as observed by Rajkai and Várallyay (1992); and 3) the soil matrix had a filtering effect, as manifested by the retention of OM (Table 5) and the notable diminution in turbidity of the leachates.

For moisture retention, it was not possible to obtain a suitable regression equation with the soil properties measured (OM, PC and CEC). Rawls *et al.*, (2003) mentioned that the effects of OM on water retention are often contradictory. In other studies on soil moisture retention and hydraulic PTFs, Wösten *et al.*, (2001) and Romano and Palladino (2002) showed that other properties, such as bulk density, porosity and soil structure (degree, size and form), were also involved. Wösten *et al.*, (2001) took into consideration the proportion of clay type (montmorillonite, illite), iron oxides and carbonate content.

Retention of dissolved organic matter

With the first layer of SWW applied, all of the columns retained 100% of the DOM, except GLha, which showed an RDOM of 79%. In the case of the second layer, the RDOM varied from 56% in LVha to 86%, 88% and 90% in LPli, CMle and VRglmo, respectively. However, for the third application, RDOM was only high in CMle and LPli (87% and 86%, respectively). In VRgl the value was 55%, while in the other groups (ARca, LVct, LVha, EPI-1, EPI-2 and EPI-3), RDOM was below 50%. This last level of application must therefore be considered as constituting a risk for underground water contamination (Table 5).

In the PFT made for the three levels of application, the relation between RDOM and PC (%), OM (%) and CEC ($\text{cmol}(+) \text{kg}^{-1}$) is determined from the following equation:

$$\text{RDOM} = 41.5 + (2.8 * \text{CEC}) - (0.81 * \text{PC}) - (3.5 * \text{OM})$$

There was a statistically significant relation between the variables at a level of confidence of 90% ($p < 0.1$). The cross validation showed an $r = 0.81$.

CEC was the soil property with the greatest influence on RDOM, as is to be expected, since molecule adsorption in the soil depends on the density of the positive charge of the organic molecules and the negative charge of the colloids (McBride, 1989). Soil CEC, PC and OM showed p values of 0.03, 0.06 and 0.15, respectively (Figure 1). As can be seen, the OM had a p value of more than 0.10, meaning it is not statistically significant, with an α value of 90% or more. However, if this variable is omitted from the model, the resulting correlation index falls substantially, so that OM must be considered as having a strong effect on RDOM.

Table 1: Characteristics of swine wastewater and its effects on soil and water bodies

| Parameter | Unit | Average | NOM-001/USDA | Water Bodies | Soils |
|--------------|--------------------|---------|--------------|--------------|-------|
| pH value | | 7 | 6-9 | - | b |
| EC* | dS m^{-1} | 4.04 | 0.75 | X | XXX |
| BOD** | mg L^{-1} | 3946.17 | 150 | XXX | b |
| COD*** | mg L^{-1} | 9960.83 | | XXX | b |
| Phosphates | mg L^{-1} | 8.71 | | P | B |
| Bicarbonates | mg L^{-1} | 137.45 | | I | X |
| Chlorides | mg L^{-1} | 138.35 | 106.36 | I | XXX |
| Sulphates | mg L^{-1} | 34.04 | | P | I |
| Nitrogen | mg L^{-1} | 806.4 | 40 | P | B |

X=harmful, XX= very harmful, XXX= extremely harmful, b= beneficial, B= very beneficial, I= indifferent and P= potentially dangerous; EC*, electrical conductivity; BOD**, biochemical oxygen demand; COD***, chemical oxygen demand.

Table 2: Physical and chemical properties of soils used in the experiments

| Soil | Sand | Silt | Clay | Textural Class | Dry Color | EC | pH | OM | CEC | Na | K | Ca | Mg | FC | PMP | WA |
|-----------------|------|------|------|----------------|------------|----------------------|------|------|------|--------------------------------------|-----|------|------|----------------|-----|----|
| | (%) | (%) | (%) | | | (dSm ⁻¹) | | % | | ------(cmol+ kg ⁻¹)----- | | | | ------(%)----- | | |
| GLha (ca-ar) | 82 | 7 | 11 | LS | 10YR5/2 | 6.3 | 8.6 | 2.7 | 3 | 2.2 | 3.8 | 13.9 | 7.3 | 32 | 12 | 19 |
| ARca | 88 | 5 | 7 | LS | 10YR6/2 | 0.3 | 8.4 | 3.5 | 2 | 2.3 | 3.2 | 13.4 | 18.9 | 33 | 12 | 21 |
| LPli | 42 | 27 | 31 | CL | 5YR4/3 | 0.33 | 7.98 | 16.4 | 35.5 | 1.7 | 3.9 | 14.6 | 16.1 | 65 | 35 | 30 |
| LVct | 18 | 17 | 65 | C | 7.5YR3/3 | 0.36 | 6.2 | 7.1 | 22.8 | 1.6 | 6.7 | 9.3 | 9.4 | 68 | 36 | 32 |
| VRgl-mo | 10 | 9 | 81 | C | 7.5YR2,5/1 | 0.42 | 7.2 | 4.5 | 36 | 1.9 | 1.4 | 15.9 | 14 | 83 | 49 | 34 |
| LVha | 6 | 17 | 77 | C | 2.5YR3/4 | 0.13 | 7.06 | 4.2 | 17.2 | 1.4 | 5.1 | 7.5 | 7.8 | 55 | 28 | 27 |
| CMle | 40 | 23 | 37 | CL | 2.5YR3/3 | 0.27 | 7.3 | 6.9 | 32 | 1.5 | 7.6 | 11.8 | 8.3 | 63 | 34 | 29 |
| EPI-1 | 34 | 21 | 45 | C | 7.5YR4/3 | 0.5 | 7.4 | 14.2 | 32 | 1.8 | 5.9 | 15.4 | 13.3 | 67 | 43 | 24 |
| EPI-2 | 52 | 18 | 30 | SCL | 7.5YR3/2 | 0.3 | 8 | 15.4 | 34.5 | 1.8 | 2.2 | 16.1 | 14 | 80 | 39 | 41 |
| EPI-3 | 10 | 16 | 74 | C | 2.5YR2,5/3 | 0.9 | 6.4 | 5.5 | 26.9 | 2.6 | 7.8 | 9.1 | 12 | 66 | 35 | 31 |

LS= Loamy sand; CL= Clay loam; C= Clay; SCL= Sandy clay loam. EC= Electrical conductivity, OM= Organic matter, CEC = Cation Exchange Capacity, FC= Field capacity, PWP= Permanent wilting point, WA= Water available.

Table 3. Moisture retention (%) in soil columns for three layers of application of wastewaters

| Soils | Application 1 | | Application 2 | | Application 3 | |
|---------|---------------|----|---------------|----|---------------|----|
| | X | sd | X | sd | X | sd |
| GLha | 60 | 9 | 35 | 4 | 23 | 4 |
| ARca | 100 | 0 | 60 | 3 | 4 | 1 |
| LPli | 100 | 0 | 65 | 1 | 5 | 2 |
| LVct | 100 | 0 | 46 | 7 | 6 | 2 |
| VRgl-mo | 100 | 0 | 50 | 3 | 14 | 1 |
| LVha | 100 | 0 | 44 | 2 | 3 | 1 |
| CMle | 100 | 0 | 54 | 4 | 3 | 0 |
| EPI-1 | 100 | 0 | 37 | 5 | 11 | 2 |
| EPI-2 | 100 | 0 | 42 | 3 | 8 | 4 |
| EPI-3 | 100 | 0 | 40 | 5 | 4 | 0 |

X= average; sd= standard deviation

Table 4. Hydraulic residence time (minutes) in soil columns for three layers of application of wastewaters

| Soils | Application 1 | | Application 2 | | Application 3 | |
|---------|---------------|----|---------------|----|---------------|----|
| | X | sd | X | sd | X | sd |
| GLha | 23 | 4 | 46 | 8 | 33 | 5 |
| ARca | 0 | | 20 | 1 | 52 | 17 |
| LPli | 0 | | 24 | 4 | 167 | 47 |
| LVct | 0 | | 22 | 3 | 23 | 6 |
| VRgl-mo | 0 | | 141 | 14 | 55 | 23 |
| LVha | 0 | | 32 | 7 | 46 | 5 |
| CMle | 0 | | 55 | 4 | 190 | 48 |
| EPI-1 | 0 | | 27 | 3 | 44 | 5 |
| EPI-2 | 0 | | 22 | 1 | 30 | 4 |
| EPI-3 | 0 | | 26 | 4 | 28 | 1 |

X= average; sd= standard deviation

Table 5. Retention of dissolved organic matter (%) in soils

| Soils | Application 1 | | Application 2 | | Application 3 | |
|---------|---------------|----|---------------|----|---------------|----|
| | X | sd | X | sd | X | sd |
| GLha | 79 | 7 | 74 | 7 | 29 | 5 |
| ARca | 100 | 0 | 74 | 0 | 31 | 11 |
| LPli | 100 | 0 | 86 | 3 | 86 | 3 |
| LVct | 100 | 0 | 63 | 9 | 42 | 6 |
| VRgl-mo | 100 | 0 | 90 | 2 | 55 | 8 |
| LVha | 100 | 0 | 56 | 7 | 12 | 6 |
| CMle | 100 | 0 | 88 | 4 | 87 | 2 |
| EPI-1 | 100 | 0 | 77 | 9 | 38 | 0 |
| EPI-2 | 100 | 0 | 57 | 8 | 32 | 9 |
| EPI-3 | 100 | 0 | 63 | 3 | 37 | 8 |

X= average; sd= standard deviation

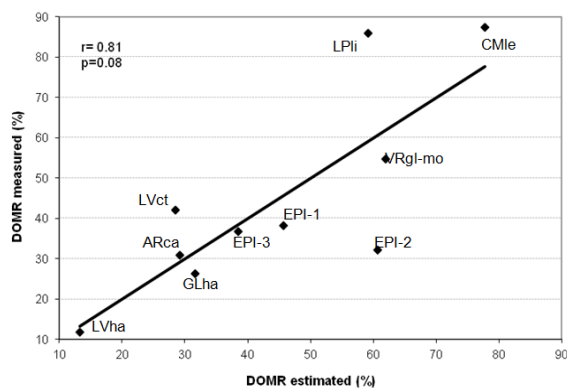


Figure 1. Cross validation of the retention of dissolved organic matter in swine wastewater in soil columns for three layers of application

Organic matter mineralisation and changes in soil salinity

As regards the SCE, each soil showed a particular mineralisation dynamics, which was not maintained with time, suggesting that each soil has its own depurative capacity. For example, the Vertisol had a high carbon evolution rate during the first week, which gradually fell to a minimum value in the fourth week.

The OM mineralisation values, measured from soil carbon evolution, showed that the soils followed three behaviour patterns as time progressed: a) increasing mineralisation, as in GLha, ARca, LPlI and EPI-2; b) constant levels of mineralisation, as in EPI-3, CMle and EPI-1; c) decreasing levels of mineralisation, as in LVct, LVha and VRgl (Table 6).

Table 6. Soil carbon evolution (mg C kg soil⁻¹) for four weeks of application of swine wastewaters

| Soil | Week 1 | | Week 2 | | Week 3 | | Week 4 | |
|---------|--------|----|--------|----|--------|----|--------|----|
| | X | sd | X | sd | X | sd | X | sd |
| GLha | 115 | 23 | 160 | 6 | 129 | 13 | 163 | 22 |
| ARca | 82 | 16 | 197 | 41 | 113 | 18 | 210 | 17 |
| LPlI | 151 | 25 | 308 | 31 | 189 | 0 | 250 | 3 |
| LVct | 159 | 32 | 218 | 40 | 112 | 19 | 98 | 9 |
| VRgl-mo | 166 | 22 | 205 | 18 | 51 | 28 | 74 | 13 |
| LVha | 183 | 23 | 201 | 16 | 62 | 8 | 77 | 33 |
| CMle | 159 | 12 | 296 | 50 | 161 | 11 | 177 | 9 |
| EPI-1 | 205 | 25 | 256 | 15 | 197 | 6 | 232 | 8 |
| EPI-2 | 165 | 37 | 350 | 65 | 174 | 8 | 275 | 12 |
| EPI-3 | 157 | 9 | 186 | 11 | 96 | 13 | 205 | 72 |

X= average; sd= standard deviation

The soil with the highest RDOM (CMle) (Table 5) was not the soil showing the greatest degree of carbon

evolution (EPI-2) (Figure 2a). The soils with the highest OM content (LPlI, EPI-1 and EPI-2) (Table 2) mineralised the greatest quantities of carbon (Figure 2a), which suggests that the addition of DOM stimulated soil microbial activity to speed up the decomposition of the original OM (Cox *et al.*, 2007). The PTF equation made with the data for the soil carbon evolution over four weeks showed that the OM content of the soil had the greatest weight in the model, followed by CEC:

$$SCE = 542.3 + (20.1*OM) + (4.6*CEC) - (2.7*PC)$$

The p value for the ANOVA was 0.10, pointing to a statistically significant relation between the variables at a 90% confidence level. The model explains 96% of the variability in the soil carbon evolution. The soil properties, OM, CEC and PC, had p values of 0.04, 0.22 and 0.07, respectively. The p value for CEC (higher than 0.10) mean that this variable was not statistically significant for an α of 90% or above. However, as in the case of RDOM, if CEC is eliminated from the model, the r decreases considerably (Figure 2a).

We expected soils with the greatest CEC to show lower rates of soil carbon evolution due to the chemical and physical protection afforded to the OM by the inorganic colloids; for example, through the adsorption of enzymes to clays. However, this was only true in the case of VRgl. The application of SWW to soils consisting of more than 65% clay very probably generates a microenvironment with a lower oxygen content, as reflected in a lower rate of OM mineralisation (Sing and Gupta, 1977).

The PANM reflected two patterns of behaviour: 1) soils with no or little mineralisation, such as GLha, ARca, LPlI, VRgl-mo, CMle and EPI-2; and 2) soils showing a significant degree of mineralisation, LVct, LVha, EPI-3 and EPI-1.

The PTF equation for PANM indicates that the OM content of the soils has the greatest weight in the model.

PANM = -8.4 + (3.45*OM) + (1.12*PC) - (2.20*CEC) The value p< 0.1 points to a significant relation between the variables at a 90% level of confidence. The model explains 88% of the variability of PANM. The soil properties, CEC, PC and OM, showed p values of 0.02, 0.005 and 0.07, respectively (Figure 2b). The negative values recorded in some soils suggest that N was not released through decomposition, but that it was fixed by the microbial communities. Beltrán *et al.*, (2005) also measured negative values for the N released in soils fertilised with sewage sludge.

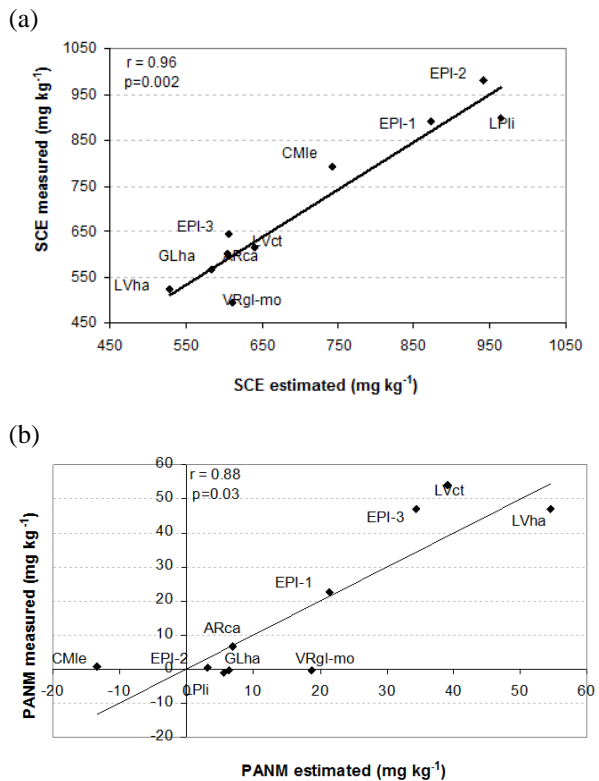


Figure 2. (a) Cross validation of the soil carbon evolution and (b) potential anaerobic nitrogen mineralisation on soils treated with swine wastewaters EC increased in all soils except GLha after the application of the SWW.

The Lithic Leptosol was among the soils with the greatest capacity to retain DOM and a high capacity to mineralise carbon, but it also presented a high risk of salinisation, since the increase in salinity was 0.72 dS m^{-1} , while in VRgl and EPI-1 the increase was 1.35 and 0.75 dS m^{-1} , respectively (Figure 3).

Overall evaluation of the effects of SWW on the soils

The multicriteria analysis grouped the soils into four categories based on the overall effects observed: a) Soils most suited to acting as receptors of SWW (Cutanic Luvisol and Epipedon-2); b) Soils showing medium suitability (Epipedon-3, Haplic Luvisol, Leptic Cambisol and Epipedon-2); c) Soils of low suitability (Calcaric Arenosol, Lithic Leptosol and Gleyic Vertisol; and d) Unsuitable soils (Haplic Gleysol) (Table 7). The multicriteria analysis also showed that soils with coarse textures, such as GL and AR, are not suited to receiving SWW or have drawbacks that prevent them from being good receptors. Soils classified as clayey show contrasting characteristics, VR being unsuitable, and LV and CM showing medium to high levels of suitability (Table 7).

In LP the degree of depuration and OM decomposition resulting from the application of the SWW was high, while N mineralisation and the effect on fertility were low and the risk of salinisation high. Moreover, the low depth of these soils (not exceeding 25 cm) is also a disadvantage, so that they must be considered unsuitable for receiving SWW, although the application of a layer not exceeding 10 cm might be acceptable in a dry period.

The VR showed a good degree of dissolved organic matter retention, mainly because of the clay types and quantities and their respective CEC, although the same characteristics do not permit adequate mineralisation of the carbon and nitrogen. Smectite is known to adsorb the extracellular enzymes secreted by saprophytic microorganisms and to reduce mineralisation (Bautista *et al.*, 2000). These soils of deficient drainage may present anaerobic conditions, which would result in a slow OM mineralization rate; furthermore, during anaerobic mineralisation, phytotoxic organic acids are produced (Bautista *et al.*, 2000). For these reasons they must be regarded as soils with a high risk of salinisation and degradation and, therefore, as being unsuitable for agricultural use.

Differences were also found among the soils with a coarse texture, such as Gleysols and Arenosols, depending on their distance from the coast. GLha is a naturally saline soil and not very deep and so cannot be considered suitable for receiving SWW. The ARca soil shows medium levels of RDOM and OM mineralisation, probably because of its high CaCO_3 content, but the fertilization value of N mineralisation is low and the risk of salinity is high. This soil, therefore, is considered unsuitable for receiving SWW.

The results of the multicriteria analysis depend on the properties and processes of the soils considered in this study. To carry out an integral evaluation of their suitability for the application of SWW for agricultural purposes, other variables should be borne in mind, such as the climate (rainfall, soil leaching index and duration of rainy season), landforms (slope, lithology, vadose zone thickness), underground waters (depth and quality) and the crops to be grown. The spatial heterogeneity of the soils of karstic zones, the presence of underground water near the surface (1-50 m) and concern for the environment (Bautista *et al.*, 2003; 2004; 2005) mean that SWW must be applied very precisely and in a manner that may differ between plots of land in the same area; that is, precision agriculture based on the management of patches of soil.

PTF and soil maps at plot level will be useful for agricultural and environmental purposes since this will enable the correct volumes to be applied to each plot.

The properties used in PTF are easily measured by conventional techniques (Anderson and Ingram, 1993; Okalebo *et al.*, 1993)

The PTF obtained in this study are only applicable to the study area and PTF developed for a particular region or based on a given database can only be applied with any degree of safety in a restricted area of soil groups and environmental conditions (Wösten *et al.*, 2001; Romano and Palladino, 2002; Merdum *et al.*, 2006; Pachepsky *et al.*, 2006;). Most PTF are regression equations derived from database referring

to a specific location and have demonstrated their capacity to predict the hydraulic behaviour of the soils of a region with an acceptable degree of accuracy and in a cost effective way, both as regards time and effort (Romano and Palladino, 2002). The discrepancies between measured and estimated soil processes must be accepted as a price that must be paid when simplified methods are used rather other methods that may be expensive and time consuming.

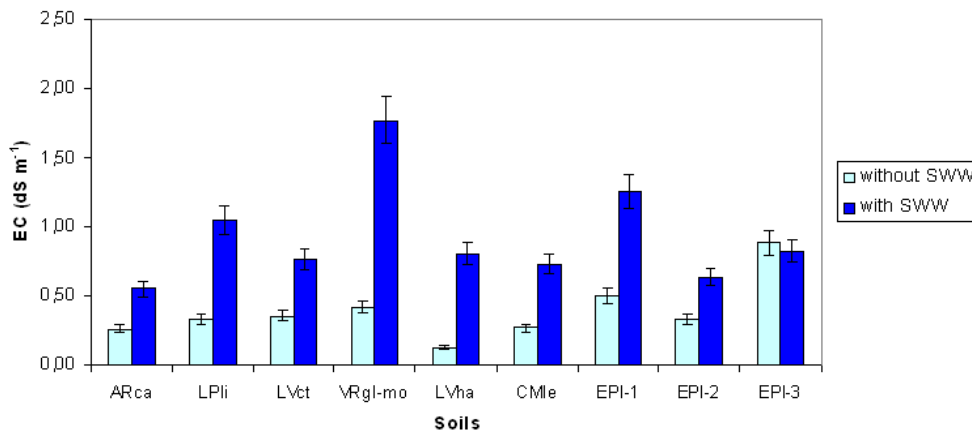


Figure 3. Increased electrical conductivity in soils by the application of swine wastewater

Table 7: Multicriteria evaluation of soils for application of swine wastewaters

| Soil unit | RDOM (deputation) | SCE (decomposition) | PANM (fertilization) | EC (salinisation) | Depth | Multi Index | Class of suitability |
|-------------|----------------------|------------------------|-------------------------|----------------------|-------|----------------|-------------------------|
| LVct | 0.48 | 0.57 | 1.00 | 0.88 | 1.00 | 0.79 | high |
| EPI-1 | 0.44 | 1.00 | 0.42 | 0.80 | 1.00 | 0.73 | high |
| EPI-3 | 0.42 | 0.49 | 0.87 | 0.87 | 0.60 | 0.65 | middle |
| LVha | 0.14 | 0.31 | 0.87 | 0.87 | 1.00 | 0.64 | middle |
| CMle | 1.00 | 0.82 | 0.01 | 0.88 | 0.45 | 0.63 | middle |
| EPI-2 | 0.37 | 0.88 | 0.01 | 0.90 | 1.00 | 0.63 | middle |
| ARca | 0.36 | 0.57 | 0.12 | 0.91 | 1.00 | 0.59 | low |
| LPli | 0.99 | 0.96 | -0.02 | 0.83 | 0.10 | 0.57 | low |
| VRgl-mo | 0.63 | 0.26 | -0.01 | 0.71 | 1.00 | 0.52 | low |
| GLha(ca-ar) | 0.33 | 0.66 | -0.01 | 0.00 | 0.50 | 0.30 | very low |

RDOM= Retention of dissolved organic matter, SCE= Soil carbon evolution, PANM= potential anaerobic nitrogen mineralisation.

CONCLUSIONS

The percentage of clay, the organic matter content and the cation exchange capacity are soil properties that influence the processes of dissolved organic matter retention and mineralisation. The same properties can be used to generate PTF that will help identify soils

from karstic zones that can be considered suitable for the application of SWW. SWW are wastes of moderate to high risk as regards soil salinisation. To benefit from their N content, SWW in layers of 5 cm or less can be used in the dry season as soil amendment.

According to the PTF and multicriteria analysis, the soils studied here can be grouped into four categories

of suitability: 1) suitable, such as LVct and EPI-1; 2) of moderate suitability, such as EPI-3, LVha, CMle and EPI-2; 3) of poor suitability, such as ARca, LPI and VRgl-mo and 4) unsuitable, such as GLha[ca-ar]. Some soils of tropical karstic zones can be used as reactors for treating wastewaters with a high organic load.

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