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SOIL HYDRAULICS ASSOCIATED WITH SOIL PHYSICAL PROPERTIES AND THEIR EFFECTS ON NITRATE LEACHING IN THE MEDITERRANEAN ZONE OF CHILE

TESIS PARA OPTAR AL GRADO DE MAGISTER EN MANEJO DE SUELOS Y AGUAS

IGNACIO FRANCISCO FUENTES SAN ROMÁN

DIRECTOR DE TESIS

MANUEL CASANOVA PINTO

PROFESORES CONSEJEROS

OSVALDO SALAZAR GUERRERO
OSCAR SEGUEL SEGUEL

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HIDRÁULICA DE SUELOS ASOCIADA A PROPIEDADES FÍSICAS Y SUS EFECTOS EN LA LIXIVIACION DE NITRATOS EN LA ZONA MEDITERRANEA DE CHILE

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Tesis presentada para optar al Grado de Magíster en Manejo de Suelos y Aguas

IGNACIO FRANCISCO FUENTES SAN ROMÁN

Director de Tesis	**Calificaciones**
Manuel Casanova Ingeniero Agrónomo MSc.	7.0
Profesores Evaluadores	
Osvaldo Salazar G. Ing. Agrónomo MSc. Ph.D.	7.0
Oscar Seguel S. Ing. Agrónomo Dr.	6.9

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PREFACE AND ACKNOWLEDGEMENTS

It is always difficult to write this part of the thesis due to a diversity of mixed feelings. On the one hand it is a pleasure, because the hard part of the work is already done, but on the other hand it is extremely difficult to list all the people who helped in accomplishment of the task in one way or another.

In the first place I want to thank all my family, especially Li, who has always supported me and encouraged me, despite the problems and hard work that this decision has cost her; to Re, my angry sister; to Cushita, "mi compañera" and to Jo, "la cashorrita". Equally important, I want to thank all my teachers who helped me in this study. To Manuel Casanova, Oscar Seguel and Osvaldo Salazar, who have worked hard designing this project and revising the manuscript. Also, I want to thank all the people who directly or indirectly participated in the study. To Kanko, my thesis partner; Xixo and Ñaño, our slaves and José, the Russian idol. Lastly, I feel a great gratitude to my friends, with whom I have shared leisure and struggle time.

We live in changing times, with crisis and agitation everywhere. There has been a collapse of the ossified state institutions of the past, which promoted a social system based on the hoarding of capital, injustice and the destruction of nature. In this global scenario, as Carlitos Marx wrote "that the fear be here left and here the cowardice becomes dead".

To my Shadow...

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CHAPTER 1. SOIL HYDRAULICS ASSOCIATED WITH SOIL PHYSICAL PROPERTIES AND THEIR EFFECTS ON NITRATE LEACHING

1.1 LITERATURE REVIEW

Soil hydraulic properties, such as the water retention curve and hydraulic conductivity, are important due to their relationship with water flow and solute transport in the vadose (unsaturated) zone. Therefore soil hydraulics must be separated from groundwater hydraulics, which also cover the water conditions in deeper aquifers. This introductory section presents a review of how soil hydraulics associated with soil physical properties affect nitrate leaching (NL). As an overview, a flow chart for soil within a particular set of climate conditions, including the factors and processes that determine NL in the soil, is presented in Figure 1.1.

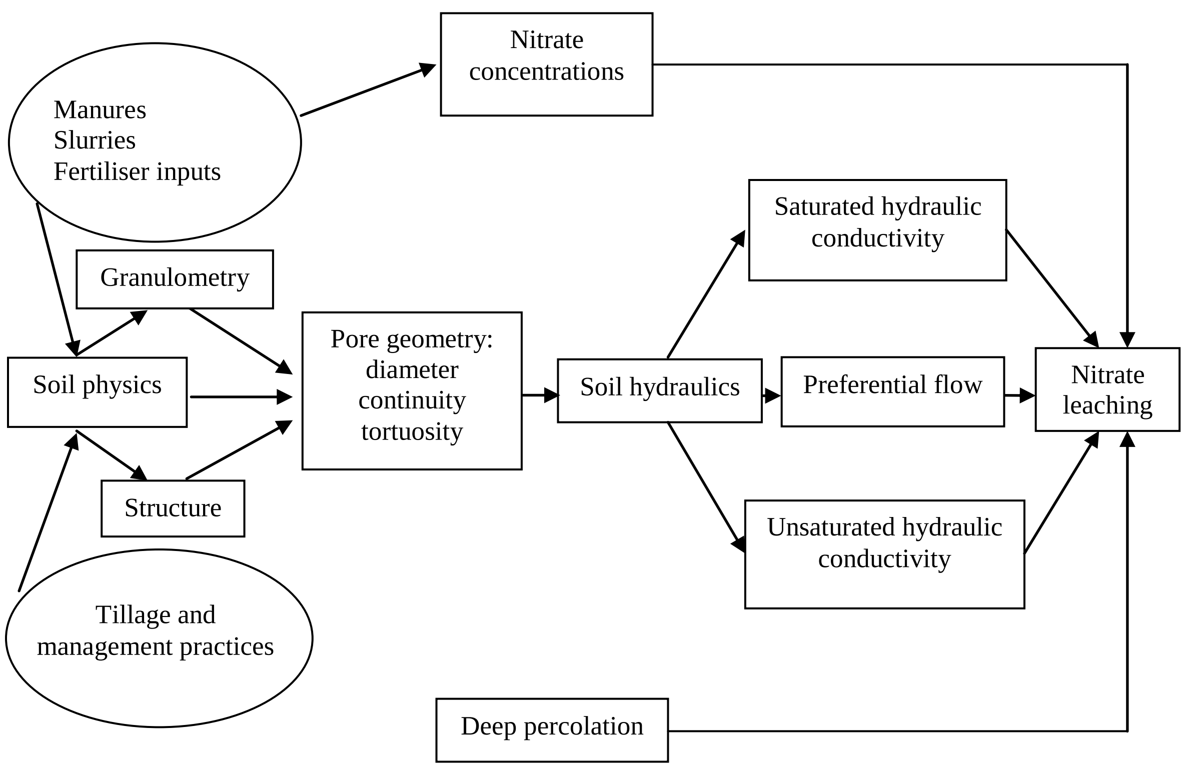


Figure 1.1. Flow chart for nitrate leaching (NL), considering the main soil processes and associated factors.

1.1.1 Agricultural management and nitrogen leaching from soil

Agricultural activities such as livestock production and crop fertilisation have the potential to contaminate surface water by runoff and groundwater by solute leaching, whereas intensive tillage and grazing promote increased runoff and leaching. These sources of pollution cannot be accurately located, being dispersed across a catchment or sub-catchment area, and are therefore considered diffuse (or non-point) sources of water pollution (Cottingham *et al.,* 2010).

The rapid intensification of livestock production systems has resulted in large quantities of organic materials being produced in limited geographical areas, but without sufficient land area to utilise these efficiently. This has led to an increasing focus on manure management. Greater livestock numbers and use of artificial fertiliser, along with higher supplementary feed inputs on farms, have resulted in marked changes in the volume, content and types of excreta produced by livestock. Therefore, particularly in the swine livestock industry, there is a need to dispose of and manage wastes safely to avoid risks to human health and derive some benefit from the wastes, turning them into a benefit for the economy of the sector (Mantovi *et al*., 2005).

Application of slurry (liquid form) and manure (solid form) to the soil not only serves to supply nutritional crop needs, but also tends to improve physical and biological soil properties. This turns the soil into a medium that favours air, water and nutrient exchange between plant roots and soil, enhancing crop development (Miller *et al*., 2002; Thomas, 2007). However, one of the negative consequences of such applications is the high risk of pollution associated with the chemical composition of the slurry/manure (Thompson *et al*., 1987; Van Es *et al*., 2004; Thomas, 2007; Sorensen and Rubek, 2012).

Over recent decades, intensive use of fertilisers and manure to increase food production has increased nitrogen (N) levels in surface water and groundwater, especially when N inputs exceed crop uptake (Harter *et al*., 2002). The N in soil undergoes a number of transformation processes (nitrification, mineralisation, denitrification, volatilisation and others) and leaching is a mechanism of soluble N removal from the soil by percolating waters (Smil, 1999; Steinfeld *et al*., 2006). In some cases, the majority of the N applied or deposited on soil is neither incorporated into the harvested plant tissues nor stored in the soil. It subsequently enters to a "N cascade", where the same N atom from atmospheric origin (N_2) has several consequences in a series of different and concatenate environmental systems (Galloway *et al*., 2003).

Leaching occurs especially when N application rate exceeds crop uptake rate (Harter *et al*., 2002). For most soils, N is mainly leached as nitrate (NO_3^-), whereas ammonium (NH_4^+) if is not immobilised or retained by soil colloids can be oxidised to NO_3^-. The presence of NO_3^- in groundwater is a potential pollution hazard and a threshold of 10 mg N-NO_3 L^{-1} for drinking water has been defined in Chile (INN, 1984) and the USA (EPA, 1987; Bohn *et al*., 2001; Sparks, 2003). Infants are especially susceptible to poisoning by nitrite (NO_2^-) or NO_3^- after its conversion to NO_2^-, and diseases such cancer, nervous system impairments (Figure 1.2) and methaemoglobinaemia (blue baby syndrome) have also been reported (Benjamin, 2005; Gehl *et al*., 2005; Powlson *et al*., 2008; Bryan and Loscalzo, 2011; Bryan and van Grinsven, 2013). In addition, eutrophication of surface waters has seriously affected the biosphere (Oviatt and Gold, 2005; Vahtera *et al*., 2007).

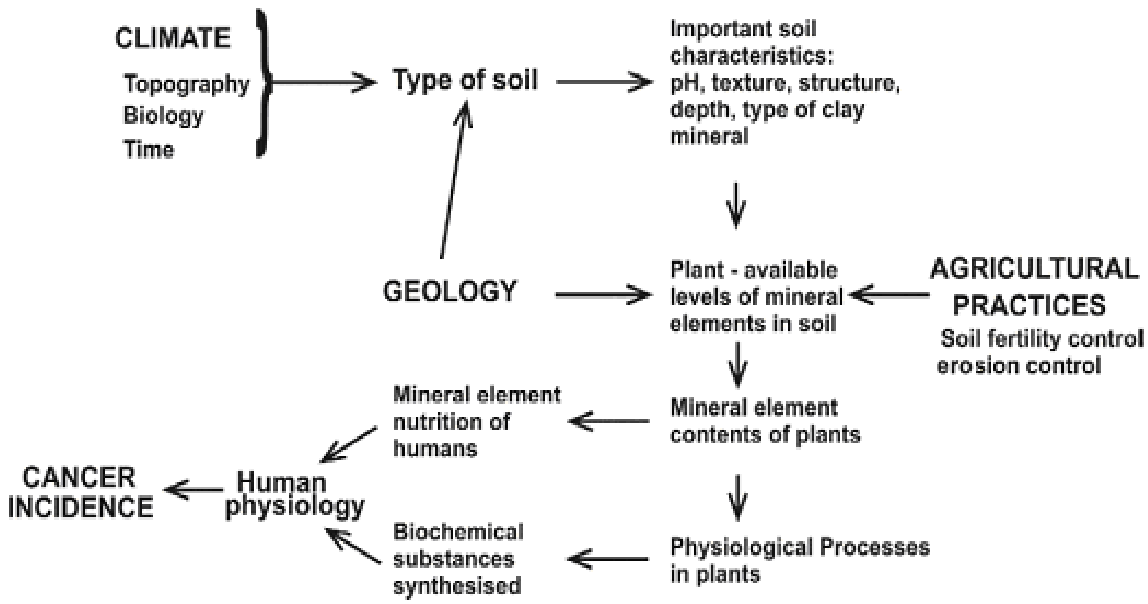


Figure 1.2. Relationship between environmental factors and cancer incidence (Dissanayake and Chandrajith, 2009).

Nitrate leaching to groundwater not only has negative health and environmental consequences, but also results in economic losses to farmers if N is not used by the growing crop (Buczko *et al*., 2010). Hence, the use and disposal of slurry and manure from the livestock industry has been examined in a number of environmental and economic studies aimed at improving welfare, human health and territorial planning, but little is known about the impact of manure management practices on water quality in the extensive alluvial aquifers underlying many basins (Harter *et al*., 2002). Climate change scenarios increase concerns about this worrying process (George *et al*., 2010).

One of the simplest ways to avoid groundwater pollution by NO_3^- through leaching is to manage and optimise the amount of nutrients applied as slurry or fertiliser by careful evaluation of soil fertility based on previous crop rotations and other data (Harter *et al*., 2002). For example, the European Union has classified the vulnerability of territorial areas according to the NO_3^- concentration and the trophic status of waters in order to introduce action programmes in these areas, limiting the doses of slurry permitted depending on the vulnerability category (Mantovi *et al*., 2005). Other studies have defined risk indices of non-point source pollution as tools for establishing fertiliser, manure or slurry restrictions, developing correct agricultural practices and decreasing N pollution of groundwater (Kucharik and Brye, 2003; Studart *et al*., 2005; Van Es and Delgado, 2006; De Paz *et al*., 2009; Buczko *et al*., 2010).

As can be inferred, a second factor necessary for preventing NL through percolating water is controlled water management (Dwivedi *et al*., 2007). Nitrate leaches mainly through irrigation water, and thus irrigation management (time, frequency and quantity) may help in controlling these losses. Although it is generally expected that excessive irrigation will result in a higher download soil water flux, and consequently a higher NL, this would be reduced if water and N uptake by the crop were to be improved through choosing a crop with a high evapotranspiration rate and using an efficient irrigation method.

According to Dinnes *et al.* (2002), the leaching problem is not solely caused by N source management or any other single factor, but rather by a combination of soil management practices and by inherent physical, chemical and biological soil characteristics. Some particular factors influencing the magnitude of NL are: (1) N fertilisation rate, time, source and method; (2) intensity of cropping and crop N uptake; (3) soil profile characteristics that affect percolation; and (4) quantity, pattern and time of rainfall and/or supplemental irrigation (Beckwith *et al.*, 1998; Havlin *et al.,* 2005). According to Mantovi *et al.* (2006) and Buczko *et al.* (2010), NL is associated with intrinsic soil properties, water budget (especially deep percolation) and management practices. The risk of groundwater pollution increases with increasing movement of water, while slower drainage rates lead to lower NL and higher NO_3^- concentrations in soils.

Considering soil properties affecting percolation and potential NO_3^- pollution risks to groundwater, Addiscott (1996) classified three general soil types affecting water and NO_3^- movement: sandy soils, aggregated soils and heavy clay soils. i) Sandy soils affect water and NO_3^- movement due to the pore size distribution, the homogeneity of which promotes high water movement through much of the soil matrix, posing a threat to the quality of underlying aquifers. ii) In aggregated soils, some of the water moves easily though inter-aggregate pores, but some moves slowly or is retained by intra-aggregate pores. In this case, part of the NO_3^- inside the soil matrix, i.e. that within aggregates, remains relatively safe, but NO_3^- lying or being carried through inter-aggregate porosity bypasses the soil matrix and is easily leached to groundwater in rainfall periods if vertical porosity dominates. This is not a general law, because form, grade and hierarchy must be considered in aggregated soils, as water and NO_3^- behaviour differ depending on those soil structure properties. iii) many heavy clay soils display shrinking and swelling behaviour. This promotes water and NO_3^- movement, mainly through preferential pathways which could connect with the drainage system. In that case, pollutants and water can easily reach the groundwater or the surface drainage network.

It must be emphasised that NO_3^- in soils can move even faster than water due to the presence of charged soil colloids, which force anions dissolved in water to remain in the centre of pores according to the maximum microscopic velocity location (Corey *et al*., 1963; Krupp *et al*., 1972). In addition, extensive research has shown that NO_3^- moves faster in coarse than in fine-textured soils (Webster *et al*., 1986; Bergström and Johansson, 1991; Vinten *et al*., 1994). For instance, sandy soils generally have a high N leaching potential (van Es and Delgado, 2006), because they need abundant N inputs to sustain optimum crop yields, which increases the movement of solutes and leaching (Lembke and Thorne, 1980; Gehl *et al*., 2005).

Knowledge of solute transport processes in soils is important to understand the problems of natural water pollution by leaching to groundwater or redistribution within the vadose zone (Lal and Shukla, 2004). In this context, leaching studies at field level are relevant to study the environmental fate and behaviour of pollutants, as they provide realistic situations and the processes that govern the transport mechanisms can be easily accommodated. Other advantages of field studies are the lack of disturbance of the soil structure within the soil profile and the ability to sample on a regular basis and to monitor the natural phenomena of rainfall and temperature, which ultimately affect the overall rate of transformation and dissipation of solute in the soil.

Due to the dependency of NL on inherent soil characteristics, climate, irrigation and management practices, it can be predicted through the use of pedotransfer functions (PTF) (Shein and Arkhangel'skaya, 2006). The NL indices obtained in this way can be useful tools in identifying risk zones and restricting fertiliser and manure applications accordingly.

Water movement in soils can occur through saturated, unsaturated and preferential flow (Kutilek and Nielsen, 1994), which results in complex and dynamic solute transport. During saturated flow all the pore space is occupied by water and such flows occur predominantly below the watertable (Hillel, 1998; Radcliffe and Rasmussen, 2002). In contrast, in unsaturated flow many pores are air-filled, the pressure head is negative and the movement occurs predominantly in the vadose zone. Both mechanisms are well understood and the literature abounds with research on the subject (e.g. Beven and German, 1982; Kung, 1990; Bootlink *et al*., 1993). As water infiltrates into the soil, it carries with it dissolved ions or it can dissolve solutes as it proceeds. Solute transport processes in soil and sediments involve convection and dispersion, which spread dissolved mass in groundwater (Leij and van Genuchten, 2002). Convection is associated with mass transport due simply to the flow of water in which the mass is dissolved, and therefore coincides with the direction and rate of groundwater flow. Dispersion includes processes such as hydrodynamic diffusion and works additively, causing a zone of mixing between a fluid of one composition adjacent to, or being displaced by, a fluid of a different composition. Thus, some of the solutes carried by water are left behind, adsorbed, taken up by plants and precipitated out of solution. The remainder are leached and move throughout the profile with water flow (Hillel, 1998; Domenico and Schwartz, 1998).

1.1.2 Preferential flow

Soil hydraulic processes have been shown to be more complex than expected in former decades, when flow theory assumed saturated, homogeneous and isotropic soil solution movement through the matrix. Later, several studies have demonstrated that in soils the water flow occurs in unsaturated and anisotrophic conditions, due to several soil inherent properties (Hillel, 1998; Radcliffe and Rasmussen, 2002; Lal and Shukla, 2004). Research in recent decades has focused on solute transport and flow through macropores (Mooney and Morris, 2008), as saturated and unsaturated flow theories and their models are unsatisfactory in predicting the entire behaviour.

Uneven and often rapid movement of water and solutes plays a major role in field leaching, associated with the rapid transport of water and solutes through cracks, biopores, fractures, funnels, wormholes and root channels in soils (Nielsen *et al*., 2010). Termed *preferential flow*, *by-pass flow* or *macropore flow*, it is now widely recognised in many parts of the world as one of the major causes of groundwater contamination by agro-chemicals and other materials (Janssen and Lennartz, 2008; Mooney and Morris, 2008; Jarvis *et al.*, 2012).

Preferential flow (PF) comprises all phenomena where water and solutes move along certain pathways, while bypassing other volume fractions of the porous soil matrix, allowing unusually rapid and deep movement of chemicals with relatively little infiltrating amounts of water (rain or irrigation). Unfortunately, PF effectively bypasses much of the soil profile within which pollutants are normally bound and/or degraded, because just a partial fraction of the total cross-section is available for flow (Radcliffe and Rasmussen, 2002). The PF is more the rule than the exception and has both environmental and human health implications, since it favours contaminant transport to groundwater without chemical or biological breakdown in the reactive upper layer of soil (Allaire *et al.*, 2009; Jarvis *et al*., 2012). Thus, a significant fraction of the contaminants quickly reaches the subsoil, where the natural attenuation processes are generally less effective (Burden and Sims, 1999; Buss *et al*., 2004; Philippot and Germon, 2005; Gadd, 2005; Rivett *et al*., 2008). In addition, PF can either enhance, or curtail, the capacity of the soil to buffer and filter, and it can compromise, or boost, other ecosystem services (Clothiers *et al.*, 2008).

Early studies of water flow in soils that demonstrated the existence of PF realised the difficulty of predicting water movement in unsaturated conditions. In fact, PF was thought to be essentially unpredictable due to the high spatial and temporal variability and the randomness of the associated processes (Beven, 1991; Jury and Flühler, 1992). This was seen as a problem, since PF is so prevalent in soils, but subsequent studies have suggested that PF, and thus unsaturated flow, may be predictable to some extent (Flury *et al*., 1994; Jarvis *et al.*, 2012).

This kind of flow occurs at two different scales: via intraaggregate and interaggregate porosity, or textural and structural porosity, respectively. The first scale is referred to as finger, funnel or heterogeneous flow in soil matrix pores at pedon scale (intraaggregate porosity), due to differences in macroscopic hydraulic characteristics (Kung, 1990; Jarvis *et al.*, 2012). In such cases, even in the absence of macropores, an unstable wetting front develops in unstructured soils and moves preferentially between separate vertical finger streams, especially towards the groundwater (Baker and Hillel, 1990; Lipsius and Mooney, 2006). For the development of unstable flow in soils, soil layering or entrapped air towards the wetting front, hydrophobic conditions associated with organic compounds and very dry soil conditions are necessary (Ritsema *et al*., 1993; Wang *et al*., 1998). The other PF at pore scale occurs via macropores (interaggregate porosity) due to great differences in permeability. Three types of macropores can be distinguished, those formed by plant roots and soil macrofauna, those formed by swelling and shrinking (drying-wetting or freezing-thawing), depending on seasonal cycles, and irregular interaggregate voids formed by tillage (Jarvis *et al*., 2012). Macropore flow is highly sensitive to the presence of initial boundary conditions and obviously depends on geometric factors of porosity (continuity, tortuosity and diameter), which are generally unknown variables and present a high spatial and temporal variability.

Although, there is no need to know the properties, characteristics and behaviour of isolated macropores, for research purposes their integrated behaviour and characteristics have been determined through studies of flow and transport at larger scales. Measured soil properties or soil morphology can explain macropore flow effects on solute transport at pedon level (Flury *et al*., 1994; Vervoort *et al*., 1999; Mooney and Morris, 2008).

Many factors in aggregation and degradation processes affect PF, including initial pedogenic factors such as climate, organisms, parent materials, time and relief (Figure 1.3). The most important process related to PF is soil aggregation and hence the formation of continuous networks of larger macropores. Thus, strong macropore flow can be expected in strongly structured soils with vertical continuous macropores and a poorly developed or degraded structure hierarchy (Jarvis *et al*., 2012). Processes involved in aggregate formation are related mainly to the soil shrinkage and expansion caused by drying-wetting seasonal cycles (Dexter, 1988; Semmel *et al*., 1990), as well as mechanisms based on organic matter factors (Cheshire 1979; Chaney and Swift, 1986). Tillage increases organic matter oxidation, with a decrease in soil friability and increased soil compaction due to repeated traffic (Watts and Dexter, 1998). Tillage also degrades the structural hierarchy and compresses soil aggregates in the plough layer, promoting stronger PF in arable soils (Jarvis, 2007; Luo *et al*., 2010). On the other hand, the large roots of some crops can enhance water and solute transport into the subsoil. Roots can also act as drying soil agents, influencing macroaggregate development (Angers and Caron, 1998). Other biotic agents that promote PF are deep burrowing by anecic earthworm species, creating conduits deep into the subsoil (Lamandé *et al*., 2003). At different flow scales (intraaggregate porosity), sandy soils without structure hierarchy show preferential finger and funnel flow, promoted by water repellency (Deurer and Bachmann, 2007). Besides, an increase in PF can be produced by the long-term use of organic amendments, which cause organic-rich topsoils to become hydrophobic when dry (Wang *et al*., 1998; Blanco-Canqui and Lal, 2009). Regardless of the origin, preferential flow with its hydrological influence is a highly transient, threshold-dependent process.

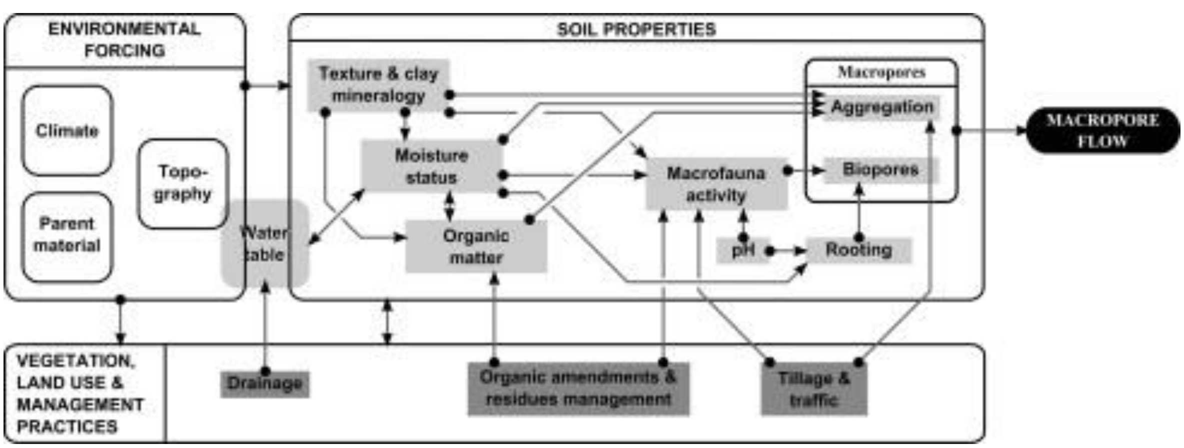


Figure 1.3. Controls on soil structure and macropore flow: a complex web of interactions between soil-forming factors (driving forces), soil properties and land management (Jarvis *et al.*, 2012).

1.1.3 Relationships between soil management and nitrate leaching

Conventional agricultural management alters soil physical properties by changing the soil structure. Application of amendment/fertiliser and tillage are two of the most common agricultural practices to make soil a suitable medium for growing crops.

Application of slurry at adequate doses can achieve satisfactory yields, substituting partially or completely the mineral fertilisers (Zebarth *et al*., 1996; Jensen *et al*., 2000) and improving soil properties (Hemmat *et al*., 2010; Melleck *et al*., 2010). However, Daudén and Quílez (2004) reported that slurry application promoted lower NO_3^- leaching than mineral fertiliser, while Thomsen (2005) observed increased NO_3^- leaching losses with increasing rates of slurry application.

Slurry application, by altering soil physical properties and soil hydraulic properties, has the potential of alter PF and associated NL. Slurry incorporation to 0-10 cm soil depth reduces soil bulk density and significantly increases soil organic carbon content (Hemmat *et al*., 2010; Melleck *et al*., 2010). It has also been reported to increase macroporosity, aggregate size and macroaggregate stability and to result in a nearly five-fold increase in saturated hydraulic conductivity (*Ks*) at doses of 180 kg ha^{-1} compared with unamended soil (Melleck *et al*., 2010). Ndiaye *et al*. (2007) found that in soils under tillage, slurry application promoted higher *Ks* in the upper horizon, with no surface runoff or ponding, and increased deep drainage flux compared with mineral fertiliser, which can promote NL if pore connection is not altered.

Tillage disrupts soil functional macroporosity, reducing its connectivity and its continuity in the plough layer (Kooistra *et al*., 1984; Cameira *et al*., 2003; Vanclooster *et al*., 2005; Buczko *et al*., 2006; Jarvis, 2007; Larsbo *et al*., 2009), while leaving intraaggregate porosity unaltered (Larsbo *et al*., 2009). Macropore space and structure depend on a dynamic balance between constructive and destructive forces and tillage practices, but wheel traffic promotes spatial and temporal variability of soil structure and soil pore properties in the plough layer by compaction (Mohanty *et al*., 1996). These changes in the soil pore network and structural stability result in altered hydraulic properties compared with untilled or reduced tillage management and hence influence the pathways of water flow and soil solute transport (Buczko *et al*., 2006; Turpin *et al*., 2007; Schwen *et al*., 2011).

Several studies have demonstrated inconsistent results regarding the impact of tillage systems on solute leaching (Logan *et al*., 1994; Randall and Iragavarapu, 1995; Weed and Kanwar, 1996; Clay *et al*., 1998; Elliot *et al*., 2000; Hangen *et al*., 2002; Zhu *et al*., 2003; Collum, 2009). For example, Besson *et al.* (2011) found significant differences in solute transport between reduced and conventional tillage (CT), with CT resulting in speedier, more homogeneous and less dispersive solute transport than reduced tillage, due to soil structure changes generated through tillage and compaction. Those authors concluded that the relationships between tillage management and solute transport are complex, scale- and time-dependent and influenced by boundary conditions and tillage practices.

Many authors report that CT can reduce NL to groundwater through soil PF and transport, by interrupting the continuity of macropores that act as PF paths (Thomas *et al*., 1973; Tyler and Thomas, 1977; Kranz and Kanwar, 1995; Elliot *et al*., 2000; Hangen *et al*., 2002; Collum, 2009). Other studies have concluded that CT has insignificant effects on leaching compared with no-till or minimal tillage systems (Logan *et al*., 1994; Clay *et al*., 1998; Zhu *et al*., 2003). Considering this lack of agreement, NL in general must be attributed to PF connectivity increases in untilled soils and hence greater solute transport, compared with higher N mineralisation, lower organic matter content and lower denitrification rates under tillage.

However, some studies suggest that although untilled soils promote higher deep percolation, CT causes higher NL (Randall and Iragavarapu, 1995; Weed and Kanwar, 1996). This may be because, on the one hand, untilled soils have higher denitrification rates, which result in the undesirable environmental impact of greenhouse gas (NH_3 and N_2O) emissions (Patni *et al*, 1998; Mkhabela *et al*., 2008). On the other hand, CT soils have weaker sorption capacity due to lower soil organic carbon content or slower microbial activity, besides increased N mineralisation (Kanwar *et al*., 1985; Drury *et al*., 1993; Ritter *et al*., 1993).

Such inconsistent results regarding the effect of tillage on solute transport in soils can be overwhelmed by the effects of climate, soil type, soil physical and chemical properties, soil historical management, plant residues and space-time variations in soil measurement conditions (Logsdon and Jaynes, 1996; Alletto *et al.*, 2010; Besson *et al*., 2011). Jarvis (2007) also include tillage characteristics (implement type, mechanical stress, plough speed and depth and machinery weight) and Strudley *et al*. (2008) take into account the spatial and temporal variability of tillage management practices.

1.1.4 Relationships between soil hydraulic properties, preferential flow, solute transport and measurement methods

Soil hydraulic properties, especially hydraulic conductivity (*Ks*), water retention capacity and PF, are particularly important because they regulate the movement and spatial distribution of water and solutes in soils. Due to material stratification by the sedimentation process (Tarbuck and Lutgens, 2005; Nichols 2009), horizonation due to pedogenetic processes (Buol *et al.*, 1973), preferred orientation of cracks of expansive clays (Van Breemen and Buurman, 2003) and soil aggregation (Hillel, 1998), most soils display hydraulic properties that are unequal in all directions. In this sense, because soil properties have a directional dependency, it can be said that soil is an anisotrophic medium (Domenico and Shwartz, 1998; Weight, 2004; Dörner and Horn, 2006). Moreover, some studies that include *Ks* measurements have found that soils vary at very short distances even within the same soil cartographical unit (Salgado, 1999; Radcliffe and Rasmussen, 2002). Therefore, soil as a heterogeneous medium by extrapolation can promote the same spatial variability in solute concentration within the soil profile (Domenico and Shwartz, 1998, Weight and Sondereger, 2000).

Despite the environmental importance of NL, its measurement is not easy. The more direct measurement methods are based on sampling of the soil solution at a given depth, determination of NO_3^- content and measurement of downward flow of this solution. The different methods of soil solution sampling, as well as their advantages and disadvantages, are discussed by Ramos and Kücke (1999). Several of the more common methods of drainage measurement or estimation are also considered, with special attention to the water and chloride balance methods, use of lysimeters and methods for hydraulic gradient and *Ks* measurement or estimation. Examples of different methods to determine NL include analyses of leached water obtained through soil suction cups, monolith lysimeters, N concentrations in groundwater, measurements of NO_3^- concentration in soil profile and analyses of percolate from tile drains (Bukzco *et al*., 2010).

There are several methods available to assess water and solute transport and to quantify PF directly and indirectly, in order to obtain a better understanding of NL. One of the direct methods for measuring solute transport is to determine the breakthrough curves on columns of undisturbed soil, without the need for PF analysis. The spread and asymmetry of these curves are good indicators of physical non-equilibrium (Jacobsen *et al*., 1992), whilst skewness of the curves is an indicator of the degree of preferential transport (Jarvis *et al*., 2012). The tension infiltrometer is another *in situ* technique that measures and characterises water transmission near to saturation tensions in soil macropores, which are considered to be important for water and solute movement. These devices can be used to characterise water flow in soils for two domain systems, soil matrix porosity and macroporosity (Cameira *et al*., 2003). Another method which when used in combination with breakthrough curves maximises the information obtained from column experiments is dye staining (Mooney and Morris, 2008; Jarvis *et al*., 2008).

Dye tracer experiments linked to image analysis of photographic snapshots allow semi-quantitative assessment of pathways (shape, width and length) and also allow different flow patterns to be classified according to pathway parameters (Weiler and Flühler, 2004). Dye staining tests can be applied to soil monoliths, field pedons or thin sections of soils, but the scale of measurement can obscure flow patterns, especially in reduced size samples. In this method, dyes are used as tracers to visualise infiltration patterns and PF pathways in the soil (Flury *et al*., 1994; Weiler and Flühler, 2004; Alaoui and Goetz, 2008; Nielsen *et al*., 2010). The criterion for dyes in soil studies is that they stain soil particles and as long as they display good visibility and contrast with soil matrix colours, they can be regarded as valuable tracers even though they display moderate sorption. Other essential characteristics of a dye tracer are low toxicity and a stable colour spectrum (Flury and Flühler, 1995). One of the most commonly used dyes is Brilliant Blue FCF (BB) because it meets these demands. BB has a higher contrast in soils compared with other common dye colours such as red, is stable, insensitive to ionic strength and pH changes (Germán-Heins and Flury, 2000) and has low toxicity (Flury and Flühler, 1995). One of the disadvantages of BB regarding sorption is that its front is limited compared with the water front due to non-linear sorption on particulate clay minerals (Flury and Flühler, 1995; Ketelsen and Meyer-Windel, 1999). A study by Kramers *et al.* (2009) showed that the dye was heterogeneously redistributed through the soil even at the relatively low irrigation intensity used, and that this effect was stronger under dry initial conditions for two of the three soils tested. It must be considered that dye tracer experiments allow the spatial variability in the flow process to be measured, and not the temporal variability, which cannot be captured by single snapshot photographs. Other limitations of dye experiments are the 2D image produced, the assumption that pores are isotrophic 3D features and the characteristics of dye tracers, which are adsorbed with different intensities to different soil constituents (Kung, 1990; Schwartz *et al*., 1999). The emerging technology of X-ray computed tomography allows 3D images of the macropore network to be created for samples large enough to be representative of the typical spatial pattern of soil macropores and at high resolution, but with access and cost difficulties (Mooney and Morris, 2008; Jarvis *et al*., 2012).

Studies of NL in Chilean soils are scarce and the few existing results contradictory. Moreover, only Blume *et al*., (2007; 2009) mention PF and dye tracer studies, but related to infiltration and runoff processes. Pollution of groundwater due to soil solute leaching, especially NO_3^-, under fertilised and amended soils, has been studied in Chile by several authors. Alfaro *et al*. (2006) found values of 66-261 kg N ha^{-1} leached for control and 150 kg N ha^{-1} fertilised lysimeters, respectively, in an Andisol receiving 1260 mm of rainfall. Other studies (Salazar *et al.*, 2010) reported values lower than 4.2 kg N ha^{-1} leached for additions of 400 kg N ha^{-1} (slurries and fertilisers) to Andisols and attributed these mainly to gaseous losses and retention characteristics of soils. Claret *et al.* (2011), on the other hand, reported NL values lower than 7.9 kg N ha^{-1} leached in an Alfisol under 1400 mm of rainfall, but without statistical differences between fertilised and control soils. However, Iriarte (2007) determined risks of NL in 27% of the soils (Mollisols, Inceptisols and Alfisols) within a sub-basin of central Chile (Region del Libertador Bernardo O' Higgins) and 63% of drinking water samples had higher concentrations than the threshold of 10 mg L^{-1} $N\text{-}NO_3$ prescribed by INN (1984). On the other hand, Arumi *et al.* (2005) observed that aquifers in the central valley of Chile do not contain significant nitrate concentrations associated with agricultural activity, inferring the existence of favourable conditions for the occurrence of natural attenuating processes such as denitrification. These contradictory pollution results across Chilean soils are mainly explained by different management practices, soil properties and water budgets.

Many works have sought to develop integrated management strategies for sustainable production and minimise NL (Di and Cameron, 2002; Dinnes *et al*., 2002; Dwivedi *et al*., 2007; Agostini *et al*., 2010). A considerable number of these NL mitigation strategies involve a range of management options such as reduced N application rates, improved timing of N application at appropriate rates and according to soil/plant tests monitoring, synchronisation of N supply with plant demands, the use of cover crops, precision agriculture, diversification of crop rotations, irrigation management practices and also applied techniques such as nitrification inhibitors, watertable management, biofilters and porous treatment walls in polluted waters, bioremediation, phytoremediation, management of riparian zones and others. However, many of these strategies are very expensive, so an efficient and integrated management plan designed according to a holistic and comprehensive knowledge of N dynamics is the best alternative to reduce NL and its impact, although it must be elaborated according to cost-effectiveness and human/environmental health.

Due to the complexity of processes governing solute and water movement in soils and its temporal and spatial variability, as discussed above, studying the synergies between pedology and soil hydraulics is key to solving problems of water quality (Jarvis *et al*., 2012). Besides, there is still a need for better understanding of the economic and environmental costs of PF and the advantages generated by soil structure development and care (Clothier *et al*., 2008).

Therefore the study described in this thesis was carried out in two basins of central Chile, San Pedro and Pichidegua, where two soils (Typic Xerochrept and Mollic Xerofluvent, respectively) were selected. Both soils are continuously cropped with maize (*Zea mays*) and amended with pig slurry. Each amended soil and their respective control (uncultivated and without pig slurry applications) were characterised in morphological, physical and hydraulic terms (3 replicates per soil). In addition, soil coring was used to obtain soil samples at 0, 25, 50 and 100 cm depth for measuring mineral N (NO_3^- and NH_4^+) concentrations. Water content was monitored and preferential flow paths were assessed with a dye tracer.

1.2 Hypothesis and objectives

As indicated above, low mean NO_3^- values in the vadose zone should not be interpreted as posing a low risk of impact to groundwater, as they may be the result of swift, unattenuated NO_3^- transport to the groundwater (the same may apply to the root zone). The starting hypothesis for this Master's thesis was thus that in coarse-textured (alluvial) soils irrigated with pig slurry, physical and hydraulic soil properties, but also preferential flow paths, mainly determine the NO_3^- leaching to groundwater.

Specific objectives of the thesis, which was carried out in the central zone of Chile during the fallow period (autumn-winter season) were:

i) To assess the relationships between morphological, physical and hydraulic soil properties and nitrate concentration distributions (Chapter 2).
ii) To evaluate preferential flow in the soils of the study areas (Chapter 3).
iii) To obtain an index based on physical and hydraulic soil properties for nitrate leaching risk to groundwater pollution (Chapter 4).

1.3 REFERENCES

Addiscott, T.M. 1996. Fertilizers and nitrate leaching. pp: 1-26. *In*: Hester, R.E., Harrison, R.M. (Eds). Agricultural Chemicals and the Environment. Issues in Environmental Science and Technology N° 5. The Royal Society of Chemistry, Cambridge. 126 p.

Agostini, F., Tei, F., Silgram, M., Farnaselli, M., Benincasa, P., Aller, M.F. 2010. Decreasing nitrate leaching in vegetable crops with better N management. pp: 147-200. *In*:

Lichtfouse, E. (Ed). Genetic Engineering, Biofertilisation, Soil Quality and Organic Farming, Sustainable Agriculture Reviews 4. Springer Science and Business Media B.V. 414 p.

Alaoui, A., Goetz, B., 2008. Dye tracers and infiltration experiments to investigate macropore flow. Geoderma 144, 279-286.

Alfaro, M., Salazar, F., Endress, D., Dumont, J., Valdebenito, A. 2006. Nitrogen leaching losses on a volcanic ash soil as affected by the source of fertilizer. Revista de la Ciencia del Suelo y Nutrición Vegetal 6, 54-63.

Allaire, S., Roulier, S., Cessna, A. 2009. Quantifying flow in soils: A review of different techniques. Journal of Hydrology 378, 179-204.

Alletto, L., Coquet, Y., Benoit, P., Heddadj, D., Barriuso, E, 2010. Tillage management effects on pesticide fate in soils: a review. Agronomy for Sustainable Development 30, 367-400.

Angers, D.A. and Caron, J. 1998. Plant-induced changes in soil structure: Processes and feedbacks. Biogeochemistry 42, 55-72.

Arumi, J., Oyarzún, R., Sandoval, M. 2005. Natural protection against groundwater pollution by nitrates in the Central Valley of Chile. Hydrological Sciences Journal 50(2), 331-340.

Baker, R.S., Hillel, D. 1990. Laboratory tests of a theory of fingering during infiltration into layered soils. Soil Science Society of America Journal 54, 20-30.

Beckwith, C.P., Cooper, J., Smith, K.A., Shepherd, M.A. 1998. Nitrate leaching loss following application of organic manures to sandy soils in arable cropping. I. Effects of application time, manure type, overwinter crop cover and nitrification inhibition. Soil Use and Management 14, 123-130.

Benjamin, N. 2005 Nitrate and health. pp: 145-162. *In*: Addiscott, T.M. (Ed). Nitrate, Agriculture and the Environment. CABI Publishing. 279 p.

Bergström, L., Johansson, R. 1991. Leaching of nitrate from monolith lysimeters of different types of agricultural soils. Journal of Environmental Quality 20, 801-807.

Besson, A., Javaux, M., Bielders, C., Vanclooster, M. 2011. Impact of tillage on solute transport in a loamy soil from leaching experiments. Soil and Tillage Research 112, 47-57.

Beven, K. 1991. Modeling preferential flow: an uncertain future?. pp: 1-11. *In*: Gish, T.J., Shirmohammadi, A. (Eds.) Preferential Flow. Proceedings of National Symposium. ASAE, Michigan, USA.

Beven, K., German, P. 1982. Macropores and water flow in soils. Water Resources Research 18, 1311-1325.

Blanco-Canqui, H**.,** Lal, R. 2009. Extent of subcritical water repellency of soils under long-term no-tillage systems on a regional scale. Geoderma 149, 171-180.

Blume, T., Zehe, E., Bronstert, A. 2007. Use of soil moisture dynamics and patterns for the investigation of runoff generation processes with emphasis on preferential flow. Hydrology and Earth System Sciences Discussions 4, 2587-2624.

Blume, T., Zehe, E., Bronstert, A. 2009. Use of soil moisture dynamics and patterns at different spatio-temporal scales for the investigation of subsurface flow processes. Hydrology and Earth System Sciences 13, 1215-1234

Bohn, H.L., McNeal, B.L., O'Connor, G.A. 2001. Soil Chemistry (3rd ed.), John Wiley & Sons, New York, 320 p.

Booltink, H.W.G., Hatano, R., Bouma, J. 1993. Measurement and simulation of bypass flow in a structures clay soil: a physico-morphological approach. Journal of Hydrology 148, 149-168.

Bryan, N., Loscalzo, J. 2011. Nitrite and Nitrate in Human Health and Disease. Bendich, A. (Ed). Humana Press - Springer Science Business Media. 306 p.

Bryan, N., van Grinsven, H. 2013. The role of nitrate in human health. Advances in Agronomy 119, 153-182.

Buczko, U., Bens, O., Huttl, R.E. 2006. Tillage effects on hydraulic properties and macroporosity in silty and sandy soils. Soil Science Society of America Journal 70, 1998-2007.

Buczko, U., Kuchenbuch, R., Lennartz, B. 2010. Assessment of the predictive quality of simple indicator approaches for nitrate leaching from agricultural fields. Journal of Environmental Management 91, 1305-1315.

Buol, S.W., Hole, F.D., McCracken, R.J. 1973. Soil Genesis and Classification. Iowa University Press, USA, 360 p.

Burden, D.S., Sims, J.L. 1999. Fundamentals of soil science as applicable to management of hazardous wastes. Environment Protection Agency. Ground Water Issue Document EPA/540/-S-98/500.

Buss, S.R., Herbert, A.W., Morgan, P., Thornton, S.F., Smith, J.W.N. 2004. A review of ammonium attenuation in soil and groundwater. Quarterly Journal of Engineering Geology and Hydrogeology 37(4), 347-359.

Cameira, M.R., Fernando, R.M., Pereira, L.S. 2003. Soil macropore dynamics affected by tillage and irrigation for a silty loam alluvial soil in southern Portugal. Soil and Tillage Research 70, 131-140.

Chaney, K., Swift, R.S. 1986. Studies on aggregate stability: II. The effect of humic substances on the stability of reformed soil aggregates. Journal of Soil Science 37, 337-343.

Cheshire, M. 1979. Nature and origins of carbohydrates in soils. Academic Press, London. 242 p.

Claret, M., Urrutia, R., Ortega, R., Best, S., Valderrama, N. 2011. Quantifying nitrate leaching in irrigated wheat with different nitrogen fertilization strategies in an Alfisol. Chilean Journal of Agricultural Research 71, 148-156.

Clay, S.A., Clay, D.E., Koskinen, W.C., Berg, R.K. 1998. Application method: impacts on atrazine and alachlor movement, weed control, and corn yield in three tillage systems. Soil and Tillage Research 48, 215-224.

Clothier, B.E., Green, S.R., Deurer, M. 2008. Preferential flow and transport in soil: progress and prognosis. European Journal of Soil Science 59, 2-13.

Collum, R. 2009. Macropore flow estimations under no-till and till systems. Catena 78, 87-91.

Corey, J., Nielsen, D., Biggar, J. 1963. Miscible displacement in saturated and unsaturated sandstone. Soil Science Society of America Proceeding 27, 258-262.

Cottinghamn R., Delfau, K.F., Garde, P. 2010. Managing diffuse water pollution in South East Queensland. An analysis of the role of the Healthy Waterways Partnership. 58 p.

Dauden, A., Quílez, D. 2004. Pig slurry versus mineral fertilization on corn yield and nitrate leaching in a Mediterranean irrigated environment. European Journal of Agronomy 21, 7-19.

De Paz, J., Delgado, J., Ramos, C., Shaffer, M., Barbarick, K. 2009. Use of a new GIS nitrogen index assessment tool for evaluation of nitrate leaching across a Mediterranean region. Journal of Hydrology 365, 183-194.

Deurer, M., Bachmann, J. 2007. Modeling water movement in heterogeneous water-repellent soil: 2. Numerical simulation. Vadose Zone Journal 6, 446-457.

Dexter, A.R. 1988. Strength of soil aggregates and of aggregate beds. pp. 35-52. *In*: Drescher, J., Horn, R., de Boodt, M. (Eds). Impact of Water and External Forces on Soil Structure. Catena Supplement 11. Catena Verlag. Reiskirchen, Germany. 171 p.

Di, H.J., Cameron, K.C. 2002. Nitrate leaching in temperate agroecosystems: sources, factors and mitigation strategies. Nutrient Cycling in Agroecosystems 46, 237-256.

Dinnes, D.L., Karlen, D.L., Jaynes, D.B., Kaspar, T.C., Hatfield, J.L., Colvin, T.S., Cambardella, C.A. 2002. Nitrogen management strategies to reduce nitrate leaching in tile-drained Midwestern soils. Agronomy Journal 94, 153-171.

Dissanayake, C.B., Chandrajith, R. 2009. Nitrates in the geochemical environment. pp: 139-155. *In:* Freiwald, A. (Ed.). Introduction to Medical Geology: focus on tropical environments. Erlangen Earth Conference Series. 297 p.

Domenico, P.A., Schwartz, F.W. 1998. Physical and Chemical Hydrogeology, (2nd ed.), John Wiley and Sons Inc., NY, 506 p.

Dörner, J., Horn, R. 2006. Anisotropy of pore functions in structural Stagnic luvisols in the weichselian moraine region in Germany. Journal Plant Nutrition Soil Science 169, 212-220.

Drury, C., Mckenney, D., Findlay, W., Gaynor, J. 1993. Influence of tillage on nitrate loss in surface runoff and tile drainage. Soil Science Society of America Journal 57, 797-802.

Dwivedi, U.N., Mishra S., Singh, P., Tripathi, R.D. 2007. Nitrate pollution and its remediation. pp: 353-389. *In*: Singh, S.N., Tripathy, R.D. (Eds.). Environmental Bioremediation Technologies. Berlin: Springer. 518 p.

Elliott, J.A., Cessna, A.J., Nicholaichuk, W., Tollefson, L.C., 2000. Leaching rates and preferential flow of selected herbicides through tilled and untilled soil. Journal of Environmental Quality 29(5), 1650–1656.

EPA. 1987. Agricultural Chemicals in Ground Water: Proposed Strategy, Office of Pesticides and Toxic Substances. Environmental Protection Agency, U.S.A., Washington, D.C., 150 p.

Flury, M., Flühler, H., Jury, W.A., Leuenberger, J. 1994. Susceptibility of soils to preferential flow of water: a field study. Water Resources Research 30 (7), 1945-1954.

Flury, M., Flühler, H. 1995. Tracer characteristics of brilliant blue FCF. Soil Science Society of America Journal 59, 22-27.

Gadd, G. 2005. Microorganisms in toxic metal-polluted soils. pp: 325-358. *In*: Buscot, F., Varma, A. (Eds.) Microorganisms in Soils: Roles in Genesis and Functions. Springer-Verlag. Leipzig, Germany. 419 p.

Galloway J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., Cosby, B.J. 2003. The nitrogen cascade. BioScience 53(4), 341-356.

Gehl, R.J., Schmidt, J.P., Stone, L.R., Schlegel, A.J. Clark, G.A. 2005. *In situ* measurements of nitrate leaching implicate poor nitrogen and irrigation management on sandy soils. Journal of Environmental Quality 34, 2243-2254.

George, G., Järvinen, M., Nõges, T., Blenckner, T., Moore, K. 2010. The impact of the changing climate on the supply and recycling of nitrate. pp: 161-178. *In*: George, D. (Ed). The Impact of Climate Change on European Lakes. Aquatic Ecology Series 4. Springer Science Business Media. 507 p.

German-Heins, J., Flury, M. 2000. Sorption of brilliant blue FCF in soils affected by pH and ionic strength. Geoderma 97, 87-101.

Hangen, E., Buczko, U., Bens, O., Brunotte, J., Hüttl, R. 2002. Infiltration patterns into two soils under conventional and conservation tillage: influence of the spatial distribution of plant root structures and soil animal activity. Soil and Tillage Research 63, 181-186.

Harter, T., Davis, H., Mathews, M., Meyer, R. 2002. Shallow groundwater quality on dairy farms with irrigated forage crops. Journal of Contaminant Hydrology 55, 287-315.

Havlin, J.L., Tisdale, S.L., Nelson, W.L., Beaton, J.D. 2005. Soil Fertility and Fertilizers. An Introduction to Nutrient Management. 7th ed. Pearson Education Inc.-Prentice All. 528 p.

Hemmat, A., Aghilinategh, N., Rezainejad, Y., Sadeghi, M. 2010. Long-term impacts of municipal solid waste compost, sewage sludge and farmyard manure application on organic carbon, bulk density and consistency limits of a calcareous soil in central Iran. Soil and Tillage Research 108, 43-50.

Hillel, D. 1998. Environmental Soil Physics. Academic Press. Boston, 771 p.

INN. 1984. Norma Chilena Oficial para Agua Potable (NCh 409). (Official Chilean Standard for Drinking Water, National Standards Institute). Instituto Nacional de Normalización. 15 p.

Iriarte, A. 2007. Evaluación espacial de la lixiviación potencial de nitratos en suelos de la subcuenca del río Cachapoal bajo. Memoria para optar al Título Profesional de Geógrafo. Universidad de Chile, Santiago. 124 p.

Janssen, M., Lennartz, B. 2008. Characterization of preferential flow pathways through paddy bunds with dye tracer tests. Soil Science Society of America Journal 72, 1756-1766.

Jacobsen, O.H., Leij, F.L. van Genuchten, M.Th. 1992. Parameter determination for chloride and tritium transport in undisturbed lysimeters during steady flow. Nordic Hydrology 23, 89-104.

Jarvis, N. 2007. A review of non-equilibrium water flow and solute transport in soil macropores: principles, controlling factors and consequences for water quality. European Journal of Soil Science 58, 523-546.

Jarvis, N.J., Etana, A., Stagnitti, F. 2008. Water repellency, near-saturated infiltration and preferential solute transport in a mcroporous clay soil. Geoderma 143, 223-230.

Jarvis, N., Moeys, J., Koestel, J., Hollis, J. 2012. Preferential flow in a pedological perspective. pp: 75-120. In: Lin, H. (Ed.) Hydropedology. Synergistic Integration of Soil Science and Hydrology. Academic Press, USA. 858 p.

Jensen, M.B., Olsen, T.B., Hansen, H.C.B., Magid, J. 2000. Dissolved and particulate phosphorus in leachate from structured soil amended with fresh cattle faeces. Nutrients Cycling in Agroecosystems 56, 253-261.

Jury, W.A., Flühler, H. 1992. Transport of chemicals through soil: mechanisms, models, and field applications. Advances in Agronomy 47, 141-201.

Kanwar, R., Baker, J., Laflen, J. 1985. Nitrate movement through the soil profile in relation to tillage system and fertilization application method. Transactions ASAE 28, 1802-1807.

Ketelsen, H., Meyer-Windel, S. 1999. Adsorption of brilliant blue FCF by soils. Geoderma 90, 131-145.

Kooistra, M.J., Bouma, J., Boersma, O.H., Jager, A. 1984. Physical and morphological characterization of undisturbed and disturbed ploughpans in a sandy loam soil. Soil and Tillage Research 4, 405-417.

Kramers, G., Richards, K.G., Holden, N.M. 2009. Assessing the potential for the occurrence and character of preferential flow in three Irish grassland soils using image analysis. Geoderma 153, 362-371.

Kranz, W., Kanwar, R. 1995. Spatial distribution of leachate losses due to preplant tillage method. pp: 107-110. *In*: Clean water - clean environment, 21st century. Team agriculture-working to protect water resources. Conference Proceedings. Kansas City, Missouri. ASAE 2, St Joseph, MI. 672 p.

Krupp, H., Biggar, S., Nielsen, D. 1972. Relative flow rates of salt in water in soil. Soil Science Society of America Proceeding 36, 412-417.

Kucharik, C., Brye, K. 2003. Integrated biosphere simulator (IBIS) yield and nitrate loss predictions for Winsconsin maize receiving varied amounts of nitrogen fertilizer. Journal of Environmental Quality 32, 247-268.

Kung, K.-J. S. 1990. Preferential flow in a sandy vadose zone: 1. Field observation. Geoderma 46, 51-71.

Kutilek, M., Nielsen, R. 1994. Soil Hydrology. Geoecology textbook. Catena Verlag, Cremlingen - Destedt, Germany, 370 p.

Lal, R., Shukla, M.K. 2004. Principles of Soil Physics. Part II. Soil Mechanics. Marcel Dekker. New York, USA, 716 p.

Lamandé, M., Hallaire, V., Curmi, P., Péres, G., Cluzeau, D. 2003. Changes of pore morphology, infiltration and earthworm community in a loamy soil under different agricultural managements. Catena 54, 637-649.

Larsbo, M., Lapen, D.R., Topp, E., Metcalfe, C., Abbaspour, K.C., Fenner, K. 2009. Simulation of pharmaceutical and personal care product transport to tile drains after biosolids application. Journal of Environmental Quality 38, 1274-1285.

Leij, J., van Genuchten, M. 2002. Solute transport. pp: 189-144. *In*: Warrick, A.W. (Ed.) Soil Physics Companion. CRC Press. Boca Raton, Florida, USA. 373 p.

Lembke, W.D., Thorne, M.D. 1980. Nitrate leaching and irrigated corn production with organic and inorganic fertilizers on sandy soil. Transactions ASAE 23, 1153-1156.

Lipsius, K., Mooney, S. 2006. Using image analysis of tracer staining to examine the infiltration patterns in a water repellent contaminated sandy soil. Geoderma 136, 865-875.

Logan, T., Eckert, D., Beak, D. 1994. Tillage, crop and climate effects on runoff and tile drainage losses of nitrate and four herbicides. Soil and Tillage Research 30, 75-103.

Logsdon, S.D., Jaynes, D.B. 1996. Spatial variability of hydraulic conductivity in a cultivated field at different times. Soil Science Society of America Journal 60, 703-709.

Luo, L.F., Lin, H., Schmidt, J. 2010. Quantitative relationships between soil macropore characteristics and preferential flow and transport. Soil Science Society of America Journal 74, 1929-1937.

Mantovi, P., Baldoni, G., Toderi, G. 2005. Reuse of liquid, dewatered and composted sewage sludge on agricultural land: effects of long-term application on soil and crop. Water Research 39, 289-296.

Mantovi, P., Fumagalli, L., Beretta, G., Guermandi, M. 2006. Nitrate leaching through the unsaturated zone following pig slurry applications. Journal of Hydrology 316, 195-212.

Mellek, J. Diecko, J., da Silva, V., Favaretto, N., Pauletti, V., Machado, F., Moretti, J. 2010. Dairy liquid manure and no-tillage: Physical and hydraulic properties and carbon stocks in a Cambisol of Southern Brazil. Soil and Tillage Research 110, 69-76.

Miller, J.J., Sweetland, N.J., Chang, C. 2002. Hydrological properties of a clay loam soil after long-term cattle manure application. Journal of Environmental Quality 31, 989-996.

Mkhabela, M., Madani, A., Gordon, R., Burton, D., Cudmore, D., Elmi, A., Hart, W. 2008. Gaseous and leaching nitrogen losses from no-tillage and conventional tillage systems following surface application of cattle manure. Soil and Tillage Research 98, 187-199.

Mohanty, B., Ankeny, M., Horton, R., Kanwar, R. 1996. Spatial analysis of hydraulic conductivity measured using disk infiltrometers. Water Resources Research 30, 2489-2498.

Mooney, S., Morris, C. 2008. A morphological approach to understanding preferential flow using image analysis with dye tracers and X-ray computed tomography. Catena 73, 204-211.

Ndiaye, B., Molenat, J., Hallaire, V., Gascuel, C., Hamon, Y. 2007. Effects of agricultural practices on hydraulic properties and water movement in soils in Brittany (France). Soil and Tillage Research 93, 251-263.

Nichols, G., 2009. Sedimentology and Stratigraphy. 2nd Ed.; Wiley-Blackwell, Chichester, 419 p.

Nielsen, M., Styczen, M., Ernstsen, V., Petersen, C., Hansen, S. 2010. Field study of preferential flow pathways in and between drain trenches. Vadose Zone Journal 9, 1073-1079.

Oviattt, C.A., Gold, A.J. 2005. Nitrate in Coastal Waters. pp: 127-144. *In*: Addiscott, T.M. (Ed). Nitrate, Agriculture and the Environment. CABI Publishing. 279 p.

Patni, N.K., Masse, L., Jui, P.Y. 1998. Groundwater quality under conventional and no-tillage: I. Nitrate, electrical conductivity, and pH. Journal of Environmental Quality 27, 869-877.

Philippot, L., Germon, J.C. 2005. Contribution of bacteria to initial input and cycling of nitrogen in soils. pp: 159-177. *In*: Buscot, F., Varma, A. (Eds.) Microorganisms in Soils: Roles in Genesis and Functions. Springer-Verlag. Leipzig, Germany. 419 p.

Powlson, D., Addiscott, T., Benjamin, N., Caassman, K., de Kok, T., van Grinsven, H., L'hirondel, J., Avery, A., van Kessel, C. 2008. When does nitrate become a risk for humans?. Journal of Environmental Quality 37 (2), 291-295.

Radcliffe, D., Rasmussen, T. 2002. Soil water movement. pp: 85-126. *In*: Warrick, A.W. (Ed.) Soil Physics Companion. CRC Press. Boca Ratón, Florida, USA. 373 p.

Ramos, C., Kücke M. 1999. Revisión crítica de los métodos de medida de la lixiviación de nitrato en suelos agrícolas. pp: 25-32. *In*: Muñoz-Carpena, R., Ritter, A., Tascón, C. (Eds.) Estudios de la Zona No Saturada del Suelo. Vol. 4. ICIA: Tenerife. España. 198 p.

Randall, G.W., Iragavarapu, T.K. 1995. Impact of long-term tillage systems for continuous corn on nitrate leaching to tile drainage. Journal of Environmental Quality 24, 360-366.

Ritter, W., Scarborough, R., Chirnside, A. 1993. Nitrate leaching under irrigated corn. Journal of Irrigation and Drainage Engineering 119, 544-553.

Ritsema, C.J., Dekker, L.W., Hendrickx, J.M.H., Hamminga, W. 1993. Preferential flow mechanism in a water repellent sandy soil. Water Resources Research 29, 2183-2193.

Rivett, M.O., Buss, S.R., Morgan, P., Smith, J.W.N., Bemment, C.D. 2008. Nitrate attenuation in groundwater: A review of biogeochemical controlling processes. Water Research 42, 4215-4232.

Salazar, F., Alfaro, M., Misselbrook, T., Lagos, J. 2010. Nitrogen leaching following a high rate of dairy slurry application on a ryegrass sward of a volcanic soil in southern Chile. pp: 48-55. *In*: Losses on application and storage. Environmental, nutrient losses, impact of storage and spreading operations. Proceedings of the 14th RAMIRAN International Conferences, Lisboa, Portugal. CD.

Salgado, L.G. 1999. Manual de Estándares Técnicos yEconómicos para Obras de Drenaje. Comisión Nacional de Riego. Universidad de Concepción, Concepción, Chile. 401 p.

Schwartz, R.C., McInnes, K.J., Juo, A.S.R., Cervantes, C.E. 1999. The vertical distribution of dye tracer in layered soil. Soil Science 164(8), 561-573.

Schwen, A., Bodner, G., Scholl, P., Buchan, G., Loiskandl, W. 2011. Temporal dynamics of soil hydraulic properties and the water-conducting porosity under different tillage. Soil and Tillage Research 113, 89-98.

Semmel, H., Horn, H., Hell, U., Dexter, A. R., Osmond, G., Schulze, E.D. 1990. The dynamics of soil aggregate formation and the effect on soil physical properties. Soil Technology 3, 113-129.

Shein, E.V., Arkhangel'skaya, T. A. 2006. Pedotransfer functions: State of the art, problems, and outlooks. Eurasian Soil Science 39, 1089-1099.

Smil, V. 1999. Nitrogen in crop production: An account of global flows. Global Biogeochemical Cycles 13, 647- 662.

Sorensen, P., Rubek, G. 2012 Leaching of nitrate and phosphorus after autumn and spring application of separated solid animal manures to winter wheat. Soil Use and Management 28, 1-11.

Sparks, D. L. 2003. Environmental Soil Chemistry. Academic Press, USA. 352 p.

Steinfeld, H., Gerber, P., Wassenaar, T., Castel, V., Rosales, M., de Haan, C. 2006. Livestock's Long Shadow: Environmental Issues and Options. Food and Agriculture Organization of the United Nations. Rome. 390 p.

Strudley, M., Green, T., Ascough, J. 2008 Tillage effects on soil hydraulic properties in space and time: State of the science. Soil and Tillage Research 99, 4-48.

Studart, R., White, R.E., Weatherley, A.J. 2005. Modelling the risk of nitrate leaching from two soils amended with five different biosolids. Revista Brasileira de la Ciencia do Solo 29, 619-626.

Tarbuck, E., Lutgens, F. 2005. Ciencias de la Tierra: Una Introducción a la Geología Física. Pearson Education (Ed.). Madrid, España, 710 p.

Thomas, G., Blevins, R., Phillips, R., McMahon, M. 1973. Effect of a killed sod mulch on nitrate movement and corn yield. Agronomy Journal 65, 736-739.

Thomas, M. 2007. Soil conditions and early crop growth after repeated manure applications. Dissertation of Master Science degree. University of Saskatchewan, Canada. 139 p.

Thompson, R.B., Ryden, J.C., Lockyer, D.R. 1987. Fate of nitrogen in cattle slurry following surface application or injection to grassland. Journal of Soil Science 38, 689-700.

Thomsen, I. 2005. Nitrate leaching under spring barley is influenced by the presence of a ryegrass catch crop: Results from a lysimeter experiment. Agriculture, Ecosystems and Environment 111, 21-29.

Turpin, K., Lapen, D., Robin, M., Topp, E., Edwards, M., Curnoe, W., Topp, G., McLaughlin, N., Coelho, B., Payne, M. 2007. Slurry-application implement tine modification of soil hydraulic properties under different soil water content conditions for silt-clay loam soils. Soil and Tillage Research 95, 120-132.

Tyler, D., Thomas, G. 1977. Lysimeter measurements of nitrate and chloride losses from soil under conventional and no-tillage corn. Journal of Environmental Quality 6, 63-66.

Vahtera, E., Conley, D., Gustafsson, B., Kuosa, H. 2007. Internal ecosystem feedbacks enhance nitrogen fixing cyanobacteria blooms and complicate management in the Baltic Sea. Ambio 36, 186-194.

van Breemen, N., Buurman, P. 2003. Soil Formation. (2nd ed.). Kluwer Academic Publishers, 415 p.

van Es, H.M., Delgado, J.E. 2006. The nitrate leaching index. pp: 1119-1121. *In*: Lal, R. (Ed). Encyclopedia of Soil Science. (2nd Ed.). Taylor and Francis CRC Press. New York, USA. 2060 p.

van Es, H.M., Schindelbeck, R.R., Jokela, W.E. 2004. Effect of manure application timing, crop, and soil type on phosphorus leaching. Journal of Environmental Quality 33, 1070-1080.

Vanclooster, M., Javaux, M., Vanderborght, J. 2005. Solute transport in soil at the core and field scale. pp: 1041-1055. *In*: Anderson, M.G., McDonnell, J.J. (Eds.), Encyclopedia of Hydrological Sciences. Wiley Online Library. 3243 p.

Vervoort, R.W., Radcliffe, D.E., West, L.T. 1999. Soil structural development and preferential solute flow. Water Resources Research 35, 913-928.

Vinten, A.J.A., Vivian, B.J., Wright, F., Howard, R.S. 1994. A comparative study of nitrate leaching from soils of differing textures under similar climatic and cropping conditions. Journal of Hydrology 159, 197-213.

Wang, Z., Feyen, J., Elrick, D.E. 1998. Prediction of fingering in porous media. Water Resources Research 34, 2183-2190.

Watts, C.W., Dexter, A.R. 1998. Soil friability: theory, measurement and the effects of management and organic carbon content. European Journal of Soil Science 49, 73-84.

Webster, C.P., Belford, R.K., Cannell, R.Q. 1986. Crop uptake and leaching losses of ^{15}N labelled fertilizer nitrogen in relation to waterlogging of clay and sandy loam soils. Plant and Soil 92, 89-101.

Weed, D., Kanwar, R. 1996. Nitrate and water present in and flowing from root-zone soil. Jounal of Environmental Quality 25, 709-719.

Weight, W.D. 2004. Manual of Applied Field Hydrogeology. McGraw-Hill Editorial. 551 p.

Weight, W.D., Sondereger, J.L. 2000. Manual of Applied Field Hydrogeology. McGraw-Hill Editorial. 608 p.

Weiler, M., Flühler, H. 2004. Inferring flow types from dye patterns in macroporous soils. Geoderma 120, 137-153.

Zebarth, B.J., Paul, J.W., Schmidt, O., McDougall, R. 1996. Influence of the time and rate of liquid–manure application on yield and nitrogen utilization of silage corn in South Coastal British Columbia. Canadian Journal of Soil Science 76, 153-164.

Zhu, Y., Fox, R., Toth, J. 2003. Tillage effects on nitrate leaching measured by pan and wick lysimeters. Soil Science Society of America Journal 67, 1517-1523.

CHAPTER 2. MORPHOLOGICAL, PHYSICAL AND HYDRAULIC PROPERTIES OF SOIL RELATED TO NITRATE DYNAMICS UNDER PIG SLURRY ADDITION

2.1 ABSTRACT

Intensive agricultural management practices, including high applications of slurry and solid manure, alters soil physical and hydraulic properties. Soil water movement governs soil solute distribution, reflecting a higher spatial and temporal variability of soil properties and overshadowing the direct effects of slurry application and tillage on solute distribution. This study assessed the effects of slurry application on physical, hydraulic and morphological soil properties and examined relationships between N dynamics and N distribution in soils depending on these soil properties.

The study was carried out in two basins of central Chile, San Pedro and Pichidegua, on Quilamuta (Typic Xerochrept) and Tinguiririca (Mollic Xerofluvent) soils, respectively. Both soils were continuously cropped with maize (*Zea mays*) and amended with pig slurry. A control site on each soil (uncultivated and without organic material applications) was also included. Three pits per soil were used for soil characterisation in terms of soil morphological, physical and hydraulic properties. Nitrogen concentrations, as nitrate (NO_3^-) and ammonium (NH_4^+), were determined in soil samples collected at 0, 25, 50 and 100 cm depth and water content was measured with a FDR ®Diviner 2000.

Various relationships between the nature and size of soil particles and pore size distribution were found. Saturated hydraulic conductivity (*Ks*) was associated with soil particle and pore characteristics. Unsaturated hydraulic conductivity (*Kns*) was dependent on hydraulic gradient and displayed high temporal variability. Soil macroaggregate stability (MDV) was better correlated with soil organic matter content (SOM) in soils with slurry application, whereas microaggregate stability (DR) correlated better with SOM on control sites. Particle size distribution also affected structure stability and hydraulic conductivity variations (ΔK). Nitrate concentrations and their variations were better associated with water content and *Kns* in San Pedro than in Pichidegua soils and were also related to sand content and total porosity. The NH_4 content was related to SOM content and MDV. Further dye staining studies, measurements of groundwater NO_3^- at different scale levels and studies under controlled conditions are needed to obtain a full understanding of the laws governing solute pattern distribution, the effect of slurry application on soil properties and NO_3^- leaching to groundwater.

Key words: Nitrate leaching, soil hydraulic properties, groundwater contamination.

2.2 INTRODUCTION

Manure and slurry additions to soil supply nutrient inputs (Zebarth *et al*., 1996; Jensen *et al*., 2000), but also modify the soil structure and its pore geometry. Consequently, a crop yield increase can be observed due to improvement of air and water movement and its interplay with soil and roots (Miller *et al*., 2002; Miller *et al*., 2005; Thomas, 2007).

The increase in crop yields in recent decades has been accompanied by an increase in fertiliser, manure and slurry applications to achieve greater food production, but with negative environmental consequences. One of the most serious environmental impacts of organic and inorganic fertiliser use is NO_3^- (nitrate) leaching and groundwater pollution (Thomsen, 2005), which can cause nitrite (NO_2^-) poisoning in infants and diseases such as cancer, nervous system impairments and methaemoglobinaemia (Gehl *et al*., 2005; Powlson *et al*., 2008). Besides eutrophication of surface waters (Vahtera *et al.*, 2007), manure and slurry application also alter physical and hydraulic soil properties and the relationships between these and leaching are not well understood.

Nitrogen compounds derived from manures or slurries undergo various transformation processes (oxidation, reduction, mineralisation, denitrification, volatilisation and others) and its forms display different behaviours depending on their oxidation state. For most soils, N is leached as NO_3^-, which is not retained (adsorbed) by most soil colloids, whereas NH_4^+ can be immobilised by plants or microorganisms, retained by soil colloids and/or oxidised to NO_3^- (Bohn *et al*., 2001).

Application of slurry or liquid manure alters topsoil physical properties (i.e. aggregate stability, macroporosity, aggregate size, infiltration rate and hydraulic conductivity) by increasing soil organic matter content, depending on application dose (Hemmat *et al*., 2010; Mellek *et al*., 2010). However, traffic and tillage practices destroy soil aggregates, altering macropore continuity in the plough layer (Kooistra *et al*., 1984; Cameira *et al*., 2003; Vanclooster *et al*., 2005; Buczko *et al*., 2006; Larsbo *et al*., 2009) and reducing water and solute transport into subsoil (Buczko *et al*., 2006; Turpin *et al*., 2007; Schwen *et al*., 2011). As a consequence of organic matter oxidation by soil tillage, N mineralisation rate increases and solutes such as NO_3^- become available.

In addition, some soil processes and management practices increase the spatial and temporal variability in physical soil properties (Mohanty *et al.*, 1996), such as soil horizonation (Buol *et al.*, 1973), stratification (Tarbuck and Lutgens, 2007; Nichols 2009), aggregation and development of cracks with preferred orientation due to expansive clays (Hillel, 1998; van Breemen and Buurman, 2003), tillage operations and slurry application (Mohanty *et al*., 1996; Strudley *et al*., 2008). Therefore, soil transference of water and solutes can become a complex process when a heterogeneous and almost unpredictable solute distribution pattern is promoted (Domenico and Shwartz, 1998).

Indeed, the principal process that determines solute transport is water movement in the soil (Hillel, 1998). Consequently, the laws governing water dynamics through saturated, unsaturated and/or preferential flow also apply to solute distribution in the soil profile. However some factors, such as tillage, SOM distribution and vegetation, can overshadow the effect of one isolated variable on the distribution of solutes in soils (Logsdon and Jaynes, 1996; Alletto *et al*., 2010; Besson *et al*., 2011).

Field-applied slurry undergoes different decomposition processes over time depending on climate characteristics, especially temperature and soil water content (Guggenberger, 2005; Havlin *et al.*, 2005). This means that the N dynamics in soil are extremely complex, with high temporal variability in different organic and mineral forms of N (Philippot and Germon, 2005), as well as their concentration and distribution, which are intimately related to the water flows that transport them (Lafolie, 1991; Chen *et al*., 2011).

The objective of this work was to assess the effect of slurry application on physical, hydraulic and morphological soil properties and look for relationships between N dynamics and N distribution in soils depending on these soil properties.

2.3 MATERIALS AND METHODS

2.3.1 Site description

The study was carried out in two soil series of the central longitudinal valley of Chile, in the commune of Pichidegua in the O'Higgins Region (UTM 0277313E, 6194387S; Datum WGS 1984 19S) and in the commune of San Pedro in the Metropolitana Region (UTM 0289587E, 6240288S; Datum WGS 1984 19S), where two experimental sites were defined corresponding to two representative cartographical units or polypedons (phases of soil series) that may pose a high potential risk of NO_3^- pollution to groundwater.

At both sites, representative soils with similar agronomic management (crops, fertilisers and organic fertiliser application) were chosen, according to information obtained from the farmers involved (Table 1). In each case, a similar control soil (without amendments and fertilisers) was also selected and characterised.

Table 2.1. General description of conditions at the two study sites in central Chile.

Sites[a]	Basin	Soil classification	Soil use[b]	Applications	Last management
PC	Pichidegua	Mollic Xerofluvent	Fallow	Control	Ploughing
PS				Pig slurry	Stubble cultivation
SC	San Pedro	Typic Xerochrept	MAP	Control	None
SS			RCB	Pig slurry	Ploughing – sowing

[a] PC: Pichidegua control; PS: Pichidegua with slurry additions; SC: San Pedro control; SS: San Pedro with slurry additions. [b] MAP: Mediterranean annual prairie; RCB: ryegrass-barley-oat mix.

A deep, stratified alluvial soil is characteristic for both sites. Cartographically, the Pichidegua site belongs to the Tinguiririca soil series, a loamy sand soil classified as a coarse loamy, mixed, thermic Mollic Xerofluvent, occupying a recent alluvial terrace position (CIREN, 1996a). The San Pedro pedon belongs to the Quilamuta soil series, a sandy loam profile classified as a coarse loamy, mixed, thermic Typic Xerochrept, located on terraces or alluvial fans, with granitic parent material (CIREN, 1996b).

The climate at both sites is semi-arid Mediterranean, with most rainfall between May and October. Hot summers with relatively cold (Pichidegua) and relatively mild (San Pedro) winters characterise both basins. In the Pichidegua basin, the maximum (January) and minimum (July) annual air temperature is 29.0 ºC and 4.9ºC, respectively, with mean annual precipitation (MAP) of 696 mm (Santibáñez and Uribe, 1993). In the San Pedro basin, the maximum and minimum annual air temperature is 31.3 ºC and 4.4ºC, respectively, with MAP of 383 mm (Santibañez and Uribe, 1990).

During the study period, the San Pedro soil (SS) was not amended with pig slurry, but it had received regular applications of pig slurry during the previous 5-year period. In Pichidegua, which was under fallow management, two applications of approximately 500 m^3 ha^{-1} pig slurry were provided during the study period through a flooding irrigation valve, and the site had received regular pig slurry applications during the previous 10-year period. The mean N concentration measured in the pig slurry applied was 1.3 g L^{-1} and the volume of slurry applied on each occasion supplied a N dose of 640 kg ha^{-1}.

2.3.2 Field and laboratory measurements and sampling for soil tests

Morphological soil profile descriptions were initially made in pits according to Schoeneberger *et al*. (2012). Each experimental unit was sampled at 0, 25, 50 and 100 cm depth (4 replicates) for basic chemical and physical characterisation during 2011. Besides data on basic soil chemical properties taken from Nájera *et al*. (2013), soil organic matter content (SOM; Sadzawka *et al*., 2006) was determined through dry calcination, water retention (pF) curves through a sand box and pressure plates, particle size distribution through the Bouyoucos hydrometer method, bulk density (*Bd*) through the clod and core methods and particle density (*Pd*) by picnometer, according to methods described by Dane and Topp (2002). Air permeability (*Ka*) was determined in undisturbed soil cores by air permeameter at 6, 33 and 100 kPa water tension according to Peth (2004).

Due to the different horizon properties (Domenico and Schwartz, 1998; Nielsen and Wendroth, 2003), hydraulic conductivity was measured in laboratory conditions on soil core samples 6 cm in diameter and 5 cm height. Saturated hydraulic conductivity was determined at five times (2, 4, 8, 24 and 30 h) by a constant head permeameter (Dane and Topp, 2002). The hydraulic conductivity variation (ΔK), which reflects the dynamic nature of soil under water flow, was defined as:

$$\Delta K = \frac{Ks2 - Ks24}{Ks2} \qquad \text{(Eq. 1)}$$

where $Ks2$ and $Ks24$ are the saturated hydraulic conductivity measured at 2 and 24 h, respectively.

Sieving in dry and wet conditions was used to calculate soil macroaggregate stability, determining the mean diameter variation (MDV) (Hartge and Horn, 1992). By means of a suspension in distilled water with and without chemical dispersion, the microaggregate stability was assessed through the dispersion ratio (DR) (Berryman *et al*., 1982).

Soil porosity is conceptually divided into two components, commonly called textural (*TP*) and structural (*SP*) porosity (Nimmo, 2004), where *TP* is the corresponding porosity if the arrangement of the particles were random. The *SP* represents non-random structural influences, including macropores, and is arithmetically defined as the difference between the *TP* and the total porosity (*Ptotal*), which was estimated with Eq. 2.

$$Ptotal = 1 - \frac{coBd}{Pd} \qquad \text{(Eq. 2)}$$

where *coBd* is the bulk density obtained through the core method and *Pd* is the particle density or specific weight determined with picnometers. Using density values, *TP* and *SP* were estimated according to Eqs. 3 and 4 (Cerisola *et al*., 2005):

$$SP = 1 - \frac{coBd}{clBd} \qquad \text{(Eq. 3)}$$

$$TP = coBd\left(\frac{1}{clBd} - \frac{1}{Pd}\right) \qquad \text{(Eq. 4)}$$

where *clBd is* the bulk density obtained through the clod method. Using volumetric water content (θ) values, which were measured from 0-100 cm depth every two weeks with a ®Diviner 2000 (Series II) device, and the Mualem-van Genuchten adjustment equation to the pF curves (combining Darcy and flux continuity equations), the unsaturated hydraulic conductivity (*Kns;* Eq. 5) was calculated (Nissen *et al*., 2006):

$$Kns = \frac{\Delta L}{\Delta t} \times \frac{\Delta \theta}{grad\psi} \qquad \text{(Eq. 5)}$$

where *Kns* is the unsaturated (or non-saturated) soil hydraulic conductivity (L T^{-1}), ΔL is the vertical distance between measured θ values (L), Δt is the time interval between measurements (T), $\Delta\theta$ is the mean variation in volumetric soil water content between two measurement dates (L^3 L^{-3}) and $grad\psi$ is the hydraulic potential gradient ($\Delta\psi/\Delta L$, L L^{-1}).

The Mualem-van Genuchten adjustment equation ($m = 1 - 1/n$, Eq. 6) applied to the pF curves is as follows (van Genuchten, 1980):

$$\theta = \frac{(\theta sat - \theta res)}{(1+|\alpha \psi|^{n})^{m}} + \theta res \qquad (\psi \leq 0, \text{Eq. } 6)$$

where θsat represents the volumetric water content at saturation, θres the residual volumetric water content at very high suction (asymptotically at infinite suction), α (L^{-1}) is inversely related to the mean soil grain size and depends on the shape of the curve, n and m are function parameters and ψ is the pressure head.

2.3.3 Ammonium (NH_4) and nitrate (NO_3) determination

Soil samples for NO_3 and NH_4 analysis (Sadsawka *et al*., 2006) were collected with a soil auger every two weeks at regular depth intervals (0-10, 25-35, 50-60 and 100-110 cm, referred to as 0, 25, 50 and 100) with 3 replicates per site and treatment. The concentrations measured were statistically correlated to unsaturated hydraulic conductivity and other physical and hydraulic soil properties assessed at the same depths.

2.3.4 Experiment design and statistical analysis

An example of an experimental unit, including spatial distribution of devices, plots and replicates, is shown in Figure 2.1. The green tubes correspond to *in situ* N mineralisation devices for nitrate leaching studies, white tubes to water content monitoring and blue tubes represent soil auger depth sampling.

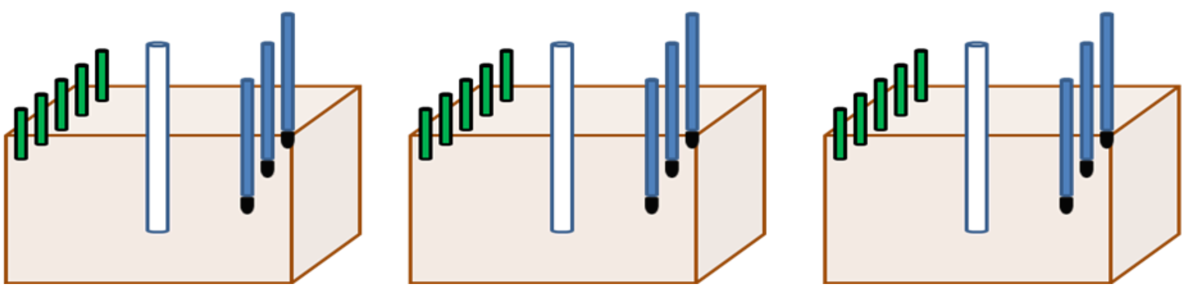


Figure 2.1. Arrangement (not to scale) of a single experimental unit with three replication plots. Green = *in situ* N mineralisation devices, white tubes = water content monitoring, blue tubes = soil auger depth sampling.

The experimental design was completely randomised. The results were analysed by Student *t*-tests for different treatments in each basin at every measurement depth (p<0.05). A multiple component test was carried out to assess the correlations between physical and hydraulic parameters and N concentrations, and a number of regressions were made between correlated variables (p<0.05 and p<0.01). For the values of *Ka*, *Ks* and *Kns*, which were non-normally distributed, a logarithmic transformation was applied. Finally, some pedotransfer functions (PTF) were obtained through a backward stepwise procedure and a least square fit model to asses *Ks*, NO_3^- and NH_4^+ in function of another soil properties.

2.4 RESULTS AND DISCUSSION

2.4.1 Soil morphology

In Pichidegua, PC soil has a dark brown colour and silty loam textural class at the surface, grading to greyish and loamy sand in depth with moderate medium subangular blocky structure and redoximorphic features from 38 cm depth, denoting an oscillating water table (Figure 2.2). Its land use capacity classification is IVw2.

The Pichidegua PS soil is sandy loam at the surface alternating to sandy in depth, moderate medium subangular blocky structures, brown to greyish colours and the same oscillating watertable and redoximorphic features from 40 cm, due its position over an old alluvial terrace. Its land use capacity is IIIw2.

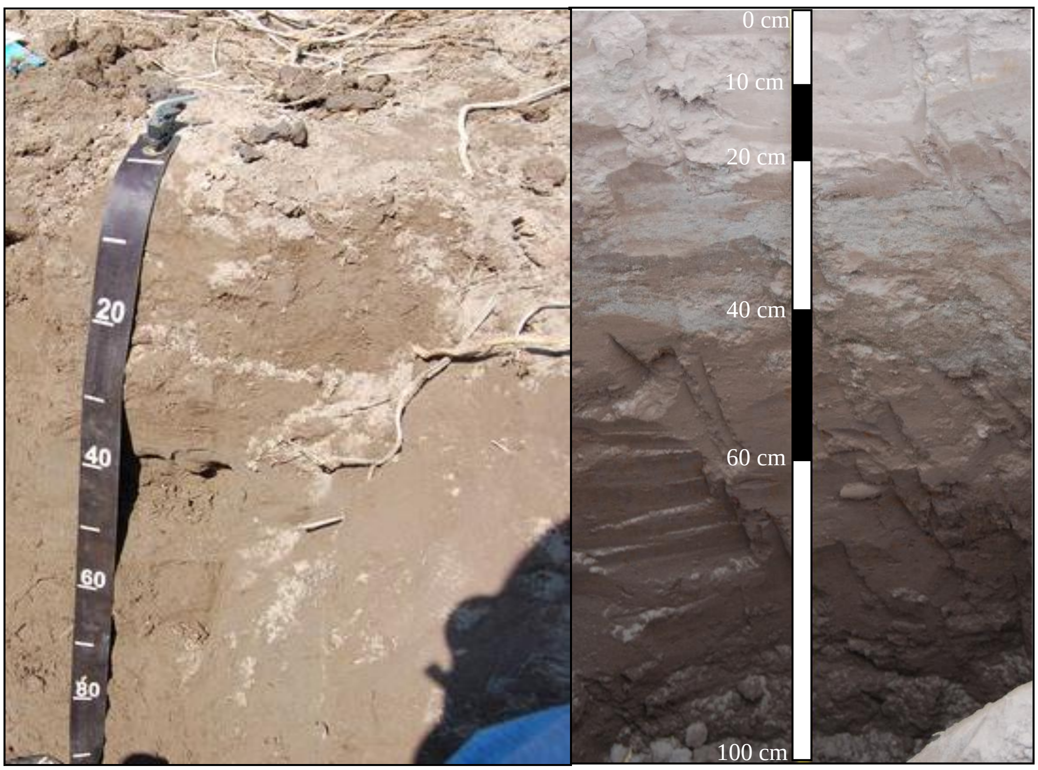


Figure 2.2. Pichidegua soil profiles (left PC; right PS), O'Higgins Region of Chile.

In general, the Pichidegua soils have very stratified deep profiles, medium to coarse textural classes and shallow redoximorphic features caused by an oscillating watertable.

In San Pedro basin, SC soil has dark yellowish colour, sandy loam textural class, weak to moderate subangular blocky structure and a land use capacity of IIs0 (Figure 2.3).

Morphologically, SS soil has dark yellowish brown colour, loam textural class at the surface and a sandy horizon near to 50 cm soil depth, with strong medium subangular blocky structure and a land use capacity of IIs0. In general, soils in San Pedro are deep, stratified, with medium to coarse texture classes and with sandy to loamy sand horizons intercalated by finer textured horizons.

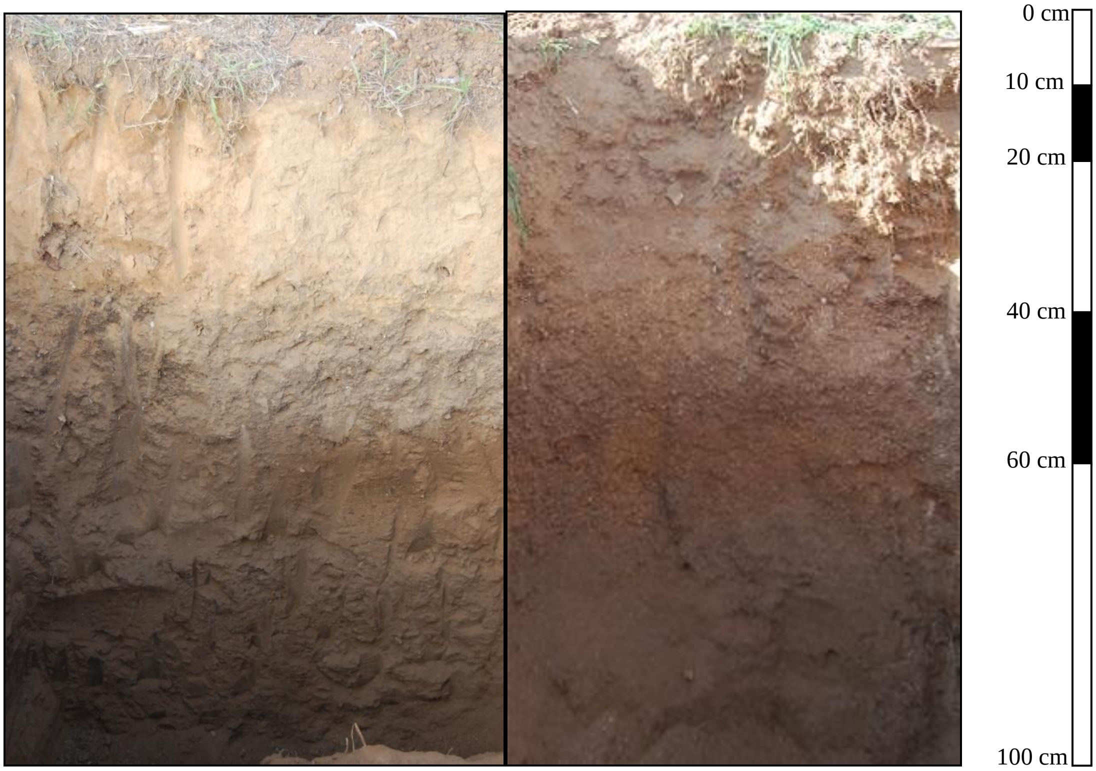


Figure 2.3. San Pedro soil profiles (left SC; right SS), Metropolitana Region of Chile. The scale is common for both profiles.

2.4.2 General characteristics of soils

Physical characterization from measurements of this study and soil chemical data (pH, ECe, CEC and N_T) taken from Nájera *et al*. (2013) are presented in Table 2.2.

Table 2.2. General characterisation of soil profiles for two basins of central Chile.

Soil[a]	Clay[b]	Sand	Silt	SOM	coBd[(c, d)]	*clBd*	*Pd*	pH	ECe	CEC	N_T
	---------------------%---------------------			-----%----	-------------------Mg m^{-3}-------------------			---	dS m^{-1}	cmol $_{(+)}$ kg^{-1}	%
PS 0	7.9 ± 1.2 a	57.9 ± 1.6 b	34.2 ± 0.9 a	5.3 ± 2.9	1.33 ± 0.09 b	1.63 ± 0.01 b	2.72 ± 0.02	5.7	11.41	16.21	0.036
PS 25	7.4 ± 1.7	58.9 ± 3.2 *	33.7 ± 2.0 a	3.2 ± 1.2	1.38 ± 0.07 b	1.54 ± 0.09 b	2.70 ± 0.01	7.0	4.22	11.71	0.012
PS 50	1.6 ± 1.6	77.8 ± 11.6 b	20.7 ± 10.2 a	0.8 ± 0.2 a	1.33 ± 0.04 b	1.45 ± 0.03	2.72 ± 0.01	7.3	1.17	14.12	0.003
PS 100	12.7 ± 0.8	33.8 ± 1.8 b	53.4 ± 2.5 a	1.4 ± 0.2	1.43 ± 0.15*	1.55 ± 0.03 b	2.72 ± 0.04	7.5	0.86	13.92	0.010
PC 0	27.5 ± 0.5 b	17.0 ± 1.5 a	55.5 ± 1.3 b	6.2 ± 1.5	1.10 ± 0.03 a	1.32 ± 0.07 a	2.70 ± 0.02	7.7	1.47	15.08	0.011
PC 25	13.5 ± 6.4	30.0 ± 16.9*	56.5 ± 13.2 b	2.0 ± 0.2	1.29 ± 0.02 a	1.34 ± 0.07 a	2.71 ± 0.01	7.9	0.65	10.44	0.009
PC 50	1.7 ± 1.0	48.0 ± 2.0 a	50.3 ± 3.1 b	1.2 ± 0.2 b	1.16 ± 0.04 a	1.31 ± 0.20	2.70 ± 0.01	7.9	0.88	14.45	0.003
PC 100	12.1 ± 2.9	23.6 ± 2.0 a	64.3 ± 4.8 b	1.9 ± 0.6	1.21 ± 0.03*	1.43 ± 0.04 a	2.72 ± 0.04	7.3	1.01	13.32	0.008
SS 0	12.6 ± 0.8 b	53.8 ± 2.2 a	33.6 ± 1.5 b	3.2 ± 0.1	1.32 ± 0.02 a	1.50 ± 0.05 a	2.68 ± 0.02	6.1	0.26	17.08	0.033
SS 25	12.3 ± 1.1 b	57.6 ± 1.9 a	30.1 ± 3.0 b	1.8 ± 0.2 b	1.41 ± 0.01	1.73 ± 0.10 b	2.72 ± 0.02	6.7	0.30	15.81	0.014
SS 50	3.5 ± 3.0 a	83.7 ± 11.7 b	12.8 ± 8.6 a	0.9 ± 0.4	1.63 ± 0.08 b	1.62 ± 0.03 b	2.73 ± 0.01	6.6	0.37	11.56	0.005
SS 100	9.0 ± 1.8	68.6 ± 6.5 b	22.3 ± 4.7 a	1.2 ± 0.4 a	1.39 ± 0.06	1.65 ± 0.10 b	2.72 ± 0.02	6.8	0.55	17.74	0.008
SC 0	7.4 ± 0.7 a	67.5 ± 4.7 b	25.0 ± 4.0 a	2.9 ± 1.2	1.43 ± 0.04 b	1.62 ± 0.07 b	2.67 ± 0.06	6.7	0.20	9.46	0.013
SC 25	8.6 ± 0.6 a	69.2 ± 2.0 b	22.2 ± 2.6 a	1.3 ± 0.2 a	1.44 ± 0.10	1.52 ± 0.07 a	2.71 ± 0.02	6.7	0.21	15.16	0.012
SC 50	9.2 ± 0.9 b	65.4 ± 1.9 a	25.4 ± 1.0 b	1.5 ± 0.3	1.39 ± 0.03 a	1.53 ± 0.07 a	2.73 ± 0.02	6.8	0.24	14.78	0.008
SC 100	11.1 ± 1.4	55.1 ± 5.2 a	33.8 ± 3.8 b	3.0 ± 0.8 b	1.34 ± 0.02	1.51 ± 0.03 a	2.72 ± 0.03	7.1	0.42	16.44	0.006

[a]PS: Pichidegua soil with slurry applications; PC: Pichidegua soil (control); SS: San Pedro soil with slurry applications; SC: San Pedro soil (control).
[b]Different lowercase letters within depths for soils (same basin) denote statistically significant differences (p<0.05).
[c]*coBd*: core bulk density; *clBd*: clod bulk density; *Pd*: particle density; ECe: electric conductivity of soil solution extract; CEC: cation exchange capacity; N_T: total nitrogen.
[d]Soil physical properties (n = 4; mean ± standard deviation), soil chemical properties (n = 1).
* Statistically significant differences by Kruskal Wallis test (p<0.05).

Pedons in both soil series generally have increasing sand content to 50 cm depth, then it decreases to 100 cm depth. An exception is SC soil, which shows constant values to 50 cm depth. The pedogenesis in alluvial terraces in Pichidegua promotes a natural soil stratification which can be seen through the variations in textural classes and horizons (Appendix).

Soil organic matter (SOM) shows similar behaviour between sites, related to organic debris deposited on the surface. The absence of significant differences in SOM between sites with and without slurry application is due to its oxidation in conventionally tilled soils (Reicosky, 2002), which is compensated by slurry applications. In addition, there is a direct relationship between SOM and clay content at depth (p<0.01).

Although organic amendments generally promote lower *Bd* values, these were generally higher under conventional tillage (CT) than at the control sites due to the external loads exerted by machinery traffic. An exception was the surface horizon of SC soil (control), where the experimental plots were established in untilled soils adjacent to a track, which promoted higher *Bd* to 25 cm depth. As reported previously in several works (Ruehlmann and Körschens, 2009; Aşkin and Özdemir, 2003), *Bd* values were directly correlated to sand content (r=0.66, p<0.01) and inversely correlated to SOM content (r=0.41, p<0.05).

Salinity and pH were altered at the soil surface due to the applications of slurry. The EC in the PS topsoil exceeded the adequate range for most crops (EC > 4 dS m^{-1}), whereas in PC topsoil the EC showed non-saline values. The pH in general was lower in PS and SS topsoils than in PC and SC topsoils, due to higher H^+ release during N mineralisation after slurry application. The chemical effect of slurry application was higher in Pichidegua soils than in San Pedro soils due to continous additions, and its effect in both soils declined with depth. N_T showed higher values in both soils under slurry addition, decreasing to 50 cm depth.

Textural porosity (*TP*) is also known as matrix, intraaggregate or intrapedal porosity, is created by the voids between primary mineral particles. In granular material without cementing agents, *TP* can be about 0.3 cm^3 cm^{-3}(Nimmo, 2004). Structural porosity (*SP*), also called interaggregate or interpedal porosity, is produced by the pores between aggregates or soil fragments. Both *TP* and *SP* vary with the horizon distribution (Table 2.3). Much of *SP* decreases with depth, where at present exogenous pedogenic factors are almost non-active, but might have promoted soil genesis in buried horizons.

Table 2.3. Pore size distribution and estimated soil porosity for two basins of central Chile.

Soil[a]	*SP*[b, c]	*TP*	*FDP*	*SDP*	*AWP*	*WPP*	*Ptotal*
	---%---		---cm^3 cm^{-3}---				---%---
PS 0	17.98 ± 5.60	32.94 ± 2.45 a	0.13 ± 0.04	0.11 ± 0.04	0.16 ± 0.03*	0.11 ± 0.03 a	50.4 ± 4.3 a
PS 25	9.99 ± 7.57	38.95 ± 6.06 a	0.14 ± 0.04	0.07 ± 0.01	0.14 ± 0.04 a	0.10 ± 0.01	45.6 ± 2.3 a
PS 50	8.30 ± 3.54	42.65 ± 2.39	0.21 ± 0.11*	0.11 ± 0.02 a	0.11 ± 0.12	0.06 ± 0.01	48.9 ± 4.2 a
PS 100	7.95 ± 10.05	39.57 ± 4.37	0.10 ± 0.04	0.06 ± 0.05	0.19 ± 0.07*	0.13 ± 0.02	47.7 ± 1.9 a
PC 0	16.23 ± 4.61	43.04 ± 4.70 b	0.15 ± 0.02	0.07 ± 0.01	0.23 ± 0.00	0.15 ± 0.01 b	60.1 ± 1.7 b
PC 25	3.53 ± 4.02	48.86 ± 4.48 b	0.09 ± 0.02	0.07 ± 0.05	0.28 ± 0.06 b	0.13 ± 0.02	57.0 ± 1.6 b
PC 50	10.37 ± 11.11	46.73 ± 12.49	0.07 ± 0.01*	0.26 ± 0.07 b	0.16 ± 0.08	0.06 ± 0.00	55.6 ± 2.9 b
PC 100	15.64 ± 1.23	39.86 ± 0.93	0.06 ± 0.01	0.04 ± 0.01	0.36 ± 0.01*	0.11 ± 0.01	56.7 ± 2.6 b
SS 0	11.59 ± 2.51	39.12 ± 2.65 b	0.15 ± 0.03	0.05 ± 0.01	0.12 ± 0.03	0.12 ± 0.00 b	43.8 ± 5.8
SS 25	18.04 ± 3.83 b	30.00 ± 4.35 a	0.15 ± 0.02	0.06 ± 0.01	0.11 ± 0.01	0.13 ± 0.00 b	44.8 ± 3.2
SS 50	0.00 ± 3.24 a	40.61 ± 0.30	0.21 ± 0.05	0.06 ± 0.02	0.05 ± 0.04	0.09 ± 0.03	40.5 ± 1.3
SS 100	15.50 ± 4.00	33.37 ± 4.57 a	0.18 ± 0.04	0.06 ± 0.01	0.08 ± 0.03	0.11 ± 0.01 a	42.5 ± 1.6
SC 0	11.86 ± 1.29	34.63 ± 1.94 a	0.11 ± 0.02	0.06 ± 0.00	0.12 ± 0.02	0.10 ± 0.01 a	38.7 ± 1.0
SC 25	5.54 ± 5.13 a	41.41 ± 3.28 b	0.17 ± 0.01	0.07 ± 0.01	0.08 ± 0.03	0.11 ± 0.01 a	43.6 ± 1.7
SC 50	8.96 ± 2.67 b	40.12 ± 3.47	0.17 ± 0.06	0.07 ± 0.01	0.09 ± 0.05	0.11 ± 0.01	43.5 ± 2.1
SC 100	11.16 ± 0.63	39.54 ± 0.73 b	0.13 ± 0.02	0.07 ± 0.01	0.11 ± 0.03	0.13 ± 0.01 b	44.4 ± 3.2

[a]PS: Pichidegua soil with slurry applications; PC: Pichidegua soil (control); SS: San Pedro soil with slurry applications; SC: San Pedro soil (control).
[b]*SP*: structural porosity; *TP*: textual porosity; *FDP*: fast draining pores (>50 µm); *SDP*: slow draining pores (50-10 µm); *AWP*: available water pores (10-0.2 µm); *WPP*: wilting point pores (<0.2 µm); *Ptotal*: total porosity (n = 4; mean ± standard deviation).
[c]Different lowercase letters within depths for soils (same basin) denote statistically significant differences (p<0.05).
*statistically significant differences by Kruskal Wallis test (p<0.05).

In the case of San Pedro soils (SS and SC), according to morphological features, SOM contents and geomorphological position, there is a soil discontinuity at depth (Soil Survey Staff, 2010). Other factors affecting textural and structural porosity include the particle size distribution, particularly in San Pedro soil (Figure 2.4), where the sand content affects *SP* due to a lower dependency on the flocculation process by matric tensions generated during the drying-wetting cycles (Fuentes, 2010). Also SOM content can affect *SP* by stabilizing soil structure (Figure 2.4, right), especially on coarse-textured soils, where slightly decomposed surface organic debris enters the soil body through interaggregate porosity (Kay and Angers, 2002). Although organic debris decomposition induces natural fault planes which can become macro and mesopores (>10 μm), these are poorly correlated according to several studies (Douglas *et al*., 1986; Kay *et al*., 1997; Kay and Angers, 2002), whereas soil pores between 0.2 and 30 μm are closely correlated to SOM (Schjønning *et al*., 1994; Emerson, 1995).

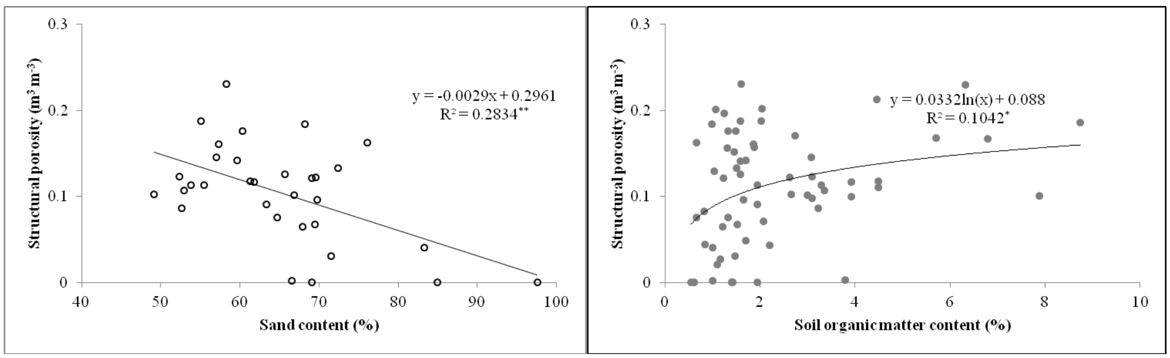


Figure 2.4. Sand content in San Pedro soil (left) and soil organic matter contents in both soil series (right) affecting soil structural porosity (*: p<0.05, **: p<0.01).

It is important to note that *TP* is considerably higher than *SP* (Table 2.3), but to obtain a better understanding of soil structure functioning, pore size distribution was characterised through pF curves.

In general, *Ptotal* was higher in Pichidegua than in San Pedro soils. As regards treatments, *Ptotal* was statistically higher in PC than PS. However, soils in both basins have a drainage porosity (*FDP* + *SDP* >15%) that favours plant development due to good air-water relations (Pagliai and Vignozzi, 2002).

Low significant differences in drainage and available water porosities between management practices were observed (Table 2.3) compared with permanent wilting point porosity, where the differences between uses were related to clay content. However, in every case pore size distribution was mainly correlated to soil particle size, SOM content and bulk density (Table 2.4).

Table 2.4. Physical soil properties and soil organic matter (SOM) contents and their relationship with pore size distribution for two soil series of central Chile.

	FDP[(a, b)]	*SDP*	*AWP*	*WPP*	*Ptotal*
clBd	$y = 0.030e^{1.0400x}$ $R^2 = 0.11$*	$y = 0.47x^2 - 1.50x + 1.27$ $R^2 = 0.14$**	$y = -0.30x + 0.61$ $R^2 = 0.21$**	-	$y = -0.48Ln(x) + 0.30$ $R^2 = 0.38$**
coBd	$y = 0.16x - 0.07$ $R^2 = 0.14$**	$y = -0.22Ln(x) + 0.15$ $R^2 = 0.16$**	$y = -0.48Ln(x) + 0.30$ $R^2 = 0.27$**	-	$y = -0.51Ln(x) + 0.63$ $R^2 = 0.55$**
Clay	-	-	$y = 0.006x + 0.09$ $R^2 = 0.18$**	$y = 0.004x + 0.073$ $R^2 = 0.67$**	$y = 0.004x + 0.434$ $R^2 = 0.16$**
Sand	$y = 0.0619e^{0,0134x}$ $R^2 = 0.39$**	-	$y = -0.004x + 0.346$ $R^2 = 0.62$**	$y = -0.001x + 0.149$ $R^2 = 0.29$**	$y = -0.003x + 0.614$ $R^2 = 0.53$**
SOM	-	-	-	$y = 0.0905x^{0.2333}$ $R^2 = 0.28$**	$y = 0.003x^2 - 0.01x + 0.48$ $R^2 = 0.11$*

[a]*FDP*: fast draining pores (>50 µm); *SDP*: slow draining pores (50-10 µm); *AWP*: available water pores (10-0.2 µm); *WPP*: wilting point pores (<0.2 µm); *Ptotal:* total porosity. (*: $p \leq 0.05$, **: $p \leq 0.01$). With 63 associated degrees of freedom.
[b]- : Non significant correlation

2.4.3 Conductive soil properties

Hydraulic conductivity and air permeability did not show significant differences ($p>0.05$) between sites with and without slurry soil application in most samples. This was mainly due to the wide variation in the results, with the standard deviation even exceeding the mean of conductivity (Table 2.5).

Table 2.5. Conductive soil properties within two soil series of central Chile.

Soil[c]	*Saturated hydraulic conductivity*[(a,b)]						*Air conductivity*		
	*Ks*2	*Ks*4	*Ks*8	*Ks*24	*Ks*30	ΔK	*Ka*6	*Ka*33	*Ka*100
	---m d^{-1}---					Dimensionless	---m d^{-1}---		
PS 0	51.57 ± 91.37	46.55 ± 85.17	18.14 ± 24.29	18.44 ± 26.96	30.53 ± 54.86	0.30 ± 0.60	16.79 ± 7.67	27.83 ± 16.24	16.06 ± 8.90
PS 25	2.97 ± 2.99	2.12 ± 1.56	1.47 ± 1.06 b	0.75 ± 0.49 b	0.58 ± 0.39	0.61 ± 0.22	13.47 ± 6.19	20.80 ± 13.82	4.62 ± 1.56
PS 50	4.53 ± 3.73	3.11 ± 2.03	2.24 ± 1.56	1.70 ± 0.92	1.90 ± 1.06	0.46 ± 0.32	17.53 ± 15.58	24.81 ± 17.63	13.62 ± 7.12
PS 100	0.37 ± 0.23	0.43 ± 0.50	0.37 ± 0.22	0.35 ± 0.17	0.49 ± 0.26	-0.03 ± 0.30	26.95 ± 9.82	19.43 ± 8.71	7.48 ± 5.56
PC 0	0.73 ± 0.80	0.63 ± 0.61	0.40 ± 0.31	0.40 ± 0.38	0.36 ± 0.34	0.15 ± 0.72	37.51 ± 15.76	15.01 ± 13.76	25.22 ± 12.26
PC 25	0.46 ± 0.71	0.24 ± 0.35	0.12 ± 0.15 a	0.11 ± 0.14 a	0.16 ± 0.18	0.25 ± 1.06	21.91 ± 14.93	11.48 ± 11.57	11.68 ± 6.50
PC 50	1.74 ± 1.35	1.55 ± 1.26	1.44 ± 1.33	1.39 ± 1.50	1.32 ± 1.31	0.32 ± 0.07	24.31 ± 15.40	11.91 ± 4.03	9.02 ± 5.91
PC 100	7.45 ± 8.59	10.75 ± 16.06	9.70 ± 15.92	8.38 ± 15.32	6.29 ± 11.67	-5.19 ± 10.09	18.69 ± 9.94	33.56 ± 20.08	25.98 ± 19.65
SS 0	14.53 ± 14.45	7.97 ± 6.76	6.84 ± 6.73	3.05 ± 3.42	2.90 ± 3.07	0.68 ± 0.40	10.31 ± 2.32	17.87 ± 20.36	7.95 ± 3.08
SS 25	1.72 ± 1.85	1.36 ± 1.49	0.56 ± 0.17	0.46 ± 0.33	0.75 ± 0.65	0.66 ± 0.23	15.70 ± 13.30	19.46 ± 12.17	10.36 ± 5.16
SS 50	38.90 ± 38.71	36.56 ± 38.35	31.01 ± 35.37	3.98 ± 4.79	3.73 ± 4.61	0.84 ± 0.10 b	26.45 ± 23.70	15.26 ± 10.31	7.36 ± 4.05
SS 100	7.87 ± 9.62	6.43 ± 8.58	2.82 ± 3.66	2.58 ± 3.50	2.83 ± 3.77	0.65 ± 0.16	31.01 ± 24.59	27.67 ± 18.63	9.69 ± 5.16
SC 0	4.57 ± 6.55	4.23 ± 6.26	3.16 ± 4.62	1.66 ± 1.95	1.90 ± 2.24	0.37 ± 0.44	19.21 ± 15.28	28.61 ± 24.90	9.55 ± 4.41
SC 25	1.21 ± 0.86	1.03 ± 0.79	0.91 ± 0.70	0.63 ± 0.26	0.62 ± 0.37	0.37 ± 0.22	7.47 ± 4.87	6.27 ± 3.21	9.10 ± 3.57
SC 50	4.25 ± 2.62	4.17 ± 2.56	3.28 ± 1.76	2.52 ± 1.15	1.85 ± 0.73	0.34 ± 0.16 a	8.11 ± 2.38	9.49 ± 7.14	17.99 ± 14.65
SC 100	8.92 ± 16.07	8.35 ± 15.31	5.23 ± 9.09	2.13 ± 3.03	2.00 ± 3.06	0.45 ± 0.24	10.84 ± 7.79	9.73 ± 4.54	15.95 ± 9.38

[a]Different lowercase letters within depths for soils (same basin) denote statistically significant differences ($p<0.05$).
[b]*Ksx* is saturated hydraulic conductivity at x hours, *Kay* is air conductivity at y water tension (kPa) and ΔK is the hydraulic conductivity variation (see Eq. 1).
[c]PS: Pichidegua soil with slurry applications; PC: Pichidegua soil (control); SS: San Pedro soil with slurry applications; SC: San Pedro soil (control; n = 4; mean ± standard deviation).

Although saturated hydraulic conductivity (*Ks*) in general tended to decrease with time at almost all depths, after 24 h it tended to stabilise. This decrease in *Ks* is associated with pore system collapse and dispersion, which alters the function of porosity, decreasing its solution transport capacity (Janssen *et al*., 2004; Osunbitan *et al*., 2005; Dörner *et al*., 2010a; Oyarzún *et al*., 2011). An exception occurred in PC at 100 cm depth, where *Ks* increased until 4 h and then decreased. In some cases *Ks* increased slightly after 24 h.

The large variation in *Ks* at different soil depths is an expression of the anisotrophic nature of pedons (Kutilek and Nielsen, 1994; Hillel, 1998; Domenico and Shwartz, 1998), responding to sedimentation and horizonation. Even with very close spatial sampling, there is a great dispersion of *Ks* values, which must be interpreted as inherent to soil heterogeneity and even associated with pore geometric characteristics (Hillel, 1998; Warrick, 2002; Dörner and Horn, 2006).

Using the mean value of *Ks*, several relationships between soil physical properties and *Ks* were found, most associated with soil particle diameter and soil pore diameter distribution (Figure 2.5).

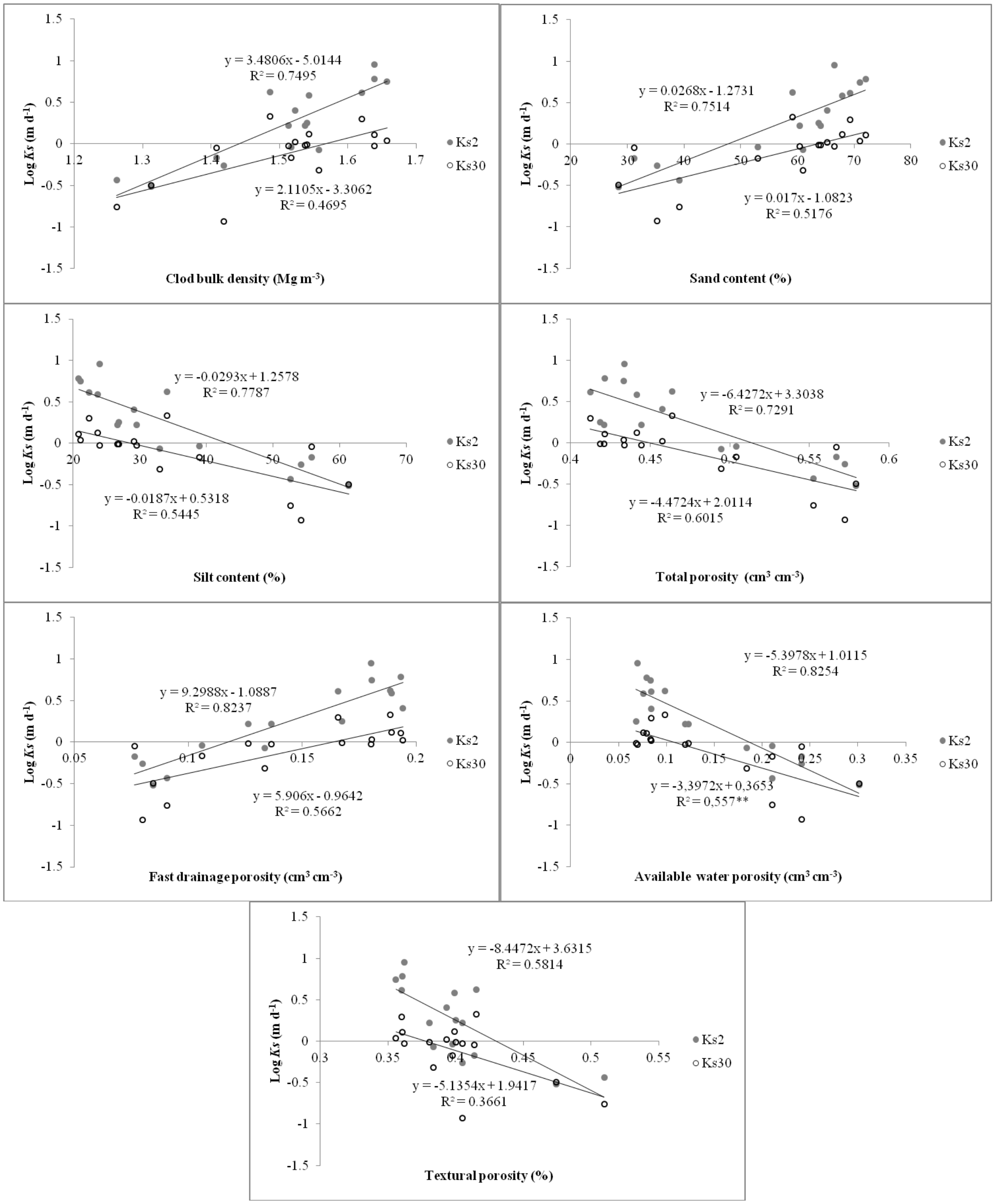


Figure 2.5. Relationships between the mean saturated hydraulic conductivity (*Ks*) at different times and other soil physical properties in two soil series of central Chile.

It must be emphasised that *Ks* depends mainly on textural and structural properties, which determine the soil skeleton and the fabric or arrangement of the skeleton, promoting the development of a complex interconnected network of voids or pores between soil particles (Berry and Reid, 1993). This confers to the soil its functionality (Dörner *et al*., 2010b). Textural properties are reflected in Figure 2.5 by sand and silt contents and *TP*, while *clBd*, fast drainage, available water and total porosity could be considered as depending simultaneously on structural and textural properties.

Although *Bd* generally showed an inverse relationship with *Ks*, the direct relationship determined by the clod method must be interpreted as inherent to soil structure development, promoting denser aggregates which leaves the inter-aggregate porosity able to increase *Ks* in soil cores. The inverse relationship between *Ptotal* and *Ks* must be related to the dependency of *Ptotal* to texture, where an increased sand content promotes low *Ptotal* and high *Ks*, while clay content increases cause the inverse relationship.

Using a backward stepwise procedure and a standard least square fit, some multiple regressions were found for *Ks*2 and *Ks*24, although the predicted expression of such fit lines showed low adjustment of parameters due to the high spatial variability of *Ks:*

$$\text{Log } Ks2 = -0.14 - 0.07\ \text{C} + 0.03\ Ka100 + 0.17\ \text{SOM} + 0.85\Delta\text{K}$$
$$p<0.0001;\ R^2=0.42;\ \text{RMSE}=0.686 \qquad \text{(Eq. 7)}$$

$$\text{Log } Ks24 = 0.90 - 3.15\ AWP - 10.11\ WPP + 0.02\ Ka100 + 0.12\ \text{SOM}$$
$$p=0.0002;\ R^2=0.31;\ \text{RMSE}=0.648 \qquad \text{(Eq. 8)}$$

where:

*Ks*2 and *Ks*24 : saturated hydraulic conductivity at 2 and 24 h, respectively ($m\ d^{-1}$)
C : clay content (%)
*Ka*100 : air conductivity at -100 kPa water pressure ($m\ d^{-1}$)
SOM : soil organic matter content (%)
ΔK : hydraulic conductivity variation (dimensionless)
AWP : available water pores ($cm^3\ cm^{-3}$)
WPP : wilting point pores ($cm^3\ cm^{-3}$).

Clay content, *AWP* and *WPP* were inversely correlated to *Ks*. Higher clay content favours *AWP* and *WPP* (see Table 2.4), where pore diameter is lower than 10 μm. Those pores are related to the storage of plant-available water and to water that is retained at high tensions (unavailable to plants) and the rate of water flow through them is very slow (Kay and Angers, 2002). *Ka*100, SOM and ΔK were directly correlated with *Ks*. *Ka* at such tension reflects pore functionality, which is also involved in *Ks*. In several studies (Lado *et al*., 2004; Nemes *et al*., 2005; Rawls *et al*., 2005), SOM has been directly correlated with *Ks* due to its effects on porosity and aggregation stability, but such a relationship at high SOM levels could have a negative correlation (Wang *et al*., 2009).

The values of *Ks* were higher at the beginning of the flow than after 24 h except in PC and PS at 100 cm depth, and the variations were higher in sites under conventional tillage with slurry additions. A relationship was found betweem ΔK and soil particle size, with higher contents of sand and lower contents of silt promoting greater ΔK (Appendix 2). At lower sand and higher silt particle contents, the values of *Ks* increased after 24 h, which can be observed by negative values of ΔK and considerably higher data dispersion. Janssen *et al.* (2004) reported that medium to coarse-textured soils under a Mediterranean climate showed dynamic behaviour, with a change in its hydraulic properties after one day of saturated flow due to the collapse of the pore system, diminishing its functionality as a conductive medium. In contrast, finer soil particles display different shapes, a greater number of contact points and even chemical affinities by ions and other particles, which confer a higher stability to structure and pore systems (Horn *et al*., 1994; Fuentes, 2010).

Air permeability (*Ka*) displayed unusual behaviour (Table 2.5), with several samples showing a *Ka* decrease with increasing soil water tensions. There was a dominance of sandy loam textural classes in the soil samples, so swelling behaviour does not explain these results. Besides, *Ka* did not show a clear relationship with soil depth, air-filled porosity or soil matric tension, but some significant correlations ($p<0.05$) between *Ka*33 and *Ks* were observed (data not shown). Anyway, results are in agreement with other study in a coarse textural soil (Seguel *et al*., 2002), where the use of cover crops on the soil dissication not necassary increased air permeability.

Some relationships between *Ka* 100 and soil particle size were also found (Appendix). Direct and inverse correlations between *Ka* and clay and sand contents were observed, which were associated with matric tensions that promote soil aggregation through drying (Semmel *et al*., 1990), promoting *SP* and pore continuity and increasing *Ka* at high tensions. Increasing values of soil porosity and continuity promoted higher *Ka*, while *coBd* values were inversely correlated with *Ka*100 (Appendix 2).

2.4.4 Unsaturated hydraulic conductivity

A significant dependency of *Kns* on the hydraulic gradient was observed (Figure 2.6). Indeed, in the coarse-textured soils there was an abrupt decrease in *Kns* at high tensions. In contrast to fine-textured soils (Ellies and Vyhmeister, 1981; Radcliffe and Rasmussen, 2002), the potential gradient determined was considerably higher, especially in San Pedro soils, where it reached almost 10^{13} hPa (Figure 2.6, right). The *Kns* was significantly lower due to the stratified nature of the profile, which leads to non-uniform pore distribution and continuity.

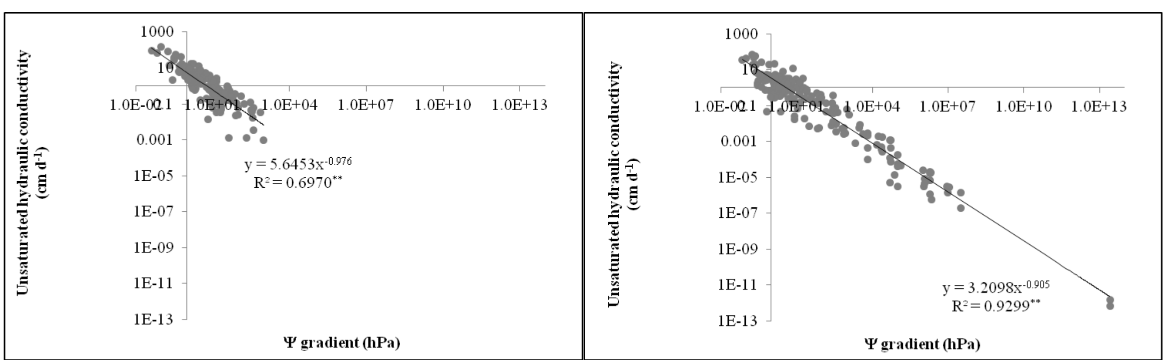


Figure 2.6. Unsaturated soil hydraulic conductivity (*Kns*) and its relationship with hydraulic potential gradient for two soil series of central Chile: Pichidegua (left) and San Pedro (right).

Pichidegua soils had higher *Kns* than San Pedro soils, principally owing to the silty loam textural classes in PC compared with the sandy loam textural classes in SC and to the finer texture in PS than in SS, causing low potential gradients. According to Radcliffe and Rasmussen (2002), fine-textured soils show higher *Kns* at high water tensions because they contain more water-filled pores and continuous water films (in clays). However, significant differences in *Kns* between our study soils with and without slurry applications were not observed.

Statistically significant ($p<0.05$) temporal variability in *Kns* was detected between plots with and without pig slurry applications on Pichidegua soils. *Kns* was considerably higher at 100 cm depth, in fine-textured horizons, than at 50 cm depth, in coarse-textured horizons (Figure 2.7). The loamy sand horizon at 50 cm depth in PS, confined between more fine-textured horizons, may pose a barrier to movement of water in unsaturated conditions and to internal drainage during infiltration (Hillel, 1998).

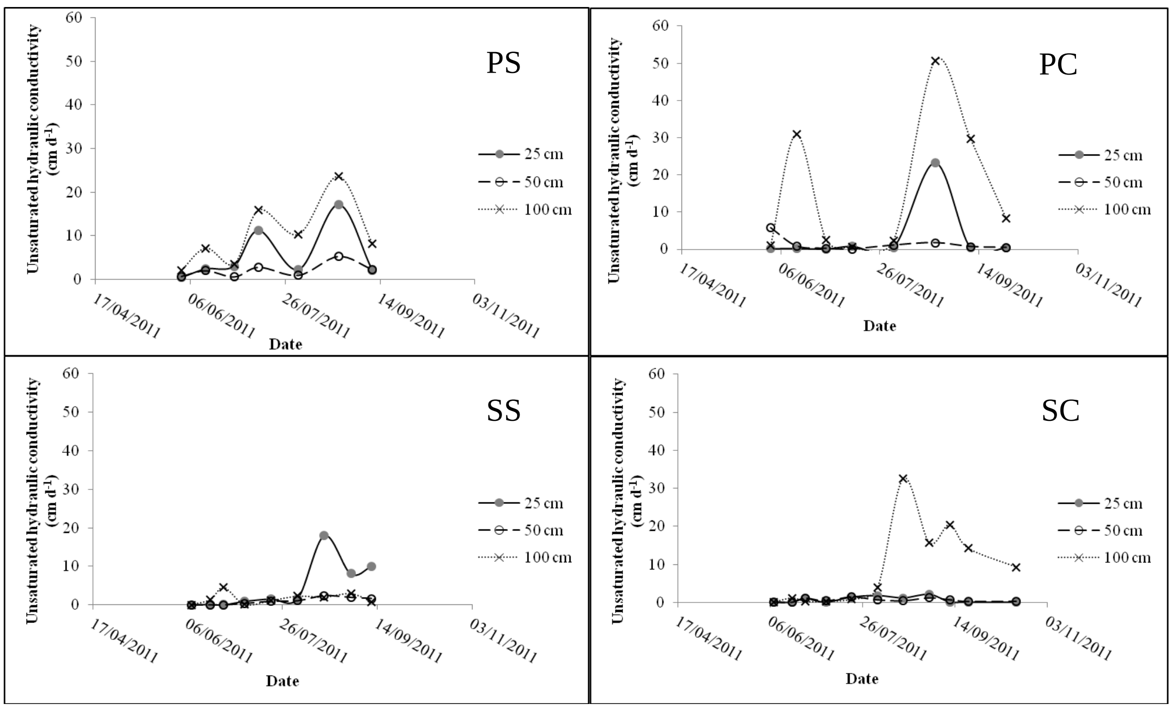


Figure 2.7. Variations in mean seasonal unsaturated hydraulic conductivity (*Kns*) at three soil depths. Above, Pichidegua soils with slurry (left) and control (right). Below, San Pedro soils with slurry (left) and control (right).

Temporal variations in *Kns* in both soil series are mainly associated with changes in natural environmental conditions due to rainfall, vegetal growth and decay, and changes in soil structure (Gupta *et al*., 2006).

2.4.5 Soil aggregate stability

High MDV (mean diameter variation) values denote low soil macroaggregate stability, which increased with soil depth in both basins, with PC and SS at 50 cm soil depths as exceptions (Table 2.6). This was reflected in low cohesion and similar mechanical behaviour in wet and dry sieving. Exogenous conditions, wetting/drying cycles, accumulation and decomposition of SOM on the soil surface have improved structure development down to C horizons (less exposed to pedogenetic processes), explaining the general tendency for MDV to vary with depth (van Breemen and Buurman, 2003; Schaetzl and Anderson, 2005).

Table 2.6. Soil aggregate stability indices for two soil series in central Chile.

Soil[a]	Soil macroaggregate stability MDV[b] (cm)	Soil microaggregate stability DR (%)
PS 0	0.50 ± 0.16 a	56.35 ± 2.11 b
PS 25	2.01 ± 0.67 a	54.22 ± 0.40 b
PS 50	2.63 ± 0.44 b	57.81 ± 9.70
PS 100	9.31 ± 2.35	32.47 ± 0.08 *
PC 0	3.36 ± 1.05 b	16.09 ± 1.49 a
PC 25	5.19 ± 0.92 b	23.43 ± 3.20 a
PC 50	0.18 ± 0.14 a	48.65 ± 0.48
PC 100	6.19 ± 1.33	24.51 ± 1.90*
SS 0	0.54 ± 0.39	61.19 ± 1.02
SS 25	6.94 ± 1.80	62.48 ± 1.52 a
SS 50	4.57 ± 2.61 a	48.68 ± 38.40
SS 100	8.40 ± 2.69	80.84 ± 7.96 b
SC 0	0.46 ± 0.19	64.70 ± 4.91
SC 25	4.74 ± 0.53	72.45 ± 3.77 b
SC 50	7.81 ± 1.03 b	71.98 ± 4.81
SC 100	8.06 ± 1.32	58.82 ± 3.70 a

[a]PS: Pichidegua soil with slurry applications; PC: Pichidegua soil (control); SS: San Pedro soil with slurry applications; SC: San Pedro soil (control). (mean ± standard deviation).
[b]Different lowercase letters within depths for soils (same basin) denote statistically significant differences (p<0.05).
* Statistically significant different values (Kruskal Wallis, p<0.05). MDV: Mean diameter variation, DR: Dispersion ratio. n = 4.

In the same way, high DR (dispersion ratio) values denote low soil microaggregate stability. Values of DR were considerably higher than MDV (Table 2.6), especially in San Pedro pedons, associated with lower soil development or changes in soil particle type, such as sand increases or SOM decreases.

In PC, the higher MDV and lower DR compared with PS were associated with reduced land use intensity and a shorter period of agricultural management. This leads to humification of SOM inputs without oxidation, as is the case in traditional agriculture (Lefroy *et al*., 1993).

It is possible that in PC, recalcitrant SOM compounds fill micropores and mesopores, conferring a higher structural stability to microaggregates compared with macroaggregates and promoting lower values of DR. Some authors have concluded that DR does not decrease with amendment addition, in contrast to MDV (Mbagwu and Ekwealor, 1990; Mbah and Onweremadu, 2009). Moreover, SOM compounds under natural conditions are translocated through pedoturbation, while under tillage such translocation occurs inside the upper 30 cm of the soil profile (Stockfisch *et al*., 1999; van Oost *et al*., 2000). Comparing both study soils with slurry applications, PS had a significantly lower MDV to 50 cm soil depth and a lower DR through the entire profile. This was related to macroaggregate stability, with more labile compounds of soil organic matter (SOM), e.g. root exudates, fungal hyphae and polysaccharides excreted by microorganisms, increasing the bonding between soil particles and thus improving structural stability (Chaney and Swift, 1986; Waters and Oades, 1991; Kay and Angers, 2002).

In San Pedro pedons there is no clear tendency in macro and microaggregate stability when conditions with and without slurry applications are compared. However, there was a tendency in SC for higher macroaggregate stability (lower MDV) and lower microaggregate stability (higher DR) with depth, except at 50 and 100 cm depth, respectively. In this case, and in both basins, the size of soil particles and its nature (mineral and organic) affected structural development (Figure 2.8).

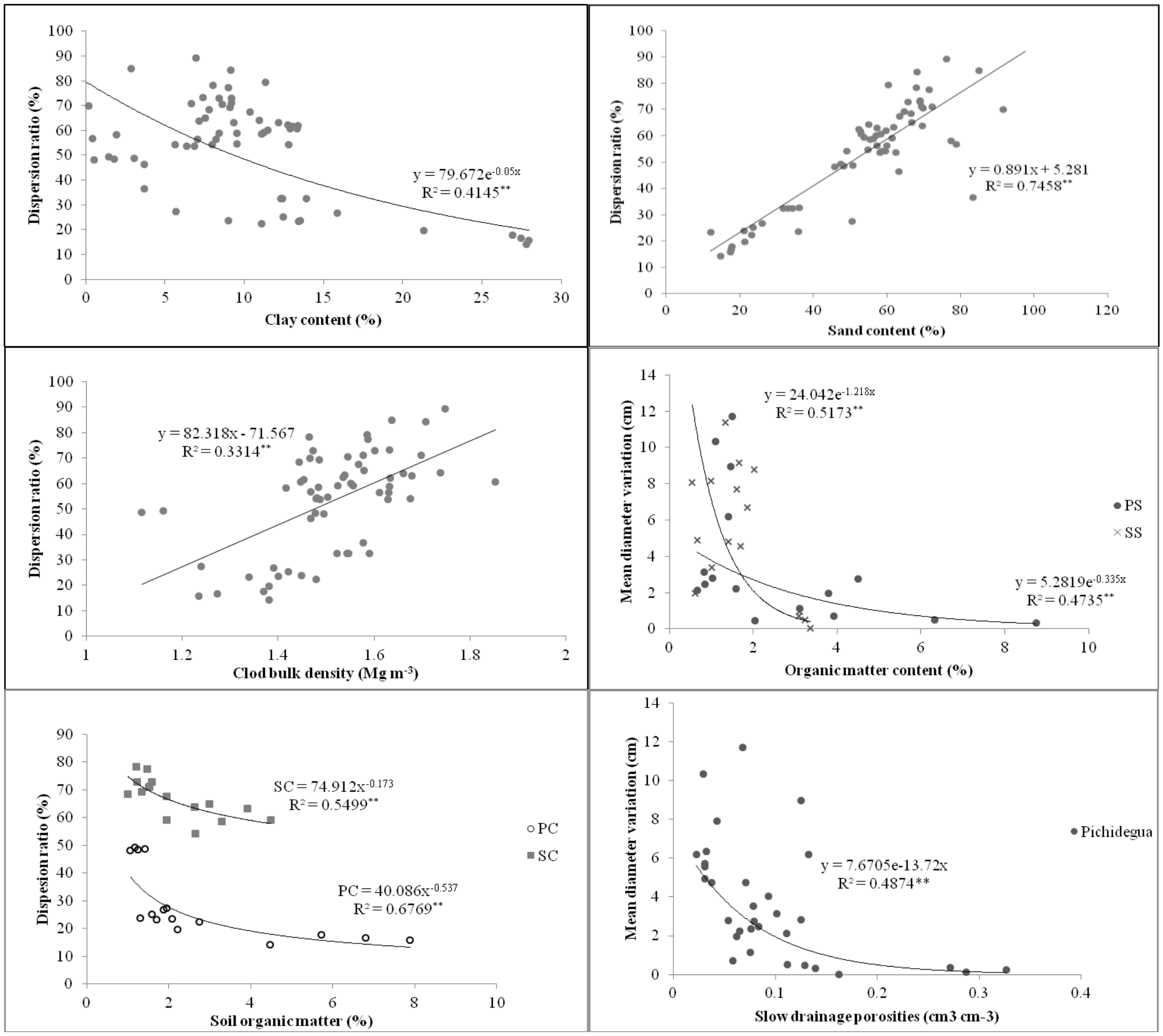


Figure 2.8. Soil physical properties and their effects on soil structural stability for two soil series of central Chile.

Soil structure development and its stability, which is dependent on the size and nature of soil particles, were also found to be associated with other physical soil properties. Clod bulk density (*clBd*) was significantly related to DR, whereas SOM reduced *Bd* and increased microaggregate stability, especially in control soils. In contrast, sand particles decreased microaggregate stability and promoted higher *clBd*. SOM also increased macroaggregate stability in soils receiving slurry applications.

The increasing macroaggregate stability with SOM addition to soils via slurry indicates that the slurry mainly contained labile fractions of SOM, which are associated with increased macroaggregate stability (>250 mm) (Puget *et al*., 1995). This is due to the function of SOM as a substrate for microbial activity, which produces microbial bonding material (Golchin *et al*., 1994; Besnard *et al*., 1996), reduces the rate of wetting and increases the resistance to stresses generated during wetting (Caron *et al*., 1996). The increasing microaggregate stability in control soils presumably demonstrates the dominance of recalcitrant compounds of SOM (Tisdall and Oades, 1982). Those recalcitrant compounds are intimately associated with the mineral phase, even occluding micropores (Kay and Angers, 2002) and are protected from breakdown due to physical protection from microbial attack. Besides, recalcitrant compounds provide long-lasting stability for microaggregates (Chaney and Swift, 1986).

In terms of soil porosity, *SDP* is positively correlated to macroaggregate stability. The *SDP* (mesopores 10-50 μm) is associated with decomposition of SOM, which besides promoting aggregate stability induces fault planes, delineating aggregate bonding and favouring slow drainage (Kay and Angers, 2002; Puget *et al*., 2005).

2.4.6 Nitrogen dynamics associated with soil hydraulics

Nitrogen dynamics measured as NO_3^- and NH_4^+ concentrations in Pichidegua soils (Figure 2.9) showed considerable oscillations during the season, with a slight increase during the spring season due to high temperatures, but with a subsequent decrease caused by immobilisation by decomposing SOM and due the lower temperatures during autumn and winter. This trend changed later, when increasing concentrations were found due to higher temperature, which promoted higher mineralisation. These results explain the increase in N concentrations with depth at the end of the measurement season, and the increase in relative proportions compared with surface contents.

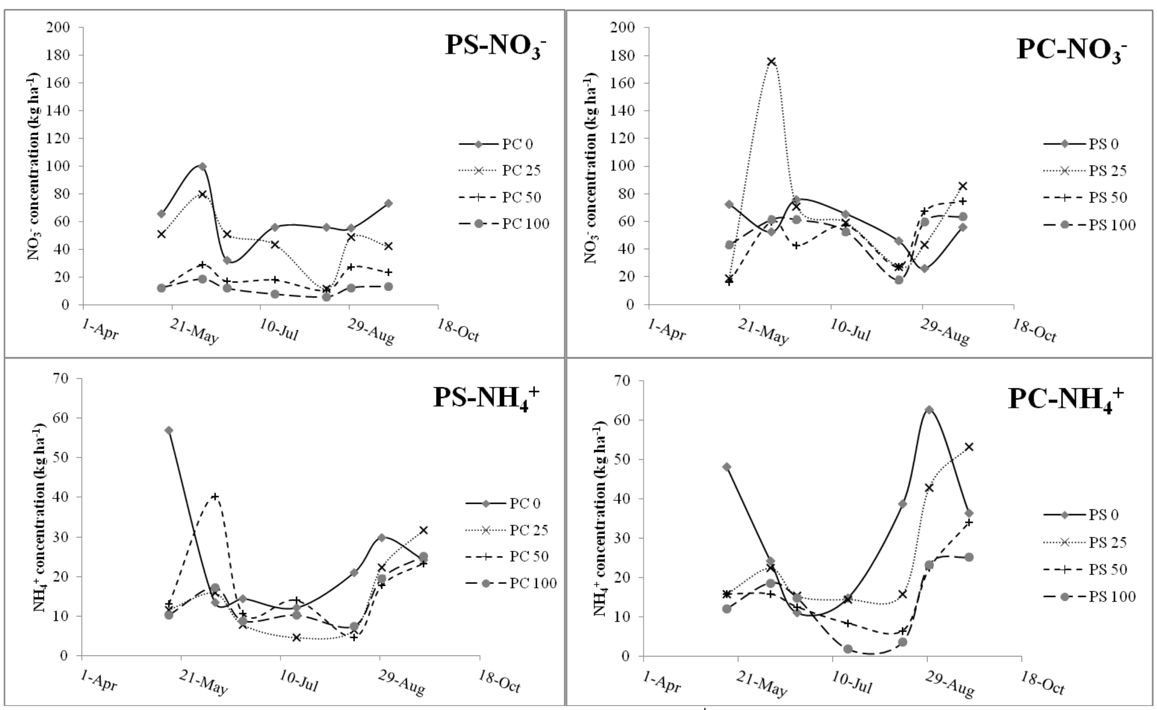


Figure 2.9. Variations in nitrogen concentration (NH_4^+ and NO_3^-) at four depth intervals (0, 25, 50 and 100 cm) in Pichidegua soils during the study period.

Despite the dependence of N forms on external factors that promote mineralisation-immobilisation, a weak relationship was found between volumetric water changes in consecutive measurement dates and NO_3^- concentration changes between measurement dates (Figure 2.10). This is related to the potential leaching of anions in soils, particularly in soils that accommodate preferential flows (Cote *et al*., 2000; Jarvis *et al*., 2012).

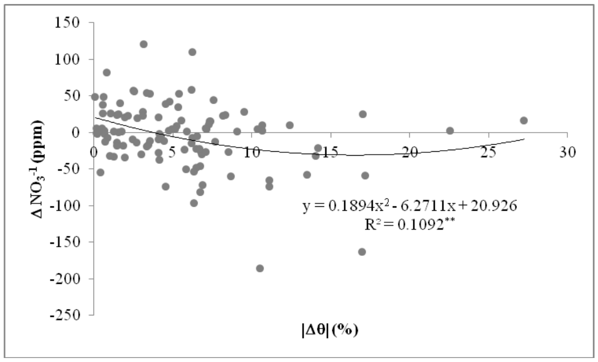


Figure 2.10. Relationship between nitrate changes (ΔNO_3^-) and water content changes ($\Delta\theta$) in Pichidegua soils.

In San Pedro soils, the concentrations of NO_3^- decreased during the season after a slight increase at the beginning of the measurement period (Figure 2.11), while NH_4^+ concentration decreased initially, with a subsequent slight increase, followed by a final decrease in concentration at the end of the measurement period.

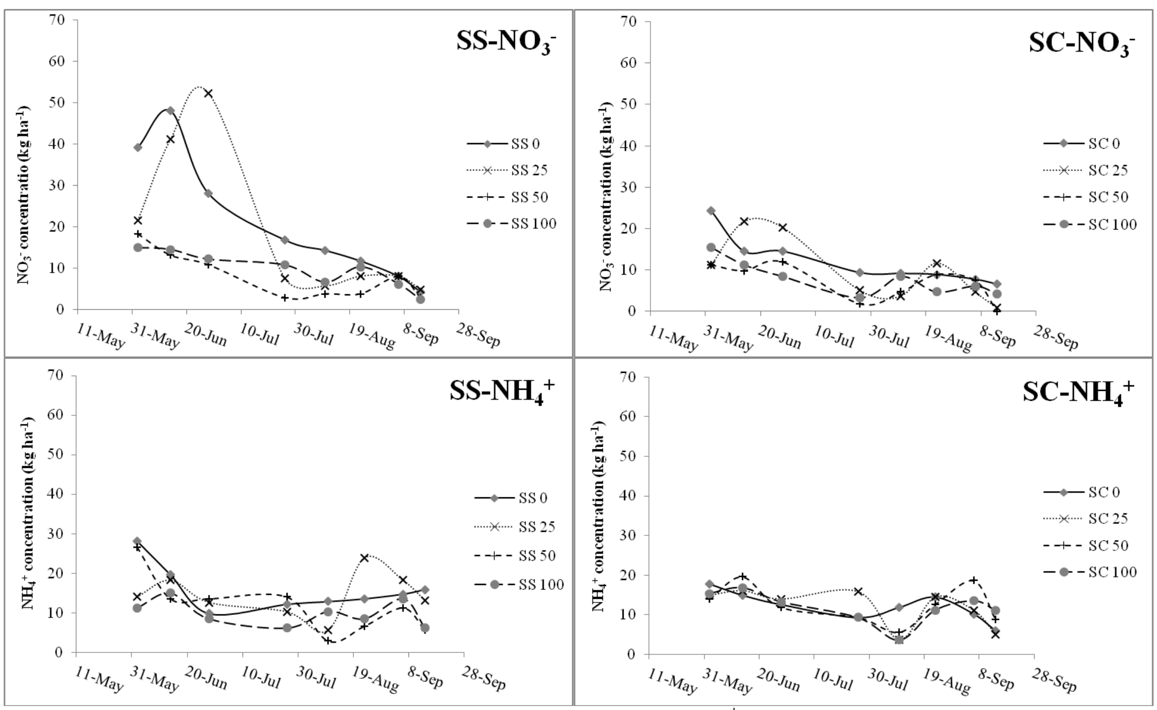


Figure 2.11. Variations in nitrogen concentration (NH_4^+ and NO_3^-) at four depth intervals (0, 25, 50 and 100 cm) in San Pedro soils during the study period.

In San Pedro soils, there was a close relationship between $\Delta\theta$ and NO_3^- concentration due to the type of flow that occurs in that soil (Figure 2.12), in which a greater part of the soil matrix participates (Fuentes *et al*., 2013). The relationship between NO_3^- and water content was not only limited to $\Delta\theta$, as *Kns* was also inversely correlated with NO_3^- concentration owing to slower flow of water in unsaturated conditions. This allowed NO_3^- to remain in the soil, as its movement through soils is dependent on water movement. This result shows that hydraulic properties and water availability govern the concentration of some solutes in soil to some degree.

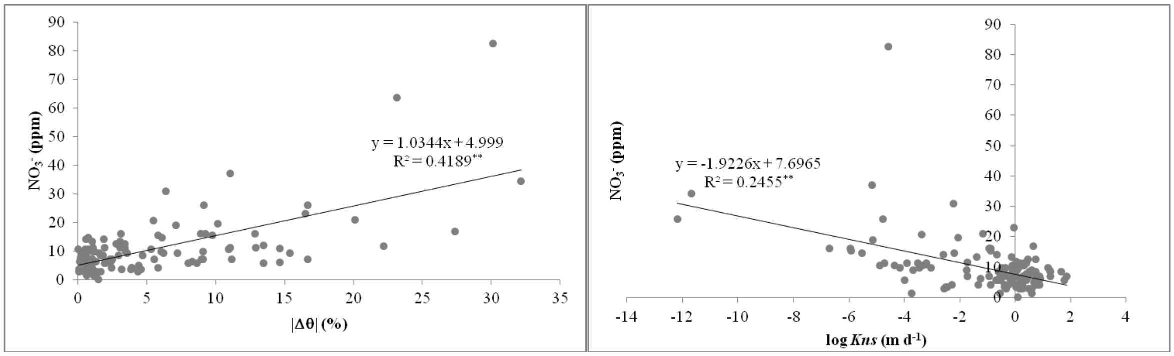


Figure 2.12. Concentration of nitrate (NO_3^-) as a function of (left) water content change ($\Delta\theta$) and (right) unsaturated hydraulic conductivity (*Kns*) in San Pedro soils.

Using some mixed stepwise fits was possible to establish pedotransfer functions (PTF) associating NO_3^- and NH_4^+ concentrations to others properties assessed:

$$[NO_3^-] = \mathit{37.06 + 136.88\ FDP - 0.69}\ \mathrm{DR} - \mathit{15.03\ Log\ (Ka100) + 1.49}\ [NH_4^+]$$
$$p<0.0001,\ R^2=0.52,\ \mathrm{RMSE}=16.86 \qquad \text{(Eq. 9)}$$

$$[NH_4^+] = \mathit{11.49 - 0.80}\ \mathrm{MDV} + \mathit{4.17\ Log\ (Ka100) + 0.15}\ [NO_3^-]$$
$$p<0.0001,\ R^2=0.45,\ \mathrm{RMSE}=5.54 \qquad \text{(Eq. 10)}$$

where:

$[NO_3^-]$	: nitrate concentration (ppm)
$[NH_4^-]$	: ammonium concentration (ppm)
FDP	: fast draining porosity ($cm^3\ cm^{-3}$)
DR	: dispersion ratio or microaggregate stability (%)
MDV	: mean diameter variation or macroaggregate stability (cm)
Ka100	: air conductivity at 100 kPa ($m\ d^{-1}$)

The NO_3^- concentration was directly correlated to *FDP* and NH_4^+ concentration, and inversely correlated to DR and *Ka100*. The NO_3^- concentration increased with increasing NH_4^+ concentration, because in oxidising conditions, mineralised nitrogen in the form of NH_4^+ is nitrified to NO_2, a precursor of NO_3^- (Havlin *et al*., 2005). *FDP* plays an important role in such oxidation processes, allowing aeration, as does microaggregate stability, which also promotes homogeneous wetting potential of the soil matrix and its interaction with solutes. *Ka100* negatively affects NO_3^- concentration due to an increase in soil permeability, which promotes NO_3^- leaching to groundwater. The NH_4^+ concentration was positively correlated with *Ka100* and NO_3^- concentration, and negatively with MDV. The relationship with *Ka100* is the reverse of that for NO_3^- due to the cationic nature of NH_4^+, which is adsorbed by soil particles, while NO_3^-, being an anion, is easily leached in highly permeable media. Macroaggregate stability promotes higher NH_4^+ concentration by increasing matrix flow, which allow solutes to interact with the soil matrix and by providing physical protection to NH_4^+ against leaching by retaining it within aggregates.

Although not included in the above PTF, a clear inverse relationship was observed between NO_3^- and sand content, while the relationship was positive with total porosity (*Ptotal*) (Figure 2.13). A low interaction of solutes with sand particles and their larger pore diameter may explain these results. On the other hand, *Ptotal* promoted higher NO_3^- concentrations by inducing a higher interaction between soil matrix and soil solution (Hillel, 1998; Leij and van Genuchten, 2002).

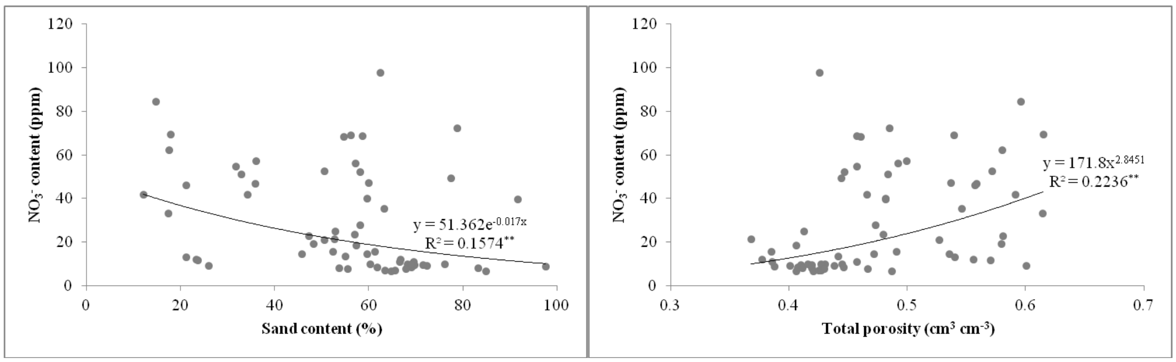


Figure 2.13. Concentration of nitrate (NO_3^-) as a function of (left) sand content and (right) total porosity in two soil series of central Chile.

The NH_4^+ content was directly associated with SOM content and inversely related with MDV (Figure 2.14). The ionised functional groups of SOM and its nitrogenate components (N source for mineralisation) can explain this relationship in the first instance (Bohn *et al*., 2001; Sparks, 2003). The inverse relationship between MDV and NH_4 indicates that higher soil macroaggregate stability (lower MDV) leads to higher NH_4 concentration. This may be related to SOM mineralisation, which besides releasing NH_4 increases the microbial biomass, its activity and its released compounds, conferring higher aggregate stability (Kandeler and Murer, 1993). Similarly, Chaney and Swift (1986) found that N and SOM contents, and other soil properties related to SOM, were correlated with aggregate stability. It can thus be concluded that soil macroaggregates have a strong cation-preserving capability.

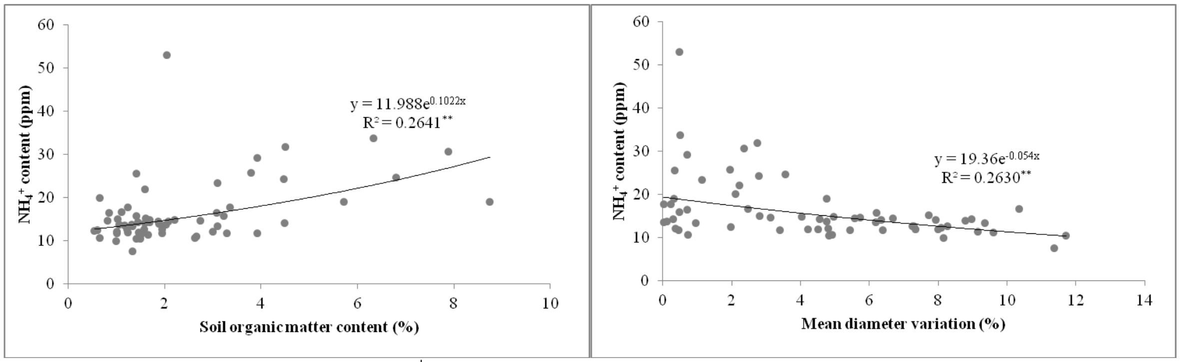


Figure 2.14. Ammonium (NH_4^+) concentration as a function of (left) soil organic matter content and (right) mean diameter variation (soil macroaggregate stability) in two soil series of central Chile.

Several previous studies have evaluated the effects of pig slurry and manure application on soil physical, hydraulic and morphological properties, but without assessing the effect on solute dynamics. For example, Hemmat *et al.* (2010) found that at 0-20 cm depth, manures increased SOM, trafficability, water content range and friability index and decreased soil bulk density (*Bd*). Melleck *et al.* (2010) noted that soil at 0-5 cm depth had increased carbon content, macroporosity, stability of macroaggregates and *Ks* and decreased *Bd* and microaggregates number after manuring, while at 10-20 cm depth significant differences were lost.

Clearly, *Ks* is a key soil property that has been directly related to the risk of N leaching, but there is a lack of field studies that assess the relationships between manure and slurry addition and soil physical and hydraulic properties and the resulting effects on solute leaching.

More studies are needed under controlled laboratory conditions and through several application seasons to assess the long-term effect of slurry or liquid manure applications on soil physical and hydraulic properties, while omitting other factors that overshadow the impact. Furthermore, for a full understanding of solute patterns in soil profiles and the relationship with soil physical properties, and to assess the risk of NL, studies are needed at different scales of solute transport and using dye staining complemented with groundwater NO_3^- measurements.

2.5 CONCLUSIONS

Under the conditions at the study sites, pig slurry addition associated with tillage practices positively altered soil physical and hydraulic properties and also increased the temporal and spatial variability of these properties, in turn increasing the pollution risk of NO_3^- to groundwater. The effects of these organic additions are additive to the existing effects of solid soil particles, which determine soil geometry and the distribution of soil pores, bulk density, conductive soil characteristics (hydraulic conductivity) and other dynamic soil properties (structure stability).

The mechanism by which pig slurry addition alters soil physical properties is mainly through increasing labile fractions of soil organic matter (SOM), which promotes macroaggregate stability. Tillage destroys structure and increases SOM oxidation and mineralisation, although these losses (occurring under intensive managements) are compensated with the use of pig slurry. The significant relationship between microaggregate stability and SOM observed within control sites (no tilled) suggests a positive effect of recalcitrant organic compounds inside aggregates. Both ploughing and pig slurry addition increase the variation in soil hydraulic conductivity after 24 h, demonstrating lower stability and faster collapse of flow pathways.

In terms of N dynamics, both soils studied showed some degree of relationship between volumetric water changes at two consecutive measurement dates and variations in NO_3^- concentrations, but the relationship was considerably higher in San Pedro soils, as demonstrated by the close relationship between unsaturated hydraulic conductivity and NO_3^- concentration. This result must be assessed and complemented by the dominant flow type to provide a full understanding of how matrix flow is related to solute distribution through the soil profile.

Sand content and total porosity were also correlated to NO_3^- concentration due to their influence on water and solute movement in the soil, whereas NH_4^+ concentration was related to SOM content and macroaggregate stability, demonstrating a combined effect of ionised functional groups in SOM and secreted polysaccharides during mineralisation processes.

Finally, more studies under controlled conditions, especially at microscopic level, are needed to complement the present findings. These should include studies about preferential flows at different scales to determine solute patterns, the factors determining those and the pollution risk of NO_3^- movement to groundwater at basin scale.

2.6 REFERENCES

Alletto, L., Coquet, Y., Benoit, P., Heddadj, D., Barriuso, E, 2010. Tillage management effects on pesticide fate in soils: a review. Agronomy for Sustainable Development 30, 367-400.

Aşkin, T., Özdemir, N., 2003. Soil bulk density as related to soil particle size distribution and organic matter content. Poljoprivreda/Agriculture 9(2), 52-55.

Berry, P., Reid, D. 1993. Mecánica de suelos. Caicedo, B., Arrieta, A. (Trads). McGraw-Hill Editorial. Bogotá, Colombia. 415 p.

Berryman, C., Davies, D., Evans, C., Harrod, M., Hughes, A., Skinner, R., Swain, R., Soane, D., 1982. Techniques for Measuring Soil Physical Properties. Formerly Advisory Paper Nº18. Reference Book 441. Ministry of Agriculture, Fisheries and Food, Sweden, 116 p.

Besnard, E., Chenu, C., Balesdent, J., Puget, P., Arrouays, D. 1996. Fate of particulate organic matter in soil aggregates during cultivation. European Journal of Soil Science 47, 495-503.

Besson, A., Javaux, M., Bielders, C., Vanclooster, M. 2011. Impact of tillage on solute transport in a loamy soil from leaching experiments. Soil and Tillage Research 112, 47-57.

Bohn, H.L., McNeal, B.L., O'Connor, G.A., 2001. Soil Chemistry, 3rd ed. John Wiley & Sons, New York, NY., 320 p.

Buczko, U., Bens, O., Huttl, R.E. 2006. Tillage effects on hydraulic properties and macroporosity in silty and sandy soils. Soil Science Society of America Journal 70, 1998-2007.

Buol, S.W., Hole, F.D., McCracken, R.J., 1973. Soil Genesis and Classification. Iowa University. Press, USA, 360 p.

Cameira, M.R., Fernando, R.M., Pereira, L.S. 2003. Soil macropore dynamics affected by tillage and irrigation for a silty loam alluvial soil in southern Portugal. Soil and Tillage Research 70, 131-140.

Caron, J., Espindola, C.R., Angers, D.A. 1996. Soil structural stability during rapid wetting: Influence of land use on some aggregate properties. Soil Science Society of America Journal 60, 901-908.

Cerisola, C.I., García, M.G., Filgueira, R.R., 2005. Distribución de la porosidad de un suelo franco arcilloso (Alfisol) en condiciones semiáridas después de 15 años bajo siembra directa. Ciencia del Suelo (Argentina) 23:167-178.

Chaney, K., Swift, R.S. 1986. Studies on aggregate stability: II. The effect of humic substances on the stability of reformed soil aggregates. Journal of Soil Science 37, 337-343.

Chen, X., Zhao, X., Wu, P., Wang, Z., Zhang, F., Zhang, Y. 2011. Water and nitrogen distribution in uncropped ridge-tilled soil under different ridge width. African Journal of Biotechnology 10(55), 11527-11536.

CIREN. 1996a. Estudio Agrológico VI región. Descripción de suelos, materiales y símbolos. Centro de Información de Recursos Naturales. Publicación Nº 114, 483 p.

CIREN. 1996b. Estudio Agrológico Región Metropolitana. Descripción de suelos, materiales y símbolos. Centro de Información de Recursos Naturales. Publicación Nº 115, 430 p.

Cote, C.M., Bristow, K.L., Ross, P.J. 2000. Increasing the efficiency of solute leaching. Soil Science Society of America Journal 43, 1100-1106.

Dane, J.H., Topp, G.C., 2002. Methods of Soil Analysis. Part 4: Physical Methods. Soil Science Society of America, Inc., Madison, WI, USA, 1692 p.

Domenico, P.A., Schwartz, F.W., 1998, Physical and Chemical Hydrogeology, 2nd ed. John Wiley and Sons Inc., New York, 506 p.

Dörner, J., Horn, R. 2006. Anisotropy of pore functions in structural stagnic luvisols in the weichselian moraine region in Germany. Journal Plant Nutrition Soil Science 169, 212-220.

Dörner, J., Dec, D., Peng, X., Horn, R. 2010a. Effect of land use change on the dynamic behaviour of structural properties of an Andisol in southern Chile under saturated and unsaturated hydraulic conditions. Geoderma 159, 189-197.

Dörner, J., Sandoval, P., Dec, D. 2010b. The role of soil structure on the pore functionality of an Ultisol. Journal of Soil Science and Plant Nutrition 10(4), 495-508.

Douglas, J.T., Jarvis, M.G., Howse, K.R., Goss, M.J. 1986 Structure of a silty soil in relation to management. Journal of Soil Science 37, 669-679.

Ellies, A., Vyhmeister, E. 1981. Algunos aspectos hídricos del horizonte superficial de tres tipos de suelos del sur de Chile. Agro Sur 9(2), 94-100.

Emerson, W.W. 1995. Water retention, organic C and soil texture. Australian Journal of Soil Research 33, 241-251.

Fuentes, I. 2010. Comportamiento mecánico de la matriz de suelo y de sus agregados individuales en función de la tensión mátrica en tres suelos de la zona central de Chile. Memoria para optar al título profesional de Ingeniero Agrónomo. Universidad de Chile, Santiago. 72 p.

Fuentes, I., Casanova, M., Salazar, O., Seguel, O., Padarian, J. 2013. Preferential flow paths in two alluvial soils with continnue pig slurry applications in central Chile. Unpublished.

Gehl, R.J., Schmidt, J.P., Stone, L.R., Schlegel, A.J. Clark, G.A., 2005. *In situ* measurements of nitrate leaching implicate poor nitrogen and irrigation management on sandy soils. Journal of Environmental Quality 34, 2243-2254.

Golchin, A., Oades, J.M., Skjemstad, J.O., Clarke, P. 1994. Soil structure and carbon cycling. Australian Journal of Soil Research 32, 1043-1068.

Guggenberger, G. 2005. Humification and Mineralization in Soils. pp: 85-106. *In*: Buscot, F., Varma, A. (Eds.) Microorganisms in Soils: Roles in Genesis and Functions. Springer-Verlag. Leipzig, Germany. 419 p.

Gupta, N., R.P. Rudra, and G. Parki. 2006. Analysis of spatial variability of hydraulic conductivity at field scale. Canadian Biosystems Engineering Journal 48, 55-62.

Hartge, K.H., Horn, R. 1992. Die physikalische Untersuchung von Boden. Ferdinand Enke Verlag, 3. Auflage, Stuttgart, Germany. 177 p.

Havlin, J.L., Tisdale, S.L., Nelson, W.L., Beaton, J.D. 2005. Soil Fertility and Fertilizers. An Introduction to Nutrient Management. 7th ed.; Pearson Education Inc.-Prentice All. 528 p.

Hemmat, A., Aghilinategh, N., Rezainejad, Y., Sadeghi, M. 2010. Long-term impacts of municipal solid waste compost, sewage sludge and farmyard manure application on organic carbon, bulk density and consistency limits of a calcareous soil in central Iran. Soil and Tillage Research 108, 43-50.

Hillel, D., 1998. Environmental Soil Physics. Academic Press. Boston, 771 p.

Horn, H., Taubner, H., Wuttke, M., Baumgartl, T. 1994. Soil physical properties related to soil structure. Soil and Tillage Research 30, 187-216.

Janssen, I., Kruemmelbein, J., Horn, R., Ellies, A. 2004. Physical and hydraulic properties of the ñadi soils in south Chile - Comparison between untilled and tilled soil. Revista de la Ciencia del Suelo y Nutrición Vegetal 4, 14-28.

Jarvis, N., Moeys, J., Koestel, J., Hollis, J. 2012. Preferential Flow in a Pedological Perspective. pp: 75-120. In: Lin, H. (Ed.) Hydropedology. Synergistic Integration of Soil Science and Hydrology. Academic Press, USA. 858 p.

Jensen, M.B., Olsen, T.B., Hansen, H.C.B., Magid, J. 2000. Dissolved and particulate phosphorus in leachate from structured soil amended with fresh cattle faeces. Nutrients Cycling in Agroecosystems 56, 253-261.

Kandeler, E., Murer, E. 1993. Aggregate stability and soil microbial processes in a soil with different cultivation. Geoderma 56, 503-513.

Kay, B.D., Angers, D.A. 2002. Soil Structure. pp: 249-283. *In*: Warrick, A.W (Ed). Soil Physics Companion. CRC Press. Boca Raton, Florida, USA. 389 p.

Kay, B.D., da Silva, A.P., Baldock, J.A. 1997. Sensitivity of soil structure to changes in organic C content: predictions using pedotransfer functions. Canadian Journal of Soil Science 77, 665-667.

Kooistra, M.J., Bouma, J., Boersma, O.H., Jager, A. 1984. Physical and morphological characterization of undisturbed and disturbed ploughpans in a sandy loam soil. Soil and Tillage Research 4, 405-417.

Kutilek, M., Nielsen, R. 1994. Soil Hydrology. Catena Verlag, Cremlingen - Destedt, Germany, 370 p.

Lado, M., Paz, A., Ben-Hur, M. 2004. Organic matter and aggregate-size interactions in saturated hydraulic conductivity. Soil Science Society of America Journal 68(1), 234-242.

Lafolie, f. 1991. Modelling water flow, nitrogen transport and root uptake including physical non-equilibrium and optimization of the root water potential. Fertilizer Research 27, 215-231.

Larsbo, M., Lapen, D.R., Topp, E., Metcalfe, C., Abbaspour, K.C., Fenner, K. 2009. Simulation of pharmaceutical and personal care product transport to tile drains after biosolids application. Journal of Environmental Quality 38, 1274-1285.

Lefroy, R.D., Blair, G.J., Strong, W.M. 1993. Changes in soil organic matter with cropping as measured by organic carbon fractions and natural isotope abundance. Plant and Soil 155/156, 399-402.

Leij, F.J., van Genuchten, M.T. 2002. Solute transport. pp: 189-248. *In*: Warrick, A.W (Ed). Soil Physics Companion. CRC Press. Boca Raton, Florida, USA. 389 p.

Logsdon, S.D., Jaynes, D.B. 1996. Spatial variability of hydraulic conductivity in a cultivated field at different times. Soil Science Society of America Journal 60, 703-709.

Mbagwu, J.S., Ekwealor, G.C. 1990. Agronomic potential of brewer's spent grain. Biological Wastes 34, 335-347.

Mbah, C.N., Onweremadu, E. 2009. Effect of organic and mineral fertilizer inputs on soil and maize grain yield in an acid ultisol in Abakaliki-South Eastern Nigeria. American-Eurasian Journal of Agronomy 2 (1), 7-12.

Mellek, J., Diecko, J., da Silva, V., Favaretto, N., Pauletti, V., Machado, F., Moretti, J. 2010. Dairy liquid manure and no-tillage: Physical and hydraulic properties and carbon stocks in a Cambisol of Southern Brazil. Soil and Tillage Research 110, 69-76.

Miller, J.J., Sweetland, N.J., Chang, C. 2002. Hydrological properties of a clay loam soil after long-term cattle manure application. Journal of Environmental Quality 31, 989-996.

Miller, J.J., Beasley, B.W., Larney, F.J., Olson, B.M. 2005. Soil salinity and sodicity after application of fresh and composted manure with straw or wood-chips. Canadian Journal of Soil Science 85, 427-438.

Mohanty, B., Ankeny, M., Horton, R., Kanwar, R. 1996. Spatial analysis of hydraulic conductivity measured using disk infiltrometers. Water Resources Research 30, 2489-2498.

Nájera, F., Salazar, O., Casanova, M. 2013. *In-situ* determination of nitrogen movement in agricultural soils with pig slurry application. Dissertation. Tesis Magíster en Manejo de Suelos y Aguas, Universidad de Chile. Unpublished.

Nemes, A., Rawls, W., Pachepsky, Y. 2005. Influence of organic matter on the estimation of saturated hydraulic conductivity. Soil Science Society of America Journal 69(4), 1330-1337.

Nichols, G., 2009. Sedimentology and Stratigraphy. 2nd Ed.; Wiley-Blackwell, Chichester, 419 p.

Nielsen, D., Wendroth, O. 2003. Spatial and Temporal Statistics-Sampling Field Soils and their Vegetation. GeoEcology Textbook, Catena-Verlag, Reiskirchen, 614 p.

Nimmo, J.R., 2004. Porosity and Pore Size Distribution. pp: 295-303. *In:* Hillel, D. (Ed) Encyclopedia of Soils in the Environment. v. 3. Elsevier, London. 600 p.

Nissen, J., Quiroz, C., Seguel, O., MacDonald, R., Ellies, A., 2006. Flujo hídrico no saturado en Andisoles. Revista de la Ciencia del Suelo y Nutrición Vegetal 6(1), 9-19.

Osunbitan, J.A., Oyedele, D.J., Adekalu, K.O. 2005. Tillage effects on bulk density hydraulic conductivity and strength of a loam sand soil in southwestern Nigeria. Soil and Tillage Research 82, 57-64.

Oyarzún, C., Frene, C., Lacrampe, G., Huber, A., Hervé, P. 2011. Propiedades hidrológicas del suelo y exportación de sedimentos en dos microcuencas de la Cordillera de la Costa en el sur de Chile con diferente cobertura vegetal. Bosque 32, 10-19.

Pagliai, M., Vignozzi, N. 2002. The Soil Pore Systems as an Indicator of Soil Quality. pp. 71-82. *In*: Pagliai, M. and Jones, R. (Eds). Sustainable Land Management - Environmental Protection. A Soil Physical Approach. IUSS – UISS – IBU, Reiskirchen, Germany. 588 p.

Peth, S. 2004. Bodenphysikalische Untersuchungen zur Trittbelastung von Bóden bei der Rentierweidewirtschaft an borealen Wald- und subarktisch-alpinen Tundrenstandorten. Dissertation in Agrarwissenschaften, Universität Christian Albrechts, Kiel, Nr. 64. 160 p.

Philippot, L., Germon, J.C. 2005. Contribution of Bacteria to Initial Input and Cycling of Nitrogen in Soils. pp: 159-177. *In*: Buscot, F., Varma, A. (Eds.) Microorganisms in Soils: Roles in Genesis and Functions. Springer-Verlag. Leipzig, Germany. 419 p.

Powlson, D., Addiscott, T., Benjamin, N., Caassman, K., de Kok, T., van Grinsven, H., L'hirondel, J., Avery, A., van Kessel, C. 2008. When does nitrate become a risk for humans? Journal of Environmental Quality 37 (2), 291-295.

Puget, P., Chenu, C., Balesdent, J. 1995. Total and young organic matter distributions in aggregates of silty cultivated soils. European Journal of Soil Science 46, 449-459.

Puget, P., Lal, R., Izaurralde, M., Post, M., Owens, L. 2005. Stock and distribution of total and corn-derived soil organic carbon in aggregate and primary particle fractions for different land use and soil management practices. Soil Science 170, 256-279.

Radcliffe, D., Rasmussen, T., 2002. Soil Water Movement. pp. 85-126. *In*: Warrick, A.W. (Ed). Soil Physics Companion. CRC Press. Boca Raton, Florida, USA. 389 p.

Rawls, W., Nemes, A., Pachepsky, Y. 2005. Effects of Soil Organic Matter on Soil Hydraulic Properties. pp: 95-114. In: Pachepsky, Y., Rawls, W. (Eds.). Development of Pedotransfer Functions in Soil Hydrology. Elsevier, Amsterdam. 542 p.

Reicosky, D. C. 2002. Long – term effect of moldboard plowing on tillage – induced CO_2 loss. pp. 87-96. *In*: J. M. Kimble, Lal, R., Follet, R. F. (Eds.), Agricultural practices and polices for carbon sequestration in soil. Lewis Publishers. Papers from symposium held July 1999 at Ohio State University, Columbus, Ohio.

Ruehlmann, J., Körschens, M., 2009. Calculating the effect of soil organic matter concentration on soil bulk density. Soil Science Society of America Journal 73, 876-885.

Sadzawka, M.A., Carrasco, M.A., Grez, R., Mora, M.L., Flores, H., Neaman, A. 2006. Métodos de análisis de suelos recomendados para los suelos de Chile. Instituto de Investigaciones Agropecuarias, Serie Actas INIA Nº 34, Santiago, Chile, 164 p.

Santibáñez, F., Uribe, J.M., 1990. Atlas Agroclimático de Chile: regiones Metropolitana y Quinta. Ministerio de Agricultura. Fondo de de Innovación Agraria. Corporación de Fomento de la Producción. Santiago de Chile. 66 p.

Santibáñez, F., Uribe, J.M., 1993. Atlas Agroclimático de Chile: regiones Sexta, Séptima, Octava y Novena. Ministerio de Agricultura. Fondo de Innovación Agraria. Corporación de Fomento de la Producción. Santiago de Chile. 99 p.

Schaetzl, R.J., Anderson, S. 2005. Soils: Genesis and Geomorphology. Cambridge University Press, UK. 832 p.

Schjonning, P., Christensen, B.T., Carstensen, B. 1994. Physical and chemical properties of a sandy loam receiving animal manure, mineral fertilizer or nor fertilizer for 90 years. European Journal of Soil Science 45, 257-268.

Schoeneberger, P.J., Wysocki, D.A., Benham, E.C. 2012. Field book for describing and sampling soils, Version 3.0. Natural Resources Conservation Service, National Soil Survey Center, Lincoln, NE. 300 p.

Schwen, A., Bodner, G., Scholl, P., Buchan, G., Loiskandl, W. 2011. Temporal dynamics of soil hydraulic properties and the water-conducting porosity under different tillage. Soil and Tillage Research 113, 89-98.

Semmel, H., Horn, H., Hell, U., Dexter, A. R., Osmond, G., Schulze, E.D. 1990. The dynamics of soil aggregate formation and the effect on soil physical properties. Soil Technology 3, 113-129.

Soil Survey Staff. 2010. Keys to Soil Taxonomy, 10th ed. USDA-Natural Resources Conservation Service, Washington, D.C., 345 p.

Sparks, D. L. 2003. Environmental Soil Chemistry. Academic Press, USA. 352 p.

Stockfisch, N., Forstreuter, T. and Ehlers, W. 1999. Ploughing effects on soil organic matter after twenty years of conservation tillage in Lower Saxony, Germany. Soil and Tillage Research 52, 91-101.

Strudley, M., Green, T., Ascough, J. 2008 Tillage effects on soil hydraulic properties in space and time: State of the science. Soil and Tillage Research 99, 4-48.

Tarbuck, E., Lutgens, F., 2007. Ciencias de la Tierra: Una Introducción a la Geología Física. Pearson Education (Ed.). Madrid, España. 710 p.

Thomas, M. 2007. Soil conditions and early crop growth after repeated manure applications. Dissertation of Master Science. University of Saskatchewan, Canada. 139 p.

Thomsen, I. 2005. Nitrate leaching under spring barley is influenced by the presence of a ryegrass catch crop: Results from a lysimeter experiment. Agriculture, Ecosystems and Environment 111, 21-29.

Tisdall, J.M., Oades, J.M. 1982. Organic matter and water-stable aggregates. Journal of Soil Science 33, 141-163.

Turpin, K., Lapen, D., Robin, M., Topp, E., Edwards, M., Curnoe, W., Topp, G., McLaughlin, N., Coelho, B., Payne, M. 2007. Slurry-application implement tine modification of soil hydraulic properties under different soil water content conditions for silt-clay loam soils. Soil and Tillage Research 95, 120-132.

Vahtera, E., Conley, D., Gustafsson, B., Kuosa, H. 2007. Internal ecosystem feedbacks enhance nitrogen fixing cyanobacteria blooms and complicate management in the Baltic Sea. Ambio 36, 186-194

van Breemen, N., Buurman, P., 2003. Soil Formation. 2nd ed.; Kluwer Academic Publishers, 415 p.

Vanclooster, M., Javaux, M., Vanderborght, J. 2005. Solute transport in soil at the core and field scale. pp: 1041-1055. *In*: Anderson, M.G., McDonnell, J.J. (Eds.). Encyclopedia of Hydrological Sciences. Wiley. 3456 p.

van Genuchten, M.Th. 1980. A Closed-form Equation for Predicting the Hydraulic Conductivity of Unsaturated Soils. Soil Science Society of America Journal 44(5), 892-898.

van Oost, K., Govers, G., and Desmet, P.J. 2000. Evaluating the effects of changes in landscape structure on soil erosion by water and tillage. Landscape Ecology 15(6), 579-591.

Wang, T., Wedin, D., Zlotnik, V. 2009. Field evidence of a negative correlation between saturated hydraulic conductivity and soil carbon in a sandy soil. Water Resources Research 45(7), W07503.

Warrick, A.W. 2002. Soil Physics Companion. CRC Press, Boca Raton. 389 p.

Waters, A.G., Oades, J.M. 1991. Organic Matter in Water-stable Aggregates, pp: 163-174. *In*: Wilson, W.S (Ed). Advances in Soil Organic Matter Research. The Impact on Agriculture and the Environment. Royal Society of Chemistry, Cambridge, UK. 400 p.

Zebarth, B.J., Paul, J.W., Schmidt, O., McDougall, R. 1996. Influence of the time and rate of liquid–manure application on yield and nitrogen utilization of silage corn in South Coastal British Columbia. Canadian Journal of Soil Science 76, 153-164.

2.7 APPENDIX

Table A1. Soil profile descriptions.

Pichidegua soil, control (PC).

Horizon	Depth (cm)	Soil description
Ap1	0 - 10	Dark brown (7.5 YR 3/3), silty loam; sticky and plastic; moderate medium subangular blocky structure; friable; common fine interstitial pores; few fine roots; clear smooth boundary.
Ap2	11 - 21	Dark brown (7.5 YR 3/3); loam; moderately sticky and plastic; moderate medium subangular blocky structure; friable; common fine and few medium interstitial pores; common fine roots; clear smooth boundary.
Bw1	21 - 29	Very dark greyish brown (10 YR 3/2); loamy sand; non-sticky and slightly plastic; moderate medium subangular blocky structure; very friable; many fine interstitial pores; few medium roots; abrupt smooth boundary.
Bw2	29 - 38	Dark yellowish brown (10 YR 4/2); sandy loam; sticky and moderately plastic; moderate coarse subangular blocky structure; very friable; common fine interstitial pores; common fine and few medium roots; very abrupt smooth boundary.
Bg1	38 - 52	Dark yellowish brown (10 YR 4/2); loamy sand; non-sticky and slightly plastic; moderate medium subangular blocky structure that breaks into fine subangular blocky structure; very friable; many fine interstitial and few medium tubular pores; few medium roots; fine common distinct pale olive brown (2.5 YR 5/6) iron depletions; clear smooth boundary.
Bg2	52 - 72	Very dark greyish brown (10 YR 3/2); loamy sand; non-sticky and slightly plastic; moderate medium subangular blocky structure; very friable; many fine interstitial and few medium tubular pores; common medium roots; fine common distinct pale olive brown (2.5 YR 5/6) iron depletions; clear smooth boundary.
Bg3	72 - 98	Dark yellowish brown (10 YR 4/2); sandy loam; slightly sticky and moderately plastic; moderate medium subangular blocky structure; very friable; many fine and few medium interstitial pores; few medium and many fine roots; medium common distinct pale olive brown (2.5 YR 5/6) iron depletions; clear smooth boundary.
Cg	98 - +120	Very dark grey (5YR 3/1); sandy loam; slightly sticky and plastic; massive; many fine interstitial pores; few medium roots.
	NB:	Watertable at 110 cm depth.

Pichidegua soil, slurry-amended (PS).

Horizon	Depth (cm)	
Ap	0 - 25	Dark greyish brown (10 YR 4/2); loamy sand; slightly sticky and slightly plastic; moderate medium subangular blocky structure; friable; many fine interstitial and common medium dendritic tubular pores; many fine and few medium roots between peds; clear smooth boundary.
Bw	25 - 40	Dark greyish brown (10 YR 4/2); loamy sand; slightly sticky and slightly plastic; moderate medium subangular blocky structure that breaks into fine moderate subangular blocky structure; friable; many fine interstitial and few medium tubular pores; few fine and medium roots; abrupt smooth boundary.
Bg1	40 - 63	Very dark greyish brown (10 YR 3/2); sandy; non-sticky and non-plastic; moderate medium subangular blocky structure; very friable; many fine interstitial pores; few fine and common medium roots; few medium faint yellowish red (5 YR 5/8) iron masses; abrupt wavy boundary.
Bg2	63 - 107	Very dark greyish brown (10 YR 3/2); sandy loam; slightly sticky and moderately plastic; moderate medium subangular blocky structure; friable; few coarse, many medium tubular and common fine interstitial pores; many coarse faint red (2.5 YR 4/6) iron masses; abrupt smooth boundary.
C	107 - +120	Dark brown (10 YR 3/3); sandy loam; moderately sticky and moderately plastic; moderate medium subangular blocky structure; friable; many fine interstitial and many medium tubular pores; fine common faint yellowish red (5 YR 4/6) iron masses.

San Pedro soil, control (SC).

Horizon	Depth (cm)	
A	0 - 22	Dark brown (10 YR 3/3); sandy loam; slightly sticky and slightly plastic; weak medium subangular blocky structure that breaks into weak fine subangular blocky structure; friable; many fine interstitial and common medium tubular pores; common fine roots; clear smooth boundary.
B1	23 - 35	90% dark yellowish brown (10 YR 3/4) and 10% very dark yellowish (10 YR 3/2); sandy loam; slightly sticky and slightly plastic; moderate medium subangular blocky structure that breaks into moderate fine subangular blocky structure; friable; many fine tubular pores; common fine roots; gradual smooth boundary.
B2	36 - 53	Very dark grey (10 YR 3/1); sandy loam; slightly sticky and slightly plastic; moderate medium subangular blocky structure; friable; many fine and medium tubular pores; common fine roots; clear smooth boundary.
Bw	54 - 65	Very dark greyish brown (10 YR 3/2); silty loam; moderately sticky and slightly plastic; moderate medium subangular blocky structure; friable; common fine vesicular and many medium tubular pores; few fine roots; gradual smooth boundary.
2Bb	66 - +120	Very dark greyish brown (10 YR 3/2); silty loam; sticky and slightly plastic; moderate medium subangular blocky structure; friable; many fine and medium tubular pores; few fine roots.

San Pedro soil, slurry-amended soil (SS).

Horizon	Depth (cm)	
Ap	0 - 26	Dark yellowish brown (10 YR 4/4) dry, dark brown (10 YR 3/3) moist; sandy loam; moderately sticky and moderately plastic; strong medium subangular blocky structure that breaks into strong medium granular structure; slightly hard; many fine interstitial and common medium vesicular pores; many fine roots; clear smooth boundary.
B	27 - 44	Dark brown (10 YR 3/3); loamy sand; slightly sticky and non plastic; weak medium subangular blocky structure; firm; many fine and medium vesicular pores; common fine roots; clear smooth boundary.
Bw	45 - 54	Dark brown (10 YR 3/3); sandy loam; slightly sticky and slightly plastic; moderate medium subangular blocky structure; firm; many fine interstitial and many medium vesicular pores; clear smooth boundary.
C	55 - 72	Dark yellowish brown (10 YR 3/3); sandy; non sticky and non plastic; single grain; loose; many fine interstitial pores; few fine roots; manganese patina over isolated gravels; abrupt smooth boundary.
2Bb	73 - +100	Dark yellowish brown (10 YR 4/4); sandy loam; sticky and moderately plastic; moderate medium subangular blocky structure; firm; many fine and medium tubular pores; few coarse roots.

Table A2. Statistically significant relationships between soil physical properties and soil conductivity properties.

	Sand	Clay	Silt	TDP (*FDP* + *SDP*)	*coBd*
	----------------------------------%----------------------------------			------cm^3 cm^{-3}-----	------Mg m^{-3}-----
ΔK	y = 0.01x - 0.17 R^2 = 0.172**	-	y = -0.01x + 0.84 R^2 = 0.156**	y = 0.45Ln(x) + 1.10 R^2 = 0.111*	-
*Ka*100 (m d^{-1})	y = -7.41Ln(x) + 41.51 R^2 = 0.13*	y = 0.63x + 6.40 R^2 = 0.162**	-	-	y = -36.06Ln(x) + 23.22 R^2 = 0.136*

*: p<0.05 and **: p<0.01.

CHAPTER 3. PREFERENTIAL FLOW PATHS IN TWO ALLUVIAL SOILS WITH LONG-TERM PIG SLURRY ADDITION IN CENTRAL CHILE

3.1 ABSTRACT

Soil hydraulics and water movement by saturated, unsaturated and preferential flow determine the complexity and dynamic patterns of solute distributions in soils. This study assessed the relationships between flow types and nitrate (NO_3^-) concentrations in two soils of central Chile under conventional agriculture management and with long-term slurry application.

The soils selected were two alluvial soils, San Pedro (SS) and Pichidegua (PS), belonging to the soil series Quilamuta (Typic Xerochrepts) and Tinguiririca (Mollic Xerofluvents) respectively, and continuously cropped with maize (*Zea mays*) and amended with pig slurry. Each soil (3 replicates) was characterised in physical and hydraulic terms. Soil NO_3^- concentration at 0, 25, 50 and 100 cm depth was determined and soil water content was measured with ®Diviner 2000 equipment every two weeks during a 6-month period (April-September 2011). A control soil with no pig slurry addition in San Pedro (SC) and Pichidegua (PC) was included. A dye tracer test using Brilliant Blue FCF was conducted on each soil and digital picture analysis was then performed to classify flow types in the soil profiles through the distribution of stained path width (SPW).

Nitrate concentration distribution showed some correlations with SPW, stained coverage and saturated hydraulic conductivity (*Ks*) in both soils, and with unsaturated hydraulic conductivity (*Kns*) in SS, where homogeneous matrix flow dominated through the entire profile. The other treatments (PS, PC and SC) displayed homogeneous matrix flow in the topsoil due to higher aggregation and tillage effects, with transition to macropore flow at depth.

Key words: Soil hydraulic properties, nitrate leaching, dye tracers, image analysis, water movement.

3.2 INTRODUCTION

Nitrate leaching (NL) and the associated groundwater pollution risk is raising considerable concerns about the environmental impacts of using pig slurry as an organic amendment on soils. Various soil factors affect the movement, pattern distribution and concentration of solutes through soils, but water movement associated with soil hydraulics is the main factor involved.

Solute distribution and water movement were once regarded as almost non-predictable processes due to the high spatial and temporal variability, but more recent research has shown that some degree of prediction is possible (Hillel, 1998; Simunek *et al*., 1998; Jarvis, 2007; Simunek and van Genuchten, 2008; Jarvis *et al.*, 2012). The difficulties in studying soil water movement and its relationships with solute transport lie in the fact that water movement occurs through at least three flow types (saturated, unsaturated and preferential flow), generating complex and dynamic interactions with solutes (Kutilek and Nielsen, 1994).

In the first decades of soil hydraulics research, water flow was assumed to be saturated, homogeneous and isotropic through the soil matrix (Hillel, 1998; Radcliffe and Rasmussen, 2002). However, it is now known that flow also occurs in unsaturated soil conditions with a rather anisotropic nature due to inherent soil properties (Beven and German, 1982; Kung, 1990; Bootlink *et al*., 1993). Over recent decades, research has focused on solute transport and flow through macropores (Mooney and Morris, 2008; Nielsen *et al.*, 2010), with saturated and unsaturated flow theories/models proving to be unsatisfactory in predicting such behaviour. A type of flow termed *preferential flow* (PF), *by-pass flow* or *macropore flow* is now widely recognised in many parts of the world as one of the major routes of groundwater contamination by agro-chemicals and other materials and is proving to be the rule rather than the exception in soil water movement (Flury *et al*., 1994; Janssen and Lennartz, 2008; Mooney and Morris, 2008; Jarvis *et al.*, 2012). This phenomenon allows unusually rapid and deep movement of chemicals with relatively small amounts of infiltrating water (rain or irrigation) and effectively bypasses much of the soil profile where pollutants are normally bound and/or degraded, because only a partial fraction of the total cross-section is available for flow (Radcliffe and Rasmussen, 2002).

This PF has both environmental and human health implications, since it allows contaminant transport to groundwater without interaction with (bypassing) the chemically and biologically reactive upper layer of soil (Allaire *et al.*, 2009; Jarvis *et al*., 2012). Thus a significant fraction of the contaminants quickly reaches the subsoil, where natural attenuation processes are generally less effective. In addition, PF can either enhance, or curtail, the capacity of the soil to buffer and filter, and it can compromise, or boost, other ecosystem services (Clothiers *et al*., 2008).

It is important to note that PF occurs at two different scales:
i) Intra-aggregate porosity: As finger, funnel or heterogeneous flow in soil matrix pores at pedon scale, due to differences in macroscopic hydraulic characteristics (Kung, 1990; Jarvis *et al.*, 2012). In this case, even in the absence of macropores, an unstable wetting front develops in unstructured soils and moves preferentially between separated vertical fingers, especially towards the groundwater (Baker and Hillel, 1990; Lipsius and Mooney, 2006). For the development of unstable flow in soils, entrapped air towards the wetting front, conditions of hydrophobia associated with organic compounds and very dry soil conditions are necessary (Ritsema *et al*., 1993; Wang *et al*.,1998).

ii) Inter-aggregate porosity at macropore scale: In this case, three different types of macropores are distinguished: a) macropores formed by plant roots and soil macrofauna; b) macropores formed by swelling and shrinking associated with drying and wetting conditions or due to freezing and thawing cycles, both dependent on seasonal cycles; and c) irregular inter-aggregate voids formed by tillage implements (Jarvis *et al*., 2012).

Thus macropore flow obviously depends on pore geometry (such as continuity, tortuosity and diameter). These are generally unknown variables and display high spatial and temporal variability.

The most important processes related to PF are associated with soil aggregation and hence the formation of continuous networks of larger macropores due to soil shrinkage/expansion caused by drying/wetting seasonal cycles (Dexter, 1988; Semmel *et al*., 1990), as well as organic matter, which stabilises soil structure (Cheshire 1979; Chaney and Swift, 1986). Thus, strong macropore flow can be expected in soils with vertical continuous macropores in a poorly developed or degraded structure hierarchy (Jarvis *et al*., 2012).

Two of the most common agricultural practices to prepare soil for growing crops are the addition of amendments (fertilisers and organic materials) and tillage, which alters the soil structure and, consequently, PF.

Tillage reduces PF paths by interrupting continuous macropores (Thomas *et al*., 1973; Tyler and Thomas, 1977; Kranz and Kanwar, 1995; Elliot *et al*., 2000; Hangen *et al*., 2002; Collum, 2009). It also promotes organic matter oxidation, with a decrease in soil friability, increasing soil compaction due to repeated traffic (Watts and Dexter, 1998) and increased mineralisation, resulting in lower water movement through PF, but with higher NO_3^- concentrations. On the other hand, according to several studies (Jarvis, 2007; Jarvis *et al*., 2007; Luo *et al*., 2010), soil fragmentation by tillage in conventional agriculture combines to degrade the structural hierarchy and promotes a coarser structure in the plough layer, causing stronger PF in arable soils. Besides tillage practices, the large roots of some agricultural crops can enhance water and solute transport into subsoil. Furthermore, since roots act as drying agents in soil, they influence macroaggregate development (Angers and Caron, 1998).

The long-term use of organic amendments produces organic-rich topsoils that can become hydrophobic when dry (Wang *et al*., 1998; Blanco-Canqui and Lal, 2009), promoting PF at different flow scales (intra-aggregate porosity). The same can occur in sandy soils without a structural hierarchy, with preferential finger and funnel flow promoted by water repellency of the sand grains (Deurer and Bachmann, 2007). Biotic factors affected by organic amendments also affect PF. For example, deep-burrowing anecic earthworm species create channels deep into the subsoil and thereby increase PF though macropores (Lamandé *et al*., 2003). Microorganisms that stabilise the soil structure increase the functionality of PF over time.

The main aim of this study was to assess the relationships between saturated, unsaturated and preferential flow with soil NO_3^- distribution in two soils of central Chile under conventional tillage and slurry applications and prone to solute leaching to groundwater.

3.3 MATERIALS AND METHODS

3.3.1 Study site and basic characterisation

The study was carried out during 2011 on two alluvial soils located in the central longitudinal valley of Chile (Pichidegua: UTM 0277313E, 6194387S and San Pedro: UTM 0289587E, 6240288S; Datum WGS 1984 19S), at two experimental sites corresponding to representative cartographical units or polypedons (phases of soil series). Laboratory measurements were carried out at the soil laboratories of the University of Chile.

At both sites, which pose a high potential risk of NO_3^- pollution to groundwater, a representative pedon was chosen. Disturbed and undisturbed soil samples (4 replicates), were taken at different depths (0-10, 25-35, 50-60 and 100-110 cm) for basic soil physical characterisation. Texture was determined using a Bouyoucos hydrometer, bulk density through the clod and the core methods and particle density by picnometer according to Dane and Topp (2002). Soil chemical characterisation was conducted according to Chilean standard methods (Sadzawka *et al*., 2006) and included soil pH_{water} 1:2.5 determined by potentiometry, soil extract electrical conductivity (ECe) by conductivimeter, total organic carbon (OC) by calcination (360°C), total N (N_T) by the Kjeldahl method, cation exchange capacity (CEC) by ammonium acetate at pH 7 and mineral N concentration (NO_3^- and NH_4^+) by the steam distillation method. In each case, a soil with repeated pig slurry applications (PS in Pichidegua and SS in San Pedro) and control soils without pig slurry applications (PC in Pichidegua and SC in San Pedro; see Table 2.1 in Chapter 2) were monitored every two weeks during a 6-month period (April-September 2011).

During the study period, the San Pedro soil was not amended with pig slurry, but it previously received repeated slurry applications through irrigation over a 5-year period. In Pichidegua, which was under fallow management, two applications of approximately 500 $m^3\ ha^{-1}$ of pig slurry each were made during the study period through a flooding irrigation valve, and the soil had received regular pig slurry applications during a previous 10-year period. The mean N concentration measured in pig slurry was 1.3 g L^{-1} and the volume of slurry applied supplied a N dose of approximately 640 kg ha^{-1} each time. According to the farmers involved, other management practices were similar at all experimental sites.

At both sites, the soils are of alluvial origin, with a deep, stratified profile. Pichidegua soil cartographically belongs to the Tinguiririca soil series, a loamy sand Mollic Xerofluvent occupying a recent alluvial terrace position (CIREN, 1996a). San Pedro soil belongs to the Quilamuta soil series, a sandy loam Typic Xerochrept developed over terraces or alluvial fans, with granitic parent material (CIREN, 1996b).

The climate at both sites is semi-arid Mediterranean, with most rainfall occurring between May and October. Hot summers and relatively cold (Pichidegua) and relatively mild (San Pedro) winters characterise the sites. At Pichidegua, the maximum (January) and minimum (July) annual air temperature is 29.0ºC and 4.9ºC, respectively, with mean annual precipitation (MAP) of 696 mm (Santibáñez and Uribe, 1993). At San Pedro, the maximum and minimum annual air temperature is 31.3ºC and 4.4ºC, respectively, with MAP of 383 mm (Santibañez and Uribe, 1990).

3.3.2 Tests of soil hydraulic properties

Saturated soil hydraulic conductivity (*Ks*) was assessed by constant load permeameter and water retention (pF) curves by pressure plates (Dane and Topp, 2002).

Soil water content (θ) was monitored with a ®Diviner 2000 (Series II) device every two weeks from topsoil to 100 cm depth. Using θ values and the Mualem-van Genuchten adjustment equation to the pF curves (combining Darcy and flux continuity equations), the unsaturated hydraulic conductivity was calculated as (Nissen *et al*., 2006):

$$Kns = \frac{\Delta L}{\Delta t}\frac{\Delta\theta}{grad\,\psi} \qquad \text{(Eq. 1)}$$

where *Kns* is the unsaturated (or non saturated) soil hydraulic conductivity (cm d^{-1}), ΔL is the vertical distance between measurements of volumetric soil water content (cm), Δt is the time interval between measurements (d), $\Delta\theta$ is the mean variation in volumetric soil water content between two measurement dates (g cm^{-3}) and $grad\,\psi$ is the hydraulic potential gradient ($\Delta\psi/\Delta L$ in cm cm^{-1}).

To obtain *Kns* through pF curves, the Mualem-van Genuchten equation (m = 1 – 1/n) was applied such that (van Genuchten, 1980):

$$\theta = \frac{(\theta sat - \theta res)}{(1+|\alpha\psi|^{n})^{m}} + \theta res \qquad \psi \leq 0 \text{ (Eq. 2)}$$

so that equation parameters were obtained: θsat is the volumetric water content at saturation, θres is the residual volumetric water content, α depends on the shape of the curve, n and m are function parameters and ψ is the pressure head (in this case matric potential with negative values).

For the values of *Ks* and *Kns*, which were non-normally distributed, logarithmic transformation was applied.

3.3.3 Ammonium (NH_4^+) and nitrate (NO_3^-) determination

Samples of soil for determination of NO_3^- and NH_4^+ concentration (Sadsawka *et al*., 2006) were collected with a soil auger every two weeks at regular interval depths (0-10, 25-35, 50-60 and 100-110 cm, which are referred here as 0, 25, 50 and 100), with 3 replicates per pedon. These concentrations were statistically correlated to unsaturated hydraulic conductivity and other physical and hydraulic soil properties assessed at the same depths.

3.3.4 Preferential flow pattern assessment with dye tracer

An examination of preferential flow (PF) pathways was carried out in open pits in each experimental unit following dye tracer application. The choice of the tracer depends on its behaviour in soil, its toxicity and stability, cost and availability. Due to its easy mobility, high contrast with the soil background colour and low toxicity (Flury and Flühler, 1995), the food dye brilliant blue (BB) was chosen for this work. According to Germán-Heins and Flury (2000), the absorption spectrum of BB is not sensitive to pH or ionic strength in aqueous solution.

Although soil pits have the disadvantage of destroying part of the preferential flow, they are inexpensive and can be used for long periods of time to characterise soil flow patterns. Moreover, soils pits allow processes that cannot be observed otherwise to be visualised and sometimes permit an understanding of connectivity between vertical and horizontal PF paths (Allaire *et al*., 2009).

After irrigation (to close to field capacity), a head of BB solution was applied at a concentration of 2.2 g L^{-1} (Nielsen *et al*., 2010) within sub-plots (metal frame square) of 1.5 m^2. The volume of solution applied was calculated to reach soil saturation at 100 cm depth. Subsequently, with the soil profile exposed, stained areas were morphometrically measured. Under natural daylight conditions and without direct radiation, the soil profile was photographed and white reflection panels were mounted on three sides of the pit to balance and compensate for differences in illumination by diffuse light. Some rulers were attached to the profile in order to correct the images geometrically and to assess the physical distribution of stained macropores (Weiler and Flühler, 2004; Alaoui and Goetz, 2008).

Before tracer (BB) application, a calibration process was carried out with 8 standard solutions (0.5, 1.0, 2.0, 4.0, 8.0, 16.0, 50.0, 100.0 g L^{-1}) in which soil samples were submerged for five days. After natural drying of soil samples, clods were photographed in similar conditions to the field experiments (Alaoui and Goetz, 2008).

Digital image analysis was carried out using image processing software (Gymp 2). Geometrical correction and maximisation of blue, green and cyan colour was carried out followed by subtraction of background colour and division of colours obtained. These images were converted to greyscale tones and a median filter of 2 cm was applied.

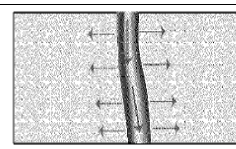
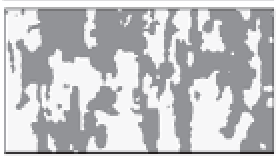
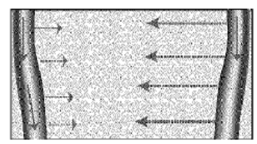
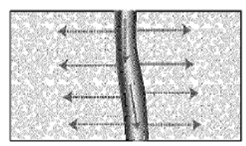
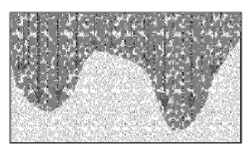
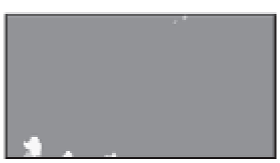
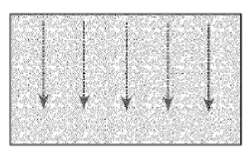
Different concentrations and unstained areas were separated by the concentration categories (*c*, obtained from the standard solutions), classifying the image into four levels according to Weiler and Flühler (2004):

i) Unstained areas (c <0.5 g L^{-1}),

ii) Low concentration ($0.5\ g\ L^{-1} \leq c < 1.0\ g\ L^{-1}$),
iii) Medium concentration ($1.0\ g\ L^{-1} \leq c \leq 3.0\ g\ L^{-1}$)
iv) High concentration ($c > 3.0\ g\ L^{-1}$).

The vertical flow was analysed (®Matlab software) according to Weiler and Flühler (2004) by the vertical dye patterns and categorised into one of the five flow types according to the percentage of stained path width (SPW) of three categories: SPW_{20}: SPW<20 mm; $SPW_{20\text{-}200}$: SPW between 20-200 mm and SPW_{200}: SPW>200 mm (Table 3.1). For this analysis, concentration categories were neglected and diagrams of stained pixels (volume density) versus soil depth were obtained.

Table 3.1. Characterisation of flow types according to stained path width (SPW).

Flow type[a]	Image sample of dye pattern	Fraction (%) of SPW for:		Flow process	Soil feature
		< 20 mm	> 200 mm		
Macropore flow with low interaction		> 50	< 20		Macropores in a poorly permeable or saturated soil matrix
Macropore flow with mixed interaction		< 50 and > 20	< 20		Macropore in a heterogeneous soil matrix or macropores with variable macropore flow
Macropore flow with high interaction		< 20	< 30		Macropores in a permeable soil matrix (texture or aggregation)
Heterogeneous matrix flow and fingering		< 20	> 30 and < 60		Spatially heterogeneous soil (texture or aggregation), water repellency or flow instability in coarse-textured or variable texture soils
Homogeneous matrix flow		< 20	> 60		Permeable soils (texture or aggregation)

[a]Adapted from Weiler and Flühler (2004) and Weiler (2001).

3.3.5 Experiment design and statistical analysis

At the experimental sites (see Figure 2.1 in Chapter 2) where the devices and plots were located, two pits were excavated between plots. The experimental design was completely randomised, with experimental sites corresponded to soil sampling units and with treatments comprising soil management practices in each soil series.

Three replicates of properties measured in field conditions were used, corresponding to three plots in each experimental unit, and 4 replicates when soil physical and hydraulic properties were assessed at laboratory level.

The results were subjected to multiple component testing to assess the correlation between hydraulic properties and NO_3^- concentration (p<0.05) and several regressions were made between correlated variables (for p<0.05 and p<0.01). In addition, some t-student tests were carried out to assess NO_3^- concentration differences between soil treatments and stepwise tests with least square fit tests to obtain a pedotransfer function of NO_3^- concentration depending on SPW, K_s and NH_4^+ concentration.

3.4 RESULTS AND DISCUSSION

3.4.1 Soil characterisation

Data on general soil chemical properties (pH, ECe, CEC and N_T) were taken from Nájera *et al.* (2013) and are presented in Table 2.2 in Chapter 2).

Most soils showed increasing sand content to 50 cm depth, and then it decreased to 100 cm depth. An exception was found in SC soil, where sand content showed a regular decrease in depth. Site position in terraces and fans of alluvial origin in both basins has led to natural soil stratification, which is evident as variations in horizon morphological properties (Fuentes *et al*., 2013).

Soil organic matter (SOM) displayed similar behaviour to sand content, related to organic debris deposited in the surface and its oxidation. Increased SOM at 100 cm depth was related to soil texture, because clay content had a direct significant relationship with SOM (p<0.01). Oxidation processes under conventionally tilled soils were apparently compensated for by slurry application, so there were no significant differences in SOM between sites with and without amendments.

Although repeated application of slurry generally leads to higher SOM accumulation and consequently lower bulk density (*Bd*), the PS and SS soils had higher *Bd* than control treatments PC and SC, probably due to the effects of the external loads exerted by agriculture machinery in conventional tillage in PS and SS. The exception occurred in SC soil, where the experimental plots were established in untilled soils adjacent to a track, which gave higher *Bd* to 25 cm depth. As reported in other studies (Arvidsson, 1998; Aşkin and Özdemir, 2003; Ruehlmann and Körschens, 2009), *Bd* values were directly correlated to sand contents (r=0.66, p<0.01) and inversely to SOM content (r=0.41, p<0.05).

Salinity and pH were altered at the soil surface due to application of slurry. The EC in PS topsoil exceeded the adequate range for most crops (EC >4 dS m^{-1}), whereas in PC the EC value was inside that range. The pH in general was lower in PS and SS topsoils than in the controls, due to the higher H^+ release during N mineralisation after slurry application. The chemical effect of slurry addition was higher in Pichidegua soils than in San Pedro soils due to higher dose applied to the former, but its effect on both soils declined with depth.

3.4.2 Soil nitrate concentration distribution

Nitrate concentrations (Table 3.2) were significantly (p<0.05) higher and showed considerably higher variation during the study period in Pichidegua (PC and PS) than in San Pedro soils. All soils and managements showed slightly higher NO_3^- concentrations at the beginning of the measurement season (May-June) due to the high temperatures, but they decreased subsequently through immobilisation. During late autumn and winter, the NO_3^- concentrations decreased due to both lower temperatures and leaching. In Pichidegua soil, this trend changed later in the season, with slightly increasing NO_3^- concentrations in September owing to the higher temperature, which promoted higher mineralization (Leirós *et al*., 1999; Sierra, 2002). In San Pedro, there was a steady regular NO_3^- concentration decrease throughout the study season.

Table 3.2. Nitrate concentration ([NO_3^-]) and ammonium concentration ([NH_4^+]) at depth in two soils of central Chile with and without slurry applications.

Soil[b]	Biweekly [NO_3^-][a] 15-May	07-Jun	21-Jun	18-Jul	16-Aug	30-Aug	20-Sep		Period mean [NO_3^-]	Period mean [NH_4^+]
	ppm									
PS 0	72.3	52.3 a	75.6	65.3	45.7	26.1	56.0		56.2 B	33.7 B
PS 25	18.7	175.9	70.9	59.3	27.1	42.9	85.9		68.7 B	25.7
PS 50	15.9	59.7	42.5	56.9	27.1	67.2 b	74.7 b		49.1 b B	16.5
PS 100	42.9	61.1 b	61.1 b	52.7	17.7 b	59.7 b	63.5 b		51.3 b B	14.3
PC 0	65.3	99.4 b	31.7	56.0	55.5	55.1	72.8		62.3 B	24.6 B
PC 25	50.9	79.8	50.9	43.4	11.2	48.5	42.0		46.7 B	14.4
PC 50	11.7	28.5	16.8	17.7	10.3	27.1 a	23.3 a		19.3 a B	17.7
PC 100	12.1	18.2 a	11.7 a	7.5	5.6 a	12.1 a	13.1 a		11.5 a	14.1
Soil	Biweekly [NO_3^-] 02-Jun	14-Jun	28-Jun	26-Jul	10-Aug	23-Aug	06-Sep	14-Sep	Period mean [NO_3^-]	Period mean [NH_4^+]
	ppm									
SS 0	39.2	48.1	28.0	16.8	14.2	11.7	7.9	4.2	21.3 A	15.8 A
SS 25	21.5	41.1 b	52.3	7.5	5.6	7.9	7.9	4.7	18.6 A	14.5
SS 50	18.2 b	13.1	10.7	2.8	3.7	3.7	7.9	2.8	7.9 A	11.7
SS 100	14.9	14.5	12.1	10.7	6.5	10.3 b	6.1	2.3	9.7 A	9.9
SC 0	24.3	14.5	14.5	9.3	9.1	8.9	7.7	6.5	11.8 A	12.2 A
SC 25	11.2	21.7 a	20.3	5.1	3.7	11.7	4.7	0.9	9.9 A	11.9
SC 50	11.2 a	9.8	11.9	1.9	4.7	8.9	7.5	0.0	7.0 A	12.6
SC 100	15.4	11.2	8.4	3.3	8.4	4.7 a	6.1	4.2	7.7	11.8

[a]Different lowercase letters at the same depth and soil (same basin) denote statistically significant differences (p<0.05) between managements, different capital letters at the same depth denote statistical differences between different soil series with the same treatment.

[b] PS: Pichidegua soil with slurry applications; PC: Pichidegua soil (control); SS: San Pedro soil with slurry applications; SC: San Pedro soil (control).

The increased NO_3^- content at depth (50 cm and 100 cm) at the end of the measurement season (Table 3.2) was presumably caused principally by leaching from the root layer. It has been demonstrated in several studies that depending on climate, mineralisation decreases considerably with soil depth (Kleber *et al*., 2000; Fu Sheng *et al*., 2005; Kheyrodin and Antoun, 2007). Dauden and Quílez (2004) and Van Es *et al*. (2006) demonstrated the risk of NL in Mediterranean zones, such as that in this study, and noted that the risk of groundwater pollution is associated with water budget and soil properties.

The NH_4^+ concentration was also significantly higher (p<0.05) at surface horizon in Pichidegua soils, compared to San Pedro soils, with higher values under slurry applications, especially in the first 30 cm of soil (Table 3.2). Soils with amendments showed a regular decrease in NH_4^+ with soil depth, whereas at control sites the concentration decrease was not as marked. Although the NH_4^+ retained at exchange sites represents a lower risk of contamination of groundwater than NO_3^-, it can be nitrified or lost to the atmosphere, depending on season and soil characteristics (Havlin *et al*., 2005).

3.4.3 Saturated hydraulic soil conductivity (*Ks*)

Soil hydraulic conductivity showed high statistical dispersion, with standard deviation values that even exceeded the mean values (see Table 2.5 without air permeability, Chapter 2) despite the spatial proximity. Thus the variation observed must be interpreted as inherent to soil heterogeneity. According to Jury *et al*. (1991) and Warrick (2002), the coefficient of variation for *Ks* ranged from 50 to 300 %, while Mallants *et al*. (1996) reported values from 105 to 619 % in a transect of a sandy loam soil with macropores, depending on the measurement scale.

Saturated soil hydraulic conductivity (*Ks*) in general tended to decrease with time at almost all depths, but after 24 h showed some stabilisation. The exception was found in PC at 100 cm depth, where *Ks* increased up to 4 h and then decreased. In some cases *Ks* increased slightly after 24 h (PS at 0 and 100 cm, PC at 25 cm, SS at 25 cm and SC at 0 cm depth), which was associated with occlusion due to pore system collapse and a subsequent small recovery in its functionality, altering the total function of porosity and decreasing its solution transport capacity. A similar effect has been reported in previous studies, some of them carried out on Andisols and Ultisols of south Chile (Ellies *et al*., 1997; Janssen *et al*., 2004; Osunbitan *et al*., 2005; Alarcón *et al*., 2010; Dörner *et al*., 2010).

The large variation in *Ks* at different depths reflects the anisotrophic nature of soil pedons, as a result of sedimentation and horizon genesis (Kutilek and Nielsen, 1994; Hillel, 1998; Domenico and Shwartz, 1998).

Various relationships between soil physical properties and *Ks* were found when using the mean values to reduce spatial variability, but most were associated with diameter of soil particles (sand and silt content) and soil porosity (clod bulk density and total porosity) as is shown in Figure 2.5 in Chapter 2.

3.4.4 Unsaturated hydraulic conductivity (*Kns*)

A significant dependency ($p<0.01$) of *Kns* on the hydraulic gradient was found (see Figure 2.6 in Chapter 2). In fact, as the soils were coarse-textured there was an abrupt decrease in *Kns* at high tensions. Fine-textured soil horizons shown higher *Kns* at high water tensions due to more water-filled pores and continuous water films (Radcliffe and Rasmussen, 2002). In contrast, as reported by Ellies and Vyhmeister (1981), the potential gradient assessed here was considerably higher, especially in San Pedro soil, reaching almost 10^{13} hPa (see Figure 2.8 in Chapter 2), and the *Kns* was significantly lower due to the stratified nature of soil profiles.

Pichidegua soils displayed higher *Kns* than San Pedro soils, principally associated with textural classes and especially high potential gradients. Only plots in PC treatment at 50 and 100 cm depths showed significant differences ($p<0.05$) in *Kns*, which confirms the stratigraphic heterogeneity of the study soils, the oscillation of the watertable and its effect on soil genesis.

Comparing plots with and without pig slurry application on Pichidegua soils, significant spatial variation in *Kns* was detected. It was considerably higher at 100 cm depth for fine-textured soil and at 50 cm depth for coarse-textured horizons (see Figure 2.7 in Chapter 2). This sandy horizon at 50 cm depth, confined between finer horizons, should constrain water movement in unsaturated conditions and internal drainage during infiltration (Hillel, 1998).

In San Pedro control soil, without slurry applications and without tillage (SC), there was significant spatial variation ($p<0.05$) in *Kns* between plots at 25 cm. Tillage of San Pedro soils with slurry application (SS) induced spatial homogenisation of soil properties by mixing upper horizons and destroying the soil structure.

At both sites, temporal variations in *Kns* during the study period were associated mainly with changes in natural environmental conditions due to rainfall, vegetal growth and decay, and changes in soil structure (Gupta *et al*., 2006).

3.4.5 Preferential flow: image analysis of stained areas

The stained areas in both Pichidegua soils were similar, although stained depth was lower in the PS treatment (Figure 3.1). This pattern was due to the higher density of upper horizons, promoted by tillage, which can lead to development of a plough pan that normally generates horizontal flow. Dimensions of soil profiles were 0.9 m width and 1.1 m depth in PS soil (under a maize crop) and 1.1 m width and 0.8 m depth in PC soil, with the watertable occurring below these depths. In both cases, the stained horizontal pattern was considerably homogeneous, with some degree of horizontal repetition through the soil profile. This was strongly dependent on soil structure with homogeneous aggregation (type and grade of soil structure) and could be considered to represent some degree of fractal geometry by presenting a pattern repetition at different scales due to soil pore geometry (Ogawa *et al*., 2002).

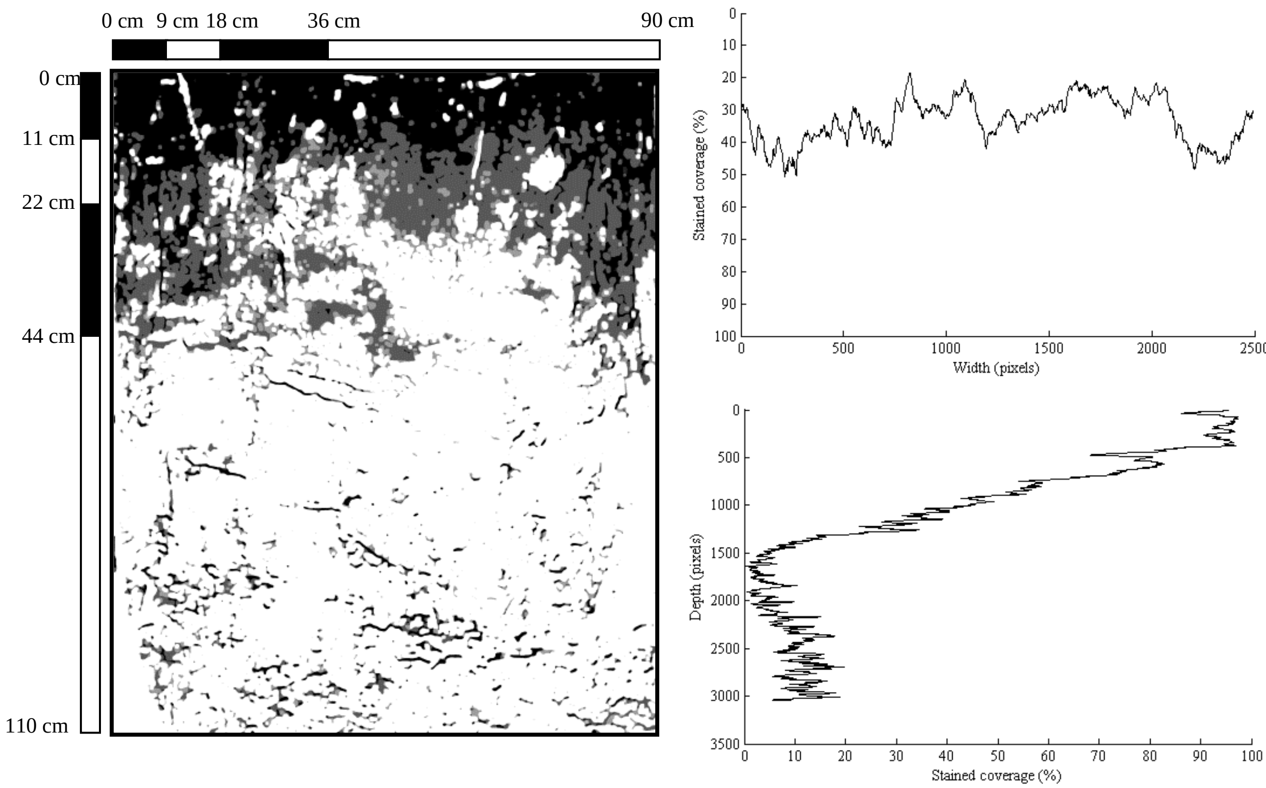


Figure 3.1. Pichidegua soil with slurry additions (PS). Left: stained profile. Above right: horizontal stained coverage pattern; below right: vertical stained coverage pattern.

Treatments PS and PC showed high concentrations of dye tracer stains in the topsoil, decreasing abruptly with depth through the soil profile, and almost disappearing at approximately 55 cm. The PS profile showed a stained area of 33.24%, while the stained area of the PC profile was 37.54%. This difference in stained area between treatments demonstrated that the solution flow through PS soil interacted to a lower degree with the soil matrix than in PC (Figure 3.2). A probable explanation is the conventional intensive tillage of PS, which has caused continuous cutting of macropores and soil compaction (Kranz and Kanwar, 1995; Elliot *et al*., 2000; Hangen *et al*., 2002; Collum, 2009), while the reduced tillage in PC and the effect of seasonal weeds and scrub resulted in conditions giving higher stain coverage.

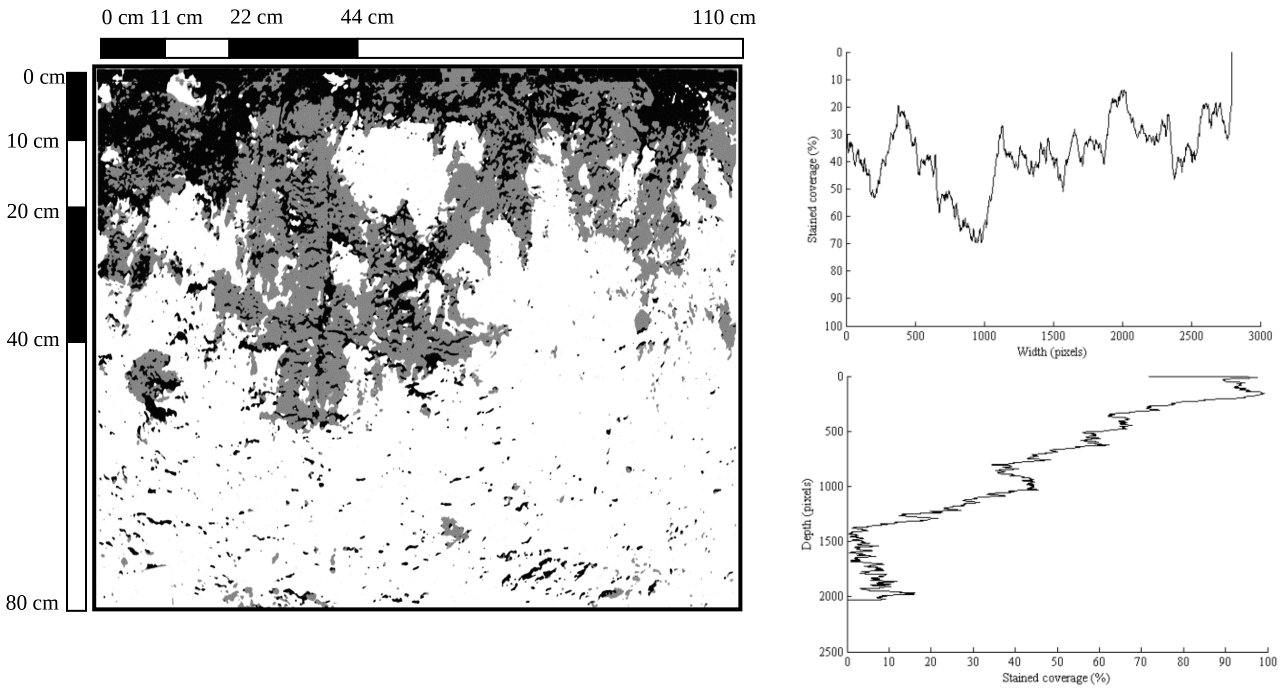


Figure 3.2. Pichidegua control soil (PC). Left: stained profile. Above right: horizontal stained coverage pattern; below right: vertical stained coverage pattern.

San Pedro soil with slurry additions (SS) had a stained area distributed across almost the entire soil profile, which covered an area 1.5 m wide and 1.2 m deep. The flow solution interacted considerably with the soil matrix, bypassing just a small fraction of the left side of soil profile, while the right side presented an area of higher concentration in the stained pattern due to flow occurring through this area, causing a higher concentration of dye tracer in the lower one-third of the soil profile. The amount of stained pixels was considerably higher than for the other profiles assessed, covering 80.06% of the total area, with an homogeneous pattern. This stained pattern is mainly explained by tillage, soil texture (Addiscott, 1996; Ogawa *et al*., 2002) and heterogeneous soil compaction under the tracks of agriculture machinery (Etana *et al.*, 2013), leaving an unstained area on the left side of the picture (Figure 3.3).

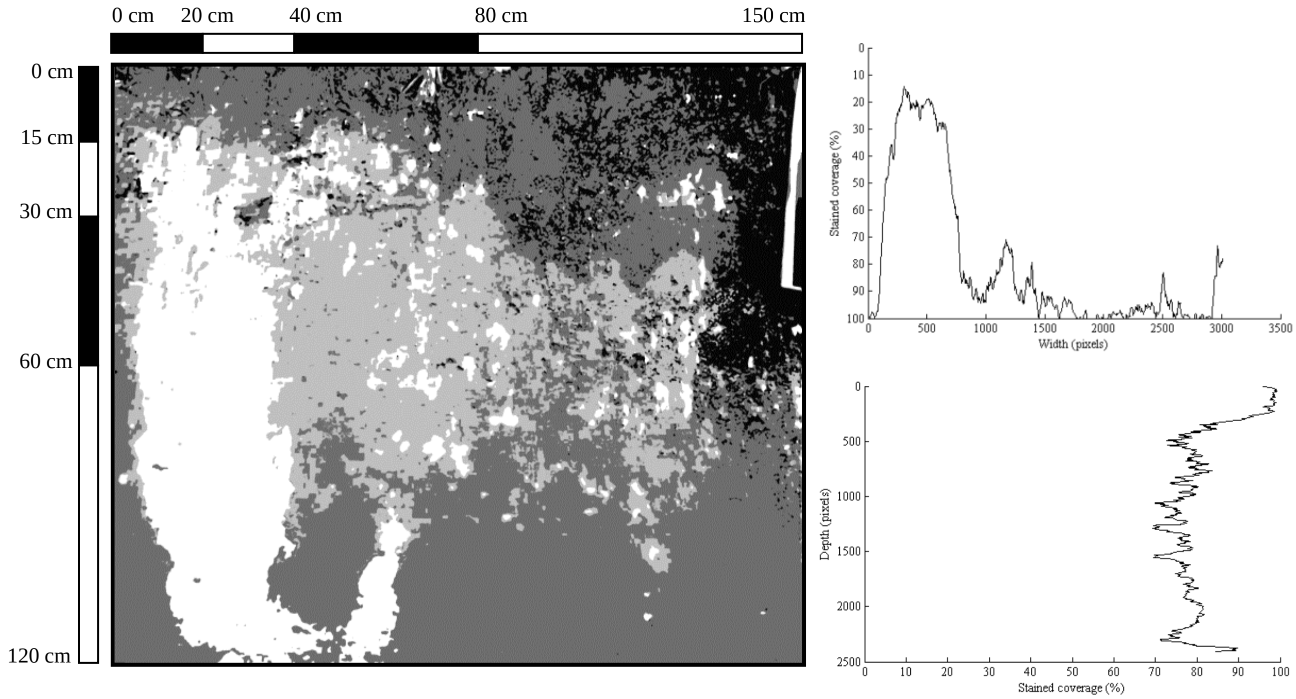


Figure 3.3. San Pedro soil with slurry additions (SS). Left: stained profile. Above right: horizontal stained coverage pattern; below right: vertical stained coverage pattern.

A typical preferential flow pattern occurred in the SC profile (Figure 3.4), where at both sides of the soil horizontal profile (1.6 m wide, 1.1 m deep) there were some thin stained paths of higher dye concentration. This pattern represented macropores created by soil aggregation, bypassing the soil solution to depth, which diminished the interaction between soil solution and soil matrix and can promote solute leaching to groundwater (Janssen and Lennartz, 2008; Mooney and Moris, 2008; Nielsen *et al*., 2010; Jarvis *et al*., 2012). The vertical pattern showed a steep decrease in stained coverage from approximately 26 cm depth, while the assessed profile covered a stained area of 42.07%.

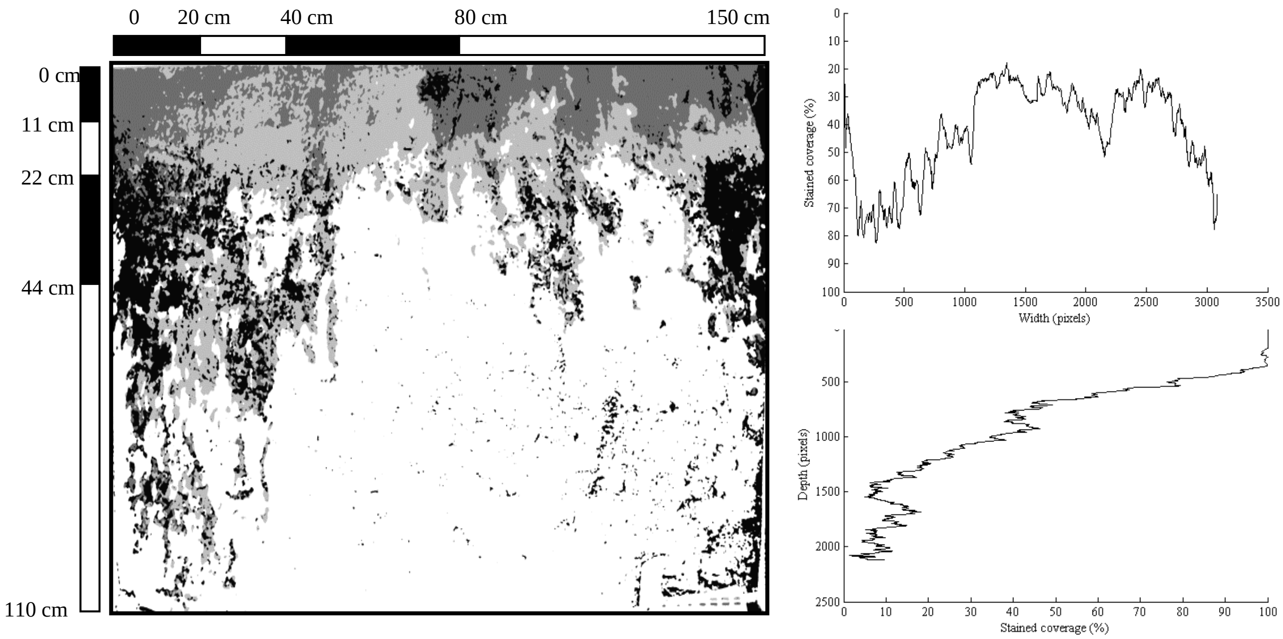


Figure 3.4. San Pedro control soil (SC). Left: stained profile. Above right: horizontal stained coverage pattern; below right: vertical stained coverage pattern.

The stained path width (SPW) vertical patterns are presented in Figure 3.5. In Pichidegua the two SPW profiles showed considerable similarities, with SPW_{200} being more homogeneous and deeper in the arable topsoil layer of PS, whilst $SPW_{20\text{-}200}$ and SPW_{20} showed a common distribution pattern in the two soil profiles (PS and PC), but with a higher proportion of $SPW_{20\text{-}200}$ in PS.

The SPW distributions in San Pedro soils showed clear differences between soil conditions (Figure 3.5). Some SPW_{200} were widespread through the entire SS vertical profile, being higher in the arable topsoil layer, whilst in SC they were confined to the top layer.

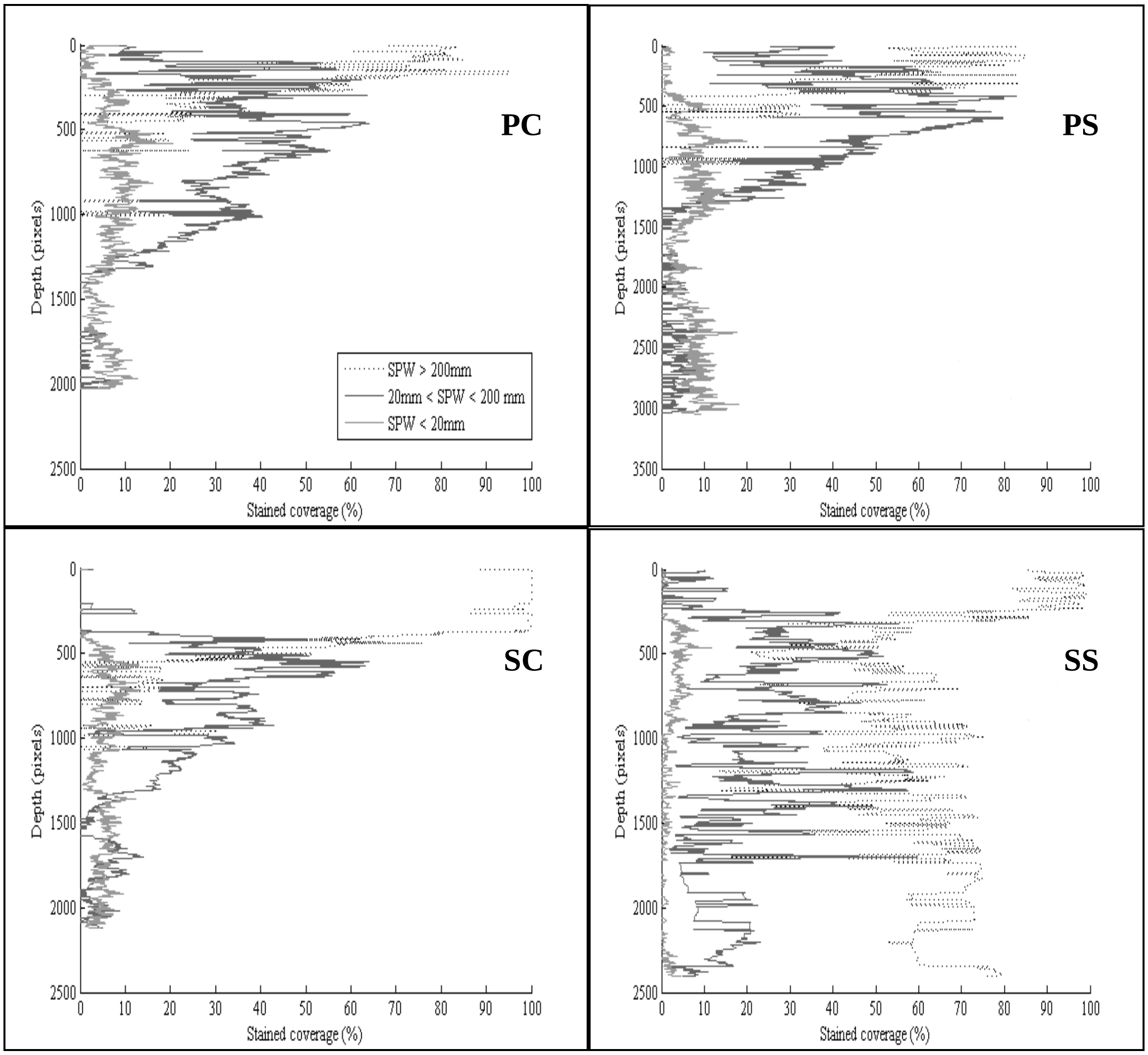


Figure 3.5. Vertical stained path width pattern distributions in soils of central Chile. Above: Pichidegua soil profiles (control on left, slurry-amended on right). Below: San Pedro soil profiles (control on left, slurry-amended on right).

Image analysis includes several steps which can be affected by subjectivity, i.e. different operators are likely to come to slightly different conclusions based on the same images (Weiler and Flühler, 2004). Therefore, summarising these results, some flow type classifications according to SPW are presented in Figure 3.6.

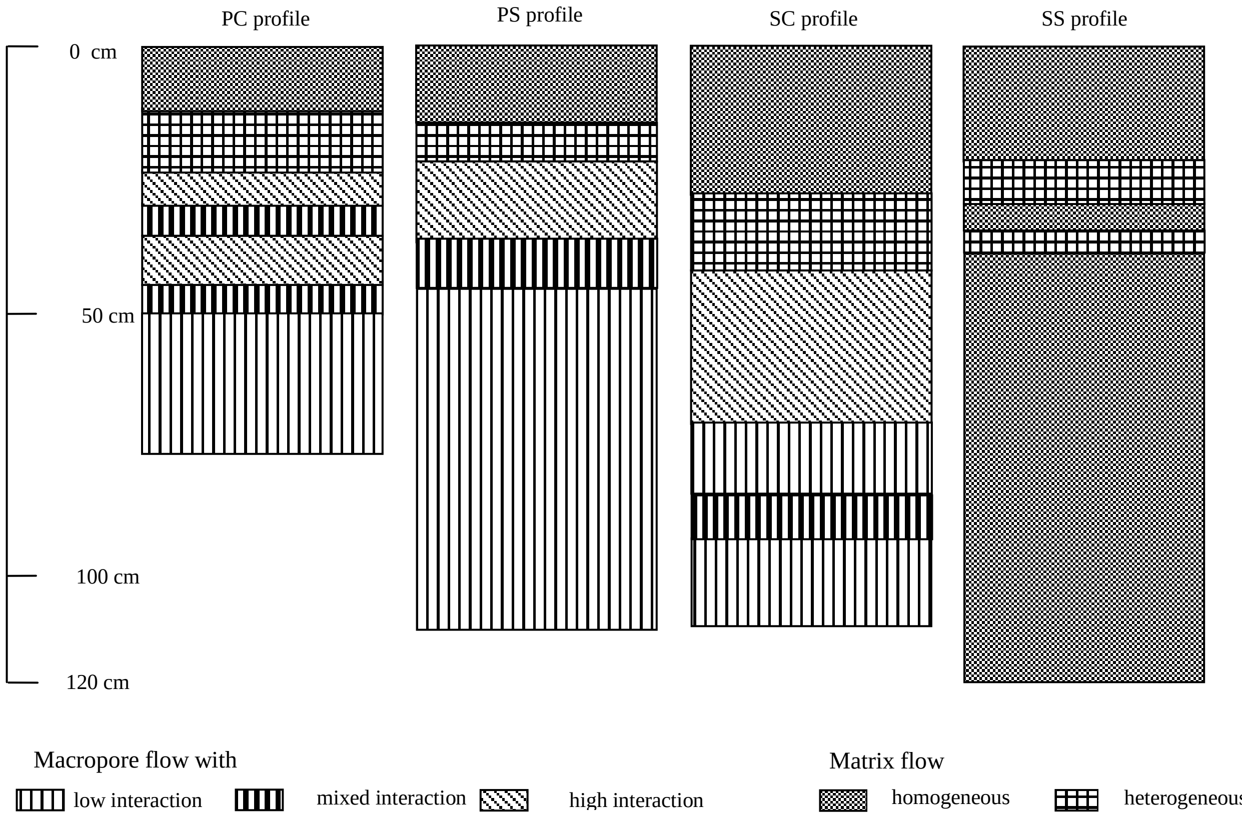


Figure 3.6. Soil solution flow types with soil depth, classified according to stained path width (SPW) distribution (Table 3.1) in two soils of central Chile using brilliant blue dye tracer.

In all profiles homogeneous matrix flow occurred in upper horizons, but was deeper in San Pedro than in Pichidegua soils. This was generally followed by heterogeneous matrix flow and solution-matrix macropore flow with different degrees of interaction. However in SS the homogeneous matrix flow extended through the entire soil profile, but was intercalated by zones of matrix heterogeneous flow. The factors inducing such matrix flow through the first 50 cm of soil are associated with tillage in the topsoil, greater soil aggregation and coarse textural classes (Addiscott, 1996; Ogawa *et al*., 2002; Jarvis *et al*., 2012). Hence, soil aggregation plays a major role in controlling flow type through soils and attention must be paid to studying its impact on the leaching of solutes and pollutants.

The distribution of coverage of stained areas and SPW classifications are shown in Table 3.3 for different sampling depths. Percentage values of SPW are with respect to stained pixels and the pixel range corresponded to 10 cm according to the size of samples and the picture scale.

Table 3.3. Stained areas and stained path width (SPW) distribution at different soil depths (cm).

Soil[a]	Stained coverage ---------%---------	Pixel interval n°	SPW_{200}[b]	$SPW_{20\text{-}200}$ ---%---	SPW_{20}
PS 0	94.1	278	63.9	35.4	0.7
PS 25	54.6	278	2.5	82.8	14.7
PS 50	5.0	278	0.0	6.8	93.2
PS 100	11.6	278	0.0	23.6	76.4
PC 0	92.8	227	73.5	24.6	1.9
PC 25	50.7	227	0.8	81.6	17.7
PC 50	20.2	227	0.0	66.8	33.2
PC 100	8.3	227	0.0	19.0	86.3
SS 0	98.2	202	95.1	4.4	0.4
SS 25	78.6	202	59.9	35.0	5.1
SS 50	74.5	202	69.1	29.6	1.4
SS 100	79.9	202	80.7	19.0	0.3
SC 0	97.8	193	99.7	0.2	0.1
SC 25	66.6	193	27.0	64.0	9.1
SC 50	31.2	193	11.7	72.2	16.1
SC 100	7.1	193	0.0	40.5	59.5

[a]PS: Pichidegua soil with slurry applications; PC: Pichidegua soil (control); SS: San Pedro soil with slurry applications; SC: San Pedro soil (control).
[b]SPW_{200}: SPW >200 mm ; $SPW_{20\text{-}200}$: 20- mm < SPW < 200 mm; SPW_{20}: SPW < 20 mm.

The pattern distribution showed a regular decrease in stained coverage with depth, especially for control sites of both basins. There was a marked decrease in SPW_{200}, but this was compensated for by a sharp increase in SPW_{20} with depth, except in SS. In general, $SPW_{20\text{-}200}$ increased between 25 and 50 cm soil depth.

3.4.6 Stained path width and its relationship with soil properties

The SPW_{200} values were related to sand content and clod bulk density (Figure 3.7). In both cases the fit found was positive quadratic, which means that there is a medium value of both properties that promoted a minimum value of SPW_{200}.

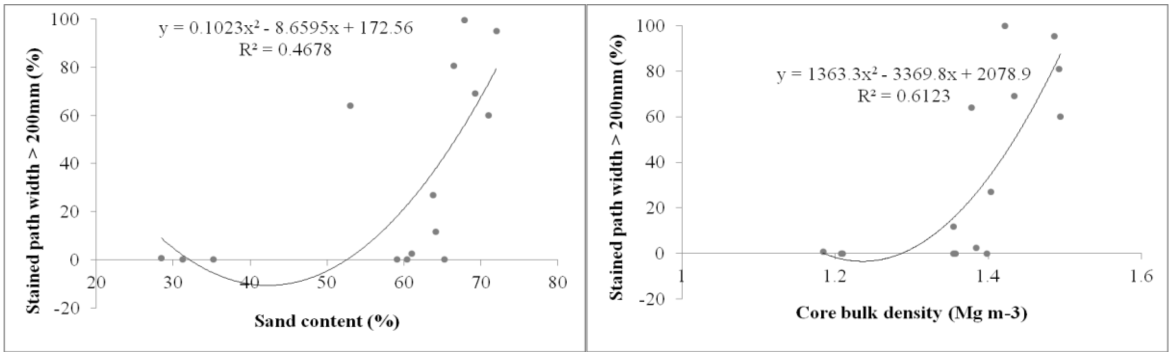


Figure 3.7. Relationships between pattern of stained path width >200 mm (SPW_{200}) and physical soil properties.

Hence, sand content could be related to matrix flow, as the soil had a predominance of SPW_{200} owing to the pore arrangement promoted. The lower SPW_{200} occurred in the range 40-50% sand content, which means that 50-60% of fine particles occluded and filled the pore space between sand particles (loam textural classes), promoting soil arrangements that prevented homogeneous matrix flow, while at lower sand contents soil structure increased, promoting slightly more homogeneous flow. A high *coBd* led to homogeneous matrix flow and a high interaction of soil solution with soil matrix due to a reduction in macropores.

Correlations were also found between *Ks* and SPW_{20}, where the fit was also positive quadratic. On the other hand, a negative exponential fit was found between *Ks* and $SPW_{20\text{-}200}$ (Figure 3.8).

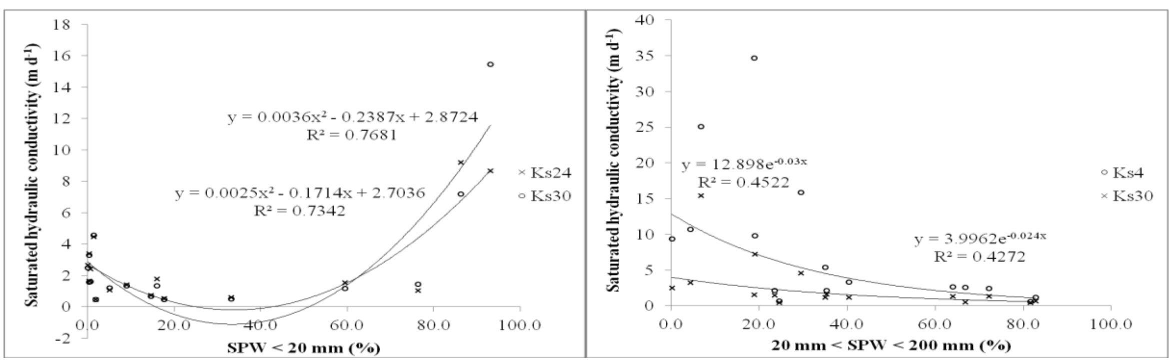


Figure 3.8. Relationship between stained path width (SPW) and saturated hydraulic conductivity (*Ks*).

In the case of SPW_{20} (Table 3.3), values approximately higher than 40% indicated greater *Ks*, due to increased vertical flow and faster flow through macropores. Similarly, values of SPW_{20} lower than 40% represented increased *Ks* due an increase in matrix flow. Lower $SPW_{20\text{-}200}$ values indicated higher *Ks* values ($Ks > 4$ m d^{-1}). Stained path widths between 20 and 200 mm indicated impeded soil water movement, allowing its interaction with the soil matrix, but under the presence of macropores, promoting intra-aggregate wetting.

3.4.7 Nitrate concentration distribution explained by soil hydraulics

Although nitrate concentration $[NO_3^-]$ cannot be explained solely by soil hydraulics because NO_3^- inputs are not considered, analysis of hydraulics can help to understand its distribution through the soil profile. In San Pedro soils, NO_3^- concentrations were related to *Kns* (see Figure 2.12 in Chapter 2). This effect was related to more homogeneous flow type, which in the case of SS was predominantly matrix homogeneous flow, decreasing NO_3^- concentrations with an increase in *Kns*. In contrast, in Pichidegua soils it was not possible to establish such relationships due to flow type transitions through the profile. However, in Pichidegua soils NO_3^- changes appeared to be related to water content variations between consecutive measurement dates.

To assess the relationship of NO_3^- concentration and hydraulic properties obtained from image analysis, some pedotransfer functions were obtained from least square fit:

$$[NO_3^-] = 578.05 + 1.12\ SC - 6.97\ SPW_{200} - 6.36\ SPW_{20\text{-}200} - 5.57\ SPW_{20} + 1.79\ [NH_4^+] \qquad \text{(Eq. 3)}$$
$$p<0.001;\ R^2=0.83;\ RMSE=11.319$$

$$[NO_3^-] = 702.09 + 1.85\ SC - 8.62\ SPW_{200} - 7.76\ SPW_{20\text{-}200} - 6.48\ SPW_{20} - 26.82\ Ks24 \qquad \text{(Eq. 4)}$$
$$p=0.0034;\ R^2=0.79;\ RMSE=12.595$$

where $[NO_3^-]$ is nitrate concentration (ppm), SC is stained coverage (%), SPW_{200} is SPW>200 mm (%), SPW_{20-200} is 20 mm<SPW<200 mm (%) and SPW_{20} is SPW<20 mm (%); $[NH_4^+]$ is the ammonium concentration (ppm) and *Ks*24 is saturated hydraulic conductivity after 24 h (m d^{-1}).

In general, NO_3^- concentration was negatively correlated with SPW and *Ks* because a reduction in water movement through the soil and a decrease in continuous vertical stained paths concentrated solutes within the soil. Nitrate concentration was positively correlated with SC, denoting higher interaction with the soil matrix.

Further studies under controlled conditions, with a higher number of stained profiles, at different sampling scales and assessing the effect of aggregation on soil hydraulics and flow type, are still needed to obtain better knowledge of the relationships between soil physical properties, flow type and nitrate distributions.

3.5 CONCLUSIONS

Hydraulic soil properties, including saturated and unsaturated hydraulic conductivity and preferential flow were shown to play a significant role in NO_3^- distribution through soil profiles. Preferential flow, determined through image analysis and measurement of stained path width (SPW), permitted flow types to be classified.

Stained path width (SPW) was related to saturated hydraulic conductivity, clod bulk density and sand content. Matrix flow types were observed through soils, especially in the upper 50 cm depth due to tillage of the topsoil, soil aggregation and soil textural class, while below this depth there was a transition to macropore flow types, except in SS pedons.

There was some temporal variation in NO_3^- concentration, with a slight increase in the temperate season and a regular decrease during autumn and winter season, due to the use of N by microorganisms when decomposing SOM, lower temperatures and leaching to below the root layer.

Unsaturated hydraulic conductivity was principally related to hydraulic gradient and proved to be associated with NO_3^- mainly in San Pedro soils, where there was dominant homogeneous matrix flow that interacted with soil to a higher degree.

Studies under controlled conditions are needed to assess the effect of aggregation on soil hydraulics and flow type and further extend knowledge of the relationships between soil physical properties, flow type and NO_3^- distribution.

3.6 REFERENCES

Addiscott, T.M. 1996. Fertilizers and nitrate leaching. pp: 1-26. *In*: Hester, R.E., Harrison, R.M. (Eds.). Agricultural chemicals and the environment. Issues in Environmental Science and Technology N° 5. The Royal Society of Chemistry, Cambridge. 126 p.

Alaoui, A., Goetz, B., 2008. Dye tracers and infiltration experiments to investigate macropore flow. Geoderma 144, 279-286.

Alarcón, C., Dörner, J., Dec, D., Balocchi, O., López, O. 2010. Efecto de dos intensidades de pastoreo sobre las propiedades hidráulicas de un Andisol (Duric Hapludand). Agro Sur 38, 30-41.

Allaire, S., Roulier, S., Cessna, A. 2009. Quantifying flow in soils: A review of different techniques. Journal of Hydrology 378, 179-204.

Angers, D.A. and Caron, J. 1998. Plant-induced changes in soil structure: Processes and feedbacks. Biogeochemistry 42, 55-72.

Arvidsson, J. 1998. Influence of soil texture and organic matter content on bulk density, air content, compression index and crop yield in field and laboratory compression experiments. Soil and Tillage Research 49, 159-170.

Aşkin, T., Özdemir, N., 2003. Soil bulk density as related to soil particle size distribution and organic matter content. Poljoprivreda/Agriculture 9(2), 52-55.

Baker, R.S., Hillel, D. 1990. Laboratory tests of a theory of fingering during infiltration into layered soils. Soil Science Society of America Journal 54, 20-30.

Beven, K., German, P. 1982. Macropores and water flow in soils. Water Resources Research 18, 1311-1325.

Blanco-Canqui, H., Lal, R. 2009. Extent of subcritical water repellency of soils under long-term no-tillage systems on a regional scale. Geoderma 149, 171-180.

Booltink, H.W.G., Hatano, R., Bouma, J. 1993. Measurement and simulation of bypass flow in a structured clay soil: a physico-morphological approach. Journal of Hydrology 148, 149-168.

Chaney, K., Swift, R.S. 1986. Studies on aggregate stability: II. The effect of humic substances on the stability of reformed soil aggregates. Journal of Soil Science 37, 337-343.

Cheshire, M. 1979. Nature and origins of carbohydrates in soils. Academic Press, London. 242 p.

CIREN. 1996a. Estudio Agrológico VI Región. Descripción de suelos materiales y símbolos. Centro de Información de Recursos Naturales. Publicación Nº 114, 483 p.

CIREN. 1996b. Estudio Agrológico Región Metropolitana. Descripción de suelos materiales y símbolos. Centro de Información de Recursos Naturales. Publicación Nº 115, 430 p.

Clothier, B.E., Green, S.R., Deurer, M. 2008. Preferential flow and transport in soil: progress and prognosis. European Journal of Soil Science 59, 2-13.

Collum, R. 2009. Macropore flow estimations under no-till and till systems. Catena 78, 87-91.

Dane, J.H., Topp, G.C. (Eds.). 2002. Methods of Soil Analysis. Part 4: Physical Methods. Soil Science Society of America, Inc., Madison, WI, USA, 1692 p.

Dauden, A., Quílez, D. 2004. Pig slurry versus mineral fertilization on corn yield and nitrate leaching in a Mediterranean irrigated environment. European Journal of Agronomy 21, 7-19.

Dexter, A.R. 1988. Strength of soil aggregates and of aggregate beds. pp. 35-52. *In*: Drescher, J., Horn, R., de Boodt, M. (Eds). Impact of Water and External Forces on Soil Structure. Catena Supplement 11. Catena Verlag. Reiskirchen, Germany. 171 p.

Deurer, M., Bachmann, J. 2007. Modeling water movement in heterogeneous water-repellent soil: 2. Numerical simulation. Vadose Zone Journal 6, 446-457.

Domenico, P.A., Schwartz, F.W. 1998. Physical and Chemical Hydrogeology, 2nd ed. John Wiley and Sons Inc., New York, 506 p.

Dörner, J., Dec, D., Peng, X., Horn, R. 2010. Effect of land use change on the dynamic behaviour of structural properties of an Andisol in southern Chile under saturated and unsaturated hydraulic conditions. Geoderma 159, 189-197.

Ellies, A., Vyhmeister, E. 1981. Algunos aspectos hídricos del horizonte superficial de tres tipos de suelos del sur de Chile. Agro Sur 9(2), 94-100.

Ellies, A., Grez, R., Ramírez, C. 1997. La conductividad hidráulica en fase saturada como herramienta para el diagnóstico de la estructura del suelo. Agro Sur 25, 51-56.

Elliott, J.A., Cessna, A.J., Nicholaichuk, W., Tollefson, L.C. 2000. Leaching rates and preferential flow of selected herbicides through tilled and untilled soil. Journal of Environmental Quality 29 (5), 1650-1656.

Etana, A., Larsbo, M., Keller, T., Arvidsson, J., Schjonning, P., Forkman, J., Jarvis, N. 2013. Persistent subsoil compaction and its effects on preferential flow patterns in a loamy till soil. Geoderma 192, 430-436.

Flury, M., Flühler, H., Jury, W.A., Leuenberger, J. 1994. Susceptibility of soils to preferential flow of water: a field study. Water Resources Research 30 (7), 1945-1954.

Flury, M., Flühler, H. 1995. Tracer characteristics of brilliant blue FCF. Soil Science Society of America Journal 59, 22-27.

Fuentes, I., Casanova, M., Salazar, O., Seguel, O. 2013. Morphological, physical and hydraulic soil properties related to nitrate dynamics under pig slurries addition. Unpublished.

Fu-sheng, C., De-hui, Z., Anand Narain, S., Guang-sheng, C. 2005. Effects of soil moisture and soil depth on nitrogen mineralization process under Mongolian pine plantations in Zhanggutai sandy land, P. R. China. Journal of Forestry Research 16, 101-104.

German-Heins, J., Flury, M. 2000. Sorption of brilliant blue FCF in soils affected by pH and ionic strength. Geoderma 97, 87-101.

Gupta, N., Rudra, R.P., Parki, G. 2006. Analysis of spatial variability of hydraulic conductivity at field scale. Canadian Biosystems Engineering 48, 55-62.

Hangen, E., Buczko, U., Bens, O., Brunotte, J., Hüttl, R. 2002. Infiltration patterns into two soils under conventional and conservation tillage: influence of the spatial distribution of plant root structures and soil animal activity. Soil and Tillage Research 63, 181-186.

Havlin, J.L., Tisdale, S.L., Nelson, W.L., Beaton, J.D. 2005. Soil Fertility and Fertilizers. An Introduction to Nutrient Management. 7th ed.; Pearson Education Inc.-Prentice All. 528 p.

Hillel, D. 1998. Environmental Soil Physics. Academic Press. Boston, 771 p.

Janssen, I., Kruemmelbein, J., Horn, R., Ellies, A. 2004. Physical and hydraulic properties of the ñadi soils in south Chile - Comparison between untilled and tilled soil. Revista de la Ciencia del Suelo y Nutrición Vegetal 4, 14-28.

Janssen, M., Lennartz, B. 2008. Characterization of preferential flow pathways through paddy bunds with dye tracer tests. Soil Science Society of America Journal 72, 1756-1766.

Jarvis, N. 2007. A review of non-equilibrium water flow and solute transport in soil macropores: principles, controlling factors and consequences for water quality. European Journal of Soil Science 58, 523-546.

Jarvis, N., Larsbo, M., Roulier, S., Lindahl, A., Persson, L. 2007. The role of soil properties in regulating non-equilibrium macropore flow and solute transport in agricultural topsoils. European Journal of Soil Science 58, 282-292.

Jarvis, N., Moeys, J., Koestel, J., Hollis, J. 2012. Preferential Flow in a Pedological Perspective. pp: 75-120. In: Lin, H. (Ed.) Hydropedology. Synergistic Integration of Soil Science and Hydrology. Academic Press, USA. 858 p.

Jury, W.A., Gardner, W.R., Gardner, H.W. 1991. Soil Physics. John Wiley and Sons, New York, USA. 328 p.

Kheyrodin, H., Antoun, H. 2007. Long – term tillage and manure effect on soil physical and chemical properties and carbon and nitrogen mineralization potentials. Iran Agricultural Research 26, 1-14.

Kleber, M., Nikolaus, P., Kuzyakov, Y., Stahr, K. 2000. Formation of mineral N (NH_4^+, NO_3^-) during mineralization of organic matter from coal refuse material and municipal sludge. Journal of Plant Nutrition and Soil Science 163, 73-80.

Kranz, W., Kanwar, R. 1995. Spatial distribution of leachate losses due to preplant tillage method. pp: 107-110. *In*: Clean water - clean environment, 21st century. Team agriculture-working to protect water resources. Conference Proceedings. Kansas City, Missouri. ASAE 2, St Joseph, MI. 168 p.

Kung, K.-J. S. 1990. Preferential flow in a sandy vadose zone: 1. Field observation. Geoderma 46, 51-71.

Kutilek, M., Nielsen, R. 1994. Soil Hydrology. Catena Verlag, Cremlingen - Destedt, Germany, 370 p.

Lamandé, M., Hallaire, V., Curmi, P., Péres, G., Cluzeau, D. 2003. Changes of pore morphology, infiltration and earthworm community in a loamy soil under different agricultural managements. Catena 54, 637-649.

Leirós, M.C., Trasar-Cepeda, S., Seoane, S., Gil-Sotres, F. 1999. Dependence of mineralization of soil organic matter on temperature and moisture. Soil Biology and Biochemistry 31, 327-335.

Lipsius, K., Mooney, S. 2006. Using image analysis of tracer staining to examine the infiltration patterns in a water repellent contaminated sandy soil. Geoderma, 136, 865-875.

Luo, L.F., Lin, H., Schmidt, J. 2010. Quantitative relationships between soil macropore characteristics and preferential flow and transport. Soil Science Society of America Journal 74, 1929-1937.

Mallants, D., Mohanty, B., Vervoort, A., Feyen, J. 1996. Spatial analysis of saturated hydraulic conductivity in a soil with macropores. Soil Technology 10, 115-131.

Mooney, S., Morris, C. 2008. A morphological approach to understanding preferential flow using image analysis with dye tracers and X-ray computed tomography. Catena 73, 204-211.

Nájera, F., Salazar, O., Casanova, M. 2013. *In situ* soil nitrogen mineralization rate after pig slurry application in the Mediterranean zone of central Chile. Unpublished.

Nielsen, M., Styczen, M., Ernstsen, V., Petersen, C., Hansen, S. 2010. Field study of preferential flow pathways in and between drain trenches. Vadose Zone Journal 9, 1073-1079.

Nissen, J., Quiroz, C., Seguel, O., MacDonald, R., Ellies, A., 2006. Flujo hídrico no saturado en Andisoles. Revista de la Ciencia del Suelo y Nutrición Vegetal 6(1), 9-19.

Ogawa, S., Baveye, P., Parlange, J., Steenhuis, T. 2002. Preferential flow in the field soils. Forma 17(1), 31-53.

Osunbitan, J.A., Oyedele, D.J., Adekalu, K.O. 2005. Tillage effects on bulk density hydraulic conductivity and strength of a loam sand soil in southwestern Nigeria. Soil and Tillage Research 82, 57-64.

Radcliffe, D., Rasmussen, T. 2002. Soil Water Movement. pp: 85-126. *In*: Warrick, A.W. (Ed). Soil Physics Companion. CRC Press. Boca Raton, Florida, USA. 389 p.

Ritsema, C.J., Dekker, L.W., Hendrickx, J.M.H., Hamminga, W. 1993. Preferential flow mechanism in a water repellent sandy soil. Water Resources Research 29, 2183-2193.

Ruehlmann, J., Körschens, M. 2009. Calculating the effect of soil organic matter concentration on soil bulk density. Soil Science Society of America Journal 73, 876-885.

Sadzawka, A., Carrasco, M.A., Grez, R., Mora, M.L., Flores, H., Neaman, A. 2006. Métodos de Análisis de Suelos Recomendados para los Suelos de Chile. Instituto de Investigaciones Agropecuarias, Serie Actas INIA Nº 34, Santiago, Chile, 164 p.

Santibáñez, F., Uribe, J.M., 1990. Atlas Agroclimático de Chile: regiones Metropolitana y Quinta. Ministerio de Agricultura. Fondo de Innovación Agraria. Corporación de Fomento de la Producción. Santiago de Chile. 66 p.

Santibáñez, F., Uribe, J.M., 1993. Atlas Agroclimático de Chile: regiones Sexta, Séptima, Octava y Novena. Ministerio de Agricultura. Fondo de Innovación Agraria. Corporación de Fomento de la Producción. Santiago de Chile. 99 p.

Semmel, H., Horn, H., Hell, U., Dexter, A.R., Osmond, G., Schulze, E.D. 1990. The dynamics of soil aggregate formation and the effect on soil physical properties. Soil Technology 3, 113-129.

Sierra, J. 2002. Nitrogen mineralization and nitrification in a tropical soil: effects of fluctuating temperature conditions. Soil Biology and Biochemistry 34, 1219-1226.

Simunek, J. van Genuchten, M.T. 2008. Modeling nonequilibrium flow and transport processes using HYDRUS. Vadose Zone Journal 7, 782-797.

Simunek, J., van Genuchten, M.T., Sejna, M. 1998. The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media. Version 2.0. IGWMC-TPS-70. International Groundwater Modeling Center, Colorado School of Mines, Golden, CO. 186 p.

Thomas, G., Blevins, R., Phillips, R., McMahon, M. 1973. Effect of a killed sod mulch on nitrate movement and corn yield. Agronomy Journal 65, 736-739.

Tyler, D., Thomas, G. 1977. Lysimeter measurements of nitrate and chloride losses from soil under conventional and no-tillage corn. Journal of Environmental Quality 6, 63-66.

van Es, H., Sogbedji, J., Schindelbeck, R. 2006. Effect of manure application timing, crop, and soil type on nitrate leaching. Journal of Environmental Quality 35, 670-679.

van Genuchten, M.Th. 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. Soil Science Society of America Journal 44(5), 892-898.

Wang, Z., Feyen, J., Elrick, D.E. 1998. Prediction of fingering in porous media. Water Resources Research 34, 2183-2190.

Warrick, A.W. 2002. Soil Physics Companion. CRC Press, Boca Raton. 389 p.

Watts, C.W., Dexter, A.R. 1998. Soil friability: theory, measurement and the effects of management and organic carbon content. European Journal of Soil Science 49, 73-84.

Weiler, M. 2001. Mechanisms controlling macropore flow during infiltration. Dye tracer experiments and simulations. Dissertation for the degree of Doctor of Technical Science. Swiss Federal Institute of Technology Zürich. Zürich, Switzerland. 172 p.

Weiler, M., Flühler, H. 2004. Inferring flow types from dye patterns in macroporous soils. Geoderma 120, 137-153.

CHAPTER 4. PHYSICAL RISK INDEX FOR GROUNDWATER POLLUTION BY SOIL NITRATE LEACHING IN CENTRAL CHILE

4.1 ABSTRACT

Nitrate leaching (NL) is a major concern due to its impact on human health and ecosystem equilibrium. Solute movement through soil is governed by various hydraulic and physical properties that determine water flow. In order to study such relationships, a risk index of groundwater pollution was developed using results from field experiments carried out on two soils under long-term pig slurry applications.

The study was carried out in two basins of central Chile, San Pedro and Pichidegua, on Quilamuta (Typic Xerochrepts) and Tinguiririca (Mollic Xerofluvents) soil series, respectively. Pichidegua soil had a maize crop in spring-summer and fallow in autumn-winter and San Pedro soil a maize crop in spring-summer and a ryegrass-barley-oat mixed crop rotation in autumn-winter. Each soil and control sites in each case (uncultivated and without pig slurry applications) were characterised in physical and hydraulic terms (4 replicates). Water content and nitrogen (N) concentration (as NO_3^- and NH_4^+) at 0, 25, 50 and 100 cm depth were determined. The water and N budgets were then drawn up using experimental and meteorological station data on water and periodic field measurements of N in soil, vegetal tissues, slurry and N mineralisation-immobilisation. Dye tracer tests were performed with brilliant blue (BB) dye and the staining patterns analysed. Some pedotransfer functions were calculated through least square fit models and artificial neural networks.

Some accurate pollution groundwater NL risk indices were obtained through pedotransfer functions, but with the disadvantage of using unusual soil properties as input information. Factors directly related to NL were textural porosity, macroaggregate stability (MDV), slow draining porosity, air conductivity at 33 kPa water tension and NO_3^- concentration, whereas wilting point porosity and stained path width >200 mm (BB tests) were inversely associated. Dye tracer tests allowed flow type to be characterised and provided a better understanding of the characteristics and pattern of water and solute movement through soil to groundwater.

Key words: Nitrate leaching index, soil hydraulic properties, soil physics, dye pattern, pedotransfer functions.

4.2 INTRODUCTION

Application of slurry (liquid manure) to soil can give satisfactory crop yields, substituting partially or completely for mineral fertilisers (Zebarth *et al.*, 1996; Jensen *et al.*, 2000;

Miller *et al*., 2002; Thomas, 2007) and improving several soil properties, although the effects depend on the rate of application (Hemmat *et al*., 2010; Melleck *et al*., 2010). Furthermore, there is a need to dispose of wastes from the pig production industry safely, to protect human health, and usefully, to provide a benefit for farm finances (Mantovi *et al*., 2005).

However, one of the major concerns about slurry application in agriculture is the potential risk of groundwater pollution through nitrate leaching (NL). Slurry has a high proportion of total N in soluble or readily mineralisable form. Studies have demonstrated that manures with a high proportion of available N (i.e. cattle/pig slurry and broiler litter) applied to a sandy soil in autumn consistently increase NL when the overwinter drainage volume is typical of the long-term average for the site studies (Daudén *et al*., 2004; Thomsen, 2005; Mantovi *et al*., 2006). Thus, such manures must be considered very risky and when used, a strategy must be formulated to limit NL from agricultural land.

Leaching of nitrate occurs especially when N application rates exceed crop uptake rates (Harter *et al*., 2002). Although N undergoes various transformation processes in soil (oxidation, reduction, mineralisation, denitrification, volatilisation and others), for most soils it is mainly leached as nitrate (NO_3^-). However, if ammonium (NH_4^+) is not immobilised or retained by soil colloids, it can be oxidised to NO_3^-. The presence of NO_3^- in groundwater is a potential pollution hazard and a threshold of 10 mg L^{-1} N-NO_3 for drinking water has been defined in Chile (INN, 1984) and in the USA (EPA, 1987; Bohn *et al*., 2001; Sparks, 2003). Infants are especially susceptible to poisoning by NO_3^- after its conversion to nitrite (NO_2^-), and links to diseases such as cancer, nervous system impairments and methaemoglobinaemia (*blue baby* syndrome) have also been reported (Benjamin, 2005; Gehl *et al*., 2005; Powlson *et al*., 2008; Bryan and Loscalzo, 2011; Bryan and van Grinsven, 2013). In addition, NL causes eutrophication of surface waters, which in coastal environments has seriously affected the biosphere (Oviatt and Gold, 2005; Vahtera *et al*., 2007).

Losses of N to groundwater not only have negative health and environmental consequences, but also represent economic losses to farmers as the N applied is not used by crops (Buczko *et al*., 2010). Hence, the use and disposal of slurry and manure from the livestock industry are currently being scrutinised in various environmental and financial studies within welfare, human health and territorial planning, but little is known about the impact of manure management practices on water quality in the extensive alluvial aquifers underlying many basins (Harter *et al*., 2002). Climate change increases the concern about this worrying process (George *et al*., 2010).

One of the simplest ways to avoid groundwater pollution by NO_3^- is by proper management and optimisation of the amount of nutrients applied through slurry or fertilisers by careful evaluation of soil fertility based on previous crop rotations and their coverage (Harter *et al*., 2002). For example, the European Union has classified the vulnerability of territorial areas according to the NO_3^- concentration and trophic status of waters and has introduced action programmes in these areas limiting the doses of slurry to different levels depending on category (Mantovi *et al*., 2005). Other strategies to reduce NL following the application of organic material to free-draining soils take account of the characteristics of the material and the climate conditions at the site (Beckwith *et al*., 1998).

According to Dinnes *et al.* (2002), the NL problem is not solely caused by either poor N source management or any other single factor, but rather by a combination of soil management practices and inherent soil physical, chemical, and biological characteristics. Some of the main factors influencing the magnitude of NL are: i) N fertilisation rate, time, source and method; ii) intensity of cropping and crop N uptake; iii) soil profile characteristics that affect percolation; and iv) quantity, pattern and time of rainfall and/or supplemental irrigation (Havlin *et al.*, 2005). Mantovi *et al*. (2006) and Buczko *et al*. (2010) report that NL is associated with intrinsic soil properties, water budget (especially deep percolation) and management practices, with the groundwater pollution risk increasing with increasing movement of water, while slower drainage results in lower NL and higher NO_3^- concentrations in soils.

Considering soil properties affecting percolation and potential NO_3^- pollution risk to groundwater, there are three general soil conditions affecting water and NO_3^- movement: sandy soils, aggregated soils and heavy clay soils (Addiscott, 1996). Sandy soils have a large pore size distribution and their homogeneity promotes high water movement through much of the soil matrix, posing a threat to the quality of underlying aquifers. In aggregated soils, part of the water moves easily though interaggregate pores, but part moves slowly or is retained by intraaggregate porosity. The NO_3^- within aggregates is retained inside the soil matrix, but NO_3^- within interaggregate pores bypasses the soil matrix and is easily leached to groundwater after rainfall if vertical porosity dominates. This is not a general law, because aggregation form, degree and hierarchy must be taken into account as these cause differences in water and NO_3^- behaviour. In heavy clay soils, many of which undergo shrinking/swelling processes, water and NO_3^- movement occurs mainly through preferential pathways and, if this connects with the drainage system, then pollutants and water can easily reach the groundwater.

There are some factors associated with hydraulic soil heterogeneity which can promote solute movement bypassing much of the soil profile, where pollutants are normally bound and/or degraded, because just a partial fraction of the total soil cross-section is available for flow (Radcliffe and Rasmussen, 2002). This is known as preferential flow (PF), which can be assessed easily through dye tracers. The presence and abundance of PF has both environmental and human health implications, since PF favours pollutant transport (such as NO_3^-) to groundwater without interaction with the chemically and biologically reactive upper layer of soil (Allaire *et al.*, 2009; Jarvis *et al*., 2012). This means that a significant fraction of contaminants quickly reaches the subsoil, where natural attenuation processes are generally less effective. By the use of pedotransfer functions (PTF; Pachepsky and Rawls, 2004; Shein and Arkhangel'skaya, 2006), NL can be predicted through physical, hydraulic and morphometric soil properties revealed from dye staining patterns, which is thus a useful tool to establish risk zone indices and to restrict fertiliser and manure applications accordingly.

A number of approaches have been used to quantify the factors influencing the transfer of NO_3^- from terrestrial to aquatic systems, including budget calculations, process-based models and statistical analyses. Moreover, various studies have defined risk indices of N diffuse pollution as tools to establish restrictions, improve efficiency and reduce environmental degradation (Studart *et al*., 2005; De Paz *et al.*, 2009; Buczko *et al.*, 2010). Therefore, the objective of the present study was to develop a risk index of groundwater NO_3^- pollution based on physical, hydraulic and morphometric soil properties determined in field experiments on two soils of central Chile under long-term pig slurry applications.

4.3 MATERIALS AND METHODS

4.3.1 Study site description

The data used for developing the risk index of groundwater NO_3^- pollution were obtained in field experiments carried out in two basins of central longitudinal valley of Chile, (Pichidegua: UTM 0277313E, 6194387S and San Pedro: UTM 0289587E, 6240288S; Datum WGS 1984 19S). These experimental sites corresponded to two representative cartographical units or polypedons (phases of soil series) that pose a high potential risk of NO_3^- leaching to groundwater.

At each site, a representative soil under conventional agriculture and with pig slurry application was chosen. These soils were defined as Pichidegua Slurry (PS), with continuous pig slurry application during a 10-year period, fallow management in late autumn and early winter and a maize crop in late winter, and San Pedro Slurry (SS), with continuous pig slurry application during a 5-year period, a maize crop in spring-summer and a ryegrass-barley-oat mixed crop rotation in autumn-winter. At each experimental site, a similar control soil (without amendments and fertilisers) was selected, characterised and defined as Pichidegua Control (PC), which had fallow management and natural weeds and scrub, and San Pedro Control (SC), which had Mediterranean annual prairie (see Table 2.1 in Chapter 2).

The soil at both experimental sites is of alluvial origin, with a deep, stratified profile. Pichidegua soils cartographically belong to the Tinguiririca soil series, loamy sand Mollic Xerofluvent occupying a recent alluvial terrace position (CIREN, 1996a). San Pedro pedons are sandy loam Typic Xerochrepts (Quilamuta soil Series) occupying terraces or fan positions, with granitic parent material (CIREN, 1996b).

A semi-arid Mediterranean climate, with most rainfall occurring between May and October, hot summers and relatively cold (Pichidegua) and relatively mild (San Pedro) winters, characterises both basins. In the Pichidegua basin, the maximum (January) and minimum (July) annual air temperature (AAT) is 29.0ºC and 4.9ºC, respectively, with mean annual precipitation (MAP) of 696 mm. In the San Pedro basin, the maximum and minimum ATT is 31.3ºC and 4.4ºC respectively, with MAP of 383 mm (Santibañez and Uribe, 1990; 1993).

4.3.2 Local water budget

At each site a simplified water budget (Figure 4.1) was defined using climate data from a nearby meteorological station (Pichidegua station, code 8001, 34°21'34"S, 71°17'59"W; San Pedro station, code 330110, 33°56'29"S,- 71°23'39"W) and according to Equation 1.

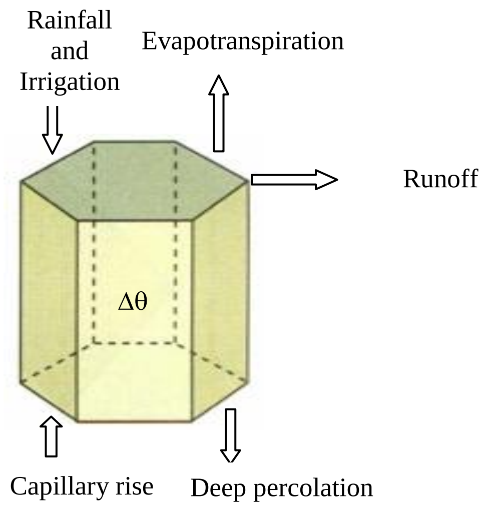


Figure 4.1. Simplified water balance for the study sites (adapted from Allen *et al*., 1998).

$$\pm DPorC = I + R - (\Delta\theta + ETc) \qquad \text{(Eq. 1)}$$

where *DPorC* (m^3 ha^{-1} or mm) is deep percolation or capillary rise (positive values represent deep percolation and negative values capillary rise), *I* and *R* are irrigation and rainfall, respectively (m^3 ha^{-1} or mm), $\Delta\theta$ is the change in volumetric soil water content (θ_{t+1}-θ_t, cm^3 cm^{-3}) and *ETc* corresponds to crop evapotranspiration (m^3 ha^{-1} or mm).

Runoff was considered negligible due to the coarse-textured upper soil and low slope (<1%). Soil water content (θ) was determined with a ®Diviner 2000 (Series II) device every two weeks.

4.3.3 Estimated nitrate leaching (NL)

Based on previous morphological descriptions, N levels were chosen to represent 0-10; 10-35; 35-60 and 60-110 cm and therefore soil sampling depth intervals for N measurement of 0-10; 25-35; 50-60 and 100-110 cm were decided. Subsequently a weighted mean was calculated to establish initial and final N (NO_3+NH_4) levels in the 0-110 cm depth interval.

Using soil coring, samples of soil were collected every two weeks from the predetermined layers for NO_3^- and NH_4^+ analyses. In San Pedro soil, vegetal tissues were collected for total N estimations and dry matter production to obtain the N exported (Sadzawka *et al*., 2007). The Pichidegua soils were under fallow during the early study period (May-September). The mean N concentration measured in the pig slurry applied was 1.3 g L^{-1} and the volume applied on each occasion was approximately 500 m^3 ha^{-1}, supplying a N dose of 640 kg ha^{-1} on 11 July and 1 August. In San Pedro soils, no slurry additions were carried out during the study period.

Every month, five covered PVC cylinders with ventilation holes (3 replicates per plot) were collected to assess *in situ* soil N mineralisation-immobilisation rates and cumulative net N mineralisation, determined as the difference between final and initial inorganic N content (Kolberg *et al*., 1997). A positive value indicated that the process of mineralisation had dominated, while a negative value denoted that immobilisation had exceeded mineralisation (Nájera *et al*., 2013).

In each experimental unit, the following N budget was used to estimate NL:

$$\mathrm{NL} = \Delta N_{NO_3+NH_4} \pm MIT - Cex - GL \qquad \text{(Eq. 2)}$$

where NL corresponds to nitrate leached from the corresponding measuring depth, $\Delta N_{NO_3+NH_4}$ represents the difference in plant-available N between two consecutive dates (Ramos and Kücke, 1999), *MIT* corresponds to the gross mineralisation-immobilisation turnover from organic N through the study season, *Cex* represents the N output due to crops (uptake and harvesting) and *GL* to gaseous losses (volatilisation and denitrification).

Nitrate leaching was then calculated as the sum of NO_3^- and NH_4^+ concentrations between consecutive dates when: a) the water budget confirmed that there was deep percolation and, b) the N difference at 100-110 cm depth was negative (N_{final} - $N_{initial}$), assuming that at such depth N was leached beyond root depth. In a modified version of the method used by Scheffer and Ortseifen (1997), *MIT* and *Cex* were subtracted from the N budget between 0-10 and 25-35 cm (Nájera *et al*., 2013) to obtain NL values, but not for deeper samples due to the decrease in mineralisation (Kleber *et al*., 2000) and plant uptake with depth.

In addition, NL obtained through the N balance was compared with the following model (Matus and Rodríguez, 1994) of NO_3^- movement in soils:

$$L=A[DP/(DP+(Wa\ Bd))]^{z} \qquad \text{(Eq. 3)}$$

where L is the amount of NL (kg N ha^{-1}) to below rooting depth z (cm), A is the annual mean amount of $N\text{-}NO_3^-$ (kg ha^{-1}) present to depth z, Wa is soil moisture content (g g^{-1}), Bd is soil bulk density (Mg m^{-3}) and DP is the percolation below depth z (cm).

4.3.4 Sampling for hydraulic and physical soil tests

Disturbed and undisturbed soil samples (4 replicates) were taken at the same depths as samples for N analysis (0-10, 25-35, 50-60 and 100-110 cm) in each pedon, for soil physical and hydraulic analyses.

Sieving in dry and wet conditions was used to calculate soil macroaggregate stability, determining the mean diameter variations (MDV) according to Hartge and Horn (1992). By means of a suspension in distilled water with and without chemical dispersion, the microaggregate stability was assessed through the dispersion ratio (DR) according to Berryman *et al*. (1982).

Soil organic matter (SOM) content was determined through calcination (360°C; Sadzawka *et al*., 2006), air permeability (*Ka*) with an air permeameter (Peth, 2004) and hydraulic conductivity (*Ks*) by constant load permeameter tests (Dane and Topp, 2002). Soil water retention curves (pF) were obtained using pressure plates, particle size distribution using a Bouyoucos hydrometer, bulk density (*Bd*) through the clod (*clBd*) and core (*coBd*) methods and particle density (*Pd*) by picnometer (Dane and Topp, 2002).

The values of *Ka* and *Ks* were logarithmically transformed for subsequent statistical analysis.

4.3.5 Preferential flow (PF) patterns

The PF pathways were examined in open pits at each experimental unit after dye tracer application. Brilliant blue (BB) dye was chosen due to its easy mobility, high contrast with the soil background colour and its low toxicity (Flury and Flühler, 1995).

After irrigation, a load of BB solution was applied within sub-plots (metal frame square) of 1.5 m^2 at a concentration of 2.2 g L^{-1}, according to Nielsen *et al*. (2010). To reach soil saturation at 100 cm depth, the volume of applied solution was calculated. Subsequently, with the soil profile exposed, stained areas were morphometrically assessed under natural daylight conditions and without direct radiation. White reflection panels were positioned on three sides of the pit to balance and compensate for differences in illumination by diffuse light and the soil profile was photographed. Some rulers were attached to the profile in order to correct the image geometrically and assess the physical distribution of stained macropores (Weiler and Flühler, 2004; Alaoui and Goetz, 2008).

Digital image analysis was performed using software Gimp 2 (GNU image manipulation programme). Geometrical correction and maximisation of blue, green and cyan colour were carried out with subsequent subtraction of background colour and the conversion of images into greyscale tones. Finally, a median filter of 2 cm was applied.

The vertical dye pattern was then analysed (Matlab software) according to Weiler and Flühler (2004) with stained path widths (SPW) <20 mm, 20-200 mm and >200 mm, obtaining SPW profiles and geometry patterns. See Chapter 3 for more details.

4.3.6 Experiment design and statistical analyses for obtaining the risk index of NL

At the experimental site (see Figure 2.1 in Chapter 2) two pits between plots were excavated to examine the soil profile. The experimental design was completely randomised, with experimental units corresponding to each soil sampling unit and with treatments corresponding to treatment (slurry addition/control) on each soil series (see Table 2.1 in Chapter 2).

A *t*-Student test was carried out for soils with contrasting slurry applications in the same soil series and multiple component testing to assess the correlation between soil properties and N budgets.

Through correlation matrix, the variables correlated with NL were identified. For this purpose, a backward stepwise analysis (p<0.05) complemented the correlation matrix to select the variables related to NL. Subsequently, through a standard least square test, some linear regression fit models were obtained, which worked as pedotransfer functions (PTF). The reason for obtaining PTF is to model and accurately predict the risk of groundwater pollution by NL. Thus it allows laborious experimental determination of NL to be replaced by mathematical equations derived from other simpler and cheaper soil property measurements, which serve as input to the model.

Besides the regression fit models obtained, some artificial neural networks (ANN) were estimated to improve the PTF. This method involves no predetermined relationships and is capable of simulating any relationship between dependent and independent variables, whether linear or not. One of the disadvantages of ANN is that its algorithms can be hardly analized (Shein and Arkhangel'skaya, 2006).

In both PTF methods used, some accuracy indices were calculated. The most obvious is the determination coefficient (R^2), which was complemented with the root mean square error (RMSE) and the sum of squared error of prediction (SSE). In the case of ANN, cross-validation was used through at least two values to validate the model.

4.4 RESULTS AND DISCUSSION

4.4.1 Water budget

Water budget results obtained through the entire period are shown in the Appendix. Negative values of deep percolation (*DP*) imply water gains by capillary rise (*C*). The *ETc* values throughout the entire period were very low due to autumn-winter climate characteristics, fallow management and the sparse vegetation during the season, except in SS.

The soil water balance is very sensitive to evapotranspiration measurements (Ramos and Kücke, 1999). Therefore, values of *ETc* in San Pedro soil, and especially in SS soil, were considerably higher than at the other site due to the presence and characteristics of the ryegrass-barley-oat crop rotation. On the other hand, *DP* was higher in PS soil, associated with fallow practices and irrigation.

4.4.2 Nitrate concentrations and leaching

Any discussion about NO_3^- leaching (NL) above the root zone could be perceived as meaningless, but it can help understand NO_3^- movement through the soil profile, which is presumably intrinsically associated with water movement. However, absolute NL must be located below root depth, where plants cannot retain it or absorb it from the soil solution. Estimated NL values are presented in Table 4.1 considering the nitrogen budget (Eq. 2). Estimated values from the Matus and Rodriguez (1994) model (Eq. 3) are also included, assuming that gaseous losses (*GL)* occur where there is no net *DP*. Data on the concentrations of N in vegetal tissues were taken from Nájera (2013).

Table 4.1. Nitrate leaching (NL) in two soils of central Chile and parameters used for this assessment.

Soil[1]	*DP*	$[NO_3^-]$[2]	NL_{model}[3]	NL_{budget}	*GL*
	mm	ppm	------------------------kg ha^{-1}	-----------------------	
PS 0	139.07	56.2 ± 9.4	58.8 ± 12.1	77.4 ± 33.6	27.4 ± 32.6
PS 25	139.07	68.7 ± 23.5	97.8 ± 29.0	99.1 ± 57.2	49.8 ± 48.2
PS 50	139.07	53.7 ± 13.8 b[4]	106.7 ± 12.8 b	86.9 ± 12.2 b	62.2 ± 30.8 b
PS 100	139.07	51.3 ± 6.8 b	48.1 ± 7.7 b	89.4 ± 4.5 b	40.6 ± 42.2
PC 0	123.81	62.3 ± 21.6	52.8 ± 18.3	82.1 ± 15.6	8.7 ± 7.5
PC 25	123.81	46.7 ± 4.4	71.9 ± 12.9	99.6 ± 9.9	30.2 ± 21.9
PC 50	123.81	18.2 ± 2.8 a	68.3 ± 13.1 a	39.3 ± 13.6 a	8.4 ± 7.9 a
PC 100	123.81	11.5 ± 1.7 a	25.2 ± 3.4 a	17.6 ± 8.3 a	2.2 ± 1.6
SS 0	43.40	21.3 ± 4.2 b	16.4 ± 3.5	18.3 ± 9.5	0.0 ± 0.0
SS 25	43.40	15.5 ± 2.2 b	9.4 ± 1.8 a	20.8 ± 11.9	0.0 ± 0.0
SS 50	43.40	7.9 ± 1.0	5.6 ± 2.1 a	24.8 ± 10.1 b	13.3 ± 7.8 a
SS 100	43.40	9.7 ± 0.2 b	1.5 ± 0.6 a	16.6 ± 6.3	13.5 ± 11.8
SC 0	78.11	11.8 ± 2.6 a	13.8 ± 1.8	8.5 ± 3.4	0.5 ± 0.6
SC 25	78.11	9.9 ± 0.8 a	19.1 ± 2.1 b	14.5 ± 4.9	10.9 ± 10.0
SC 50	78.11	7.0 ± 0.4	16.4 ± 0.7 b	5.8 ± 4.7 a	26.2 ± 2.4 b
SC 100	78.11	7.7 ± 0.8 a	7.8 ± 1.5 b	17.0 ± 7.8	12.0 ± 5.0

[1]PS: Pichidegua soil with slurry applications; PC: Pichidegua soil (control); SS: San Pedro soil with slurry applications; SC: San Pedro soil (control)
[2] Mean annual nitrate concentrations taken in soil auger samples (samples of 0.1 m).
[3](Matus and Rodríguez, 1994)
[4]Different lowercase letters between soils (same soil series) denote statistically significant differences ($p<0.05$).

In Pichidegua soils, NL below 50 cm depth was considerably higher in PS than control soil (PC), associated with slurry applications and irrigation (higher *DP*). In San Pedro soils, although higher [NO_3^-] in SS was observed, simulated NL results were the opposite to the expected, with higher values in SC (high *DP*) than in SS. However, values obtained from the NO_3^- budget showed significant differences at 50 cm depth, with higher NL from 50 cm depth in SS. The low NL differences within San Pedro (SS and SC) and even their simulated higher values in SC are associated with high *ETc* (ryegrass-barley-oat mix) in SS, which served to pump moisture to the atmosphere and confine solutes, preventing their movement into the deep subsoil. The absence of irrigation and slurry applications in SS during the measurement period also contributed to the results obtained.

The NL values were within the range reported in some other studies in Chile (Alfaro *et al*., 2006). Those authors found NL values of 66-261 kg ha^{-1} for control and 150 kg ha^{-1} fertilised soil in lysimeters filled with an Andisol and 1,260 mm of rainfall. However, the NL values determined here were considerably higher than those obtained by Salazar *et al.* (2010), who reported values <4.2 kg N ha^{-1} for addition of 400 kg N ha^{-1} (slurry and artificial fertilisers), also in Andisols, mainly explained by gaseous losses and retention characteristics of soils. On the other hand, Claret *et al.* (2011) reported NL values <7.9 kg N ha^{-1} in an Alfisol under 1,400 mm of rainfall, but without statistical differences between fertilised and control soils. Iriarte (2007) reported risks of NL of 27% in soils (Mollisols, Inceptisols and Alfisols) within a sub-basin of central Chile (Region VI, Libertador Bernardo O' Higgins) and 63% of drinking water samples analysed showed higher concentrations than the threshold of 10 mg N-NO_3 L^{-1} prescribed by the INN (1984). In contrast, Arumi *et al.* (2005) observed that aquifers in the central valley of Chile do not contain significant nitrate concentrations associated with agricultural activity, inferring the existence of favourable conditions for the occurrence of natural attenuating processes such as denitrification. These contradictory NL results across Chilean soils are mainly explained by different management practices, soil properties and water budgets.

Estimated gaseous losses (*GL*) of N showed considerably higher deviation than NL and were greater in PS than in PC, increasing until 50 cm and 25 cm depth, respectively, and decreasing subsequently. Restricted soil drainage and anoxic conditions in Pichidegua soils resulted in high values of denitrification. In San Pedro soils, *GL* were higher below 50 cm depth, but minimal above this depth due to oxidative conditions and soil structure development, as explained by Laudone *et al*. (2011) in a model to predict denitrification and N_2O emissions depending on soil structure.

Assessing both estimation methods (Figure 4.2) by a comparison of the regression line of observed versus predicted values through a conditional sum of squares, there were no statistical differences (p<0.05) between the intersect and the slope of the fit line and the 1:1 line of observed:predicted. Thus NL_{model} and NL_{budget} assess the same phenomenon, with low differences in the observed results.

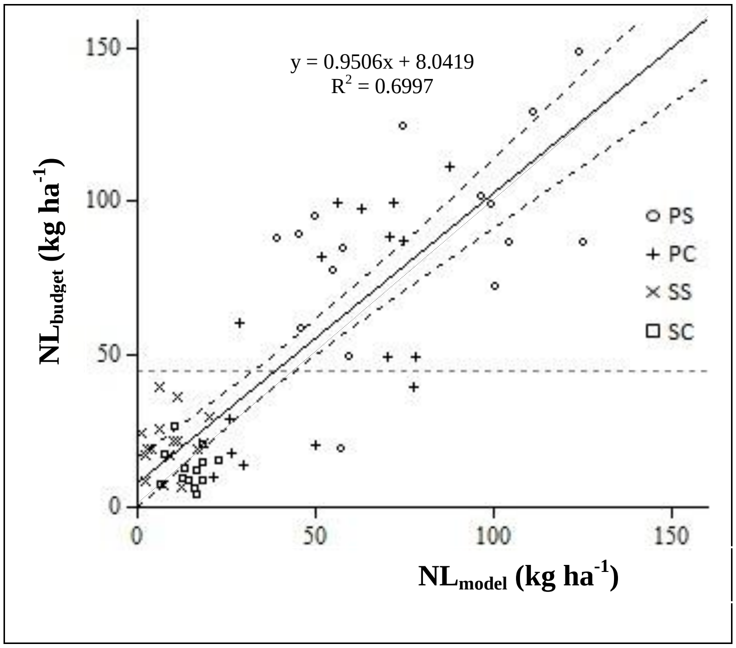


Figure 4.2. Regression analysis between nitrate leaching estimated by nitrogen budget and a model defined by Matus and Rodriguez (1994). The dashed line parallel to the x-axis represents the mean NL_{budget}.

It should be noted that at lower values of NL, the model underestimated the nitrate leached obtained by the N budget. This was not necessarily a problem of the model, but may have been caused by a methodological error during soil sampling. More studies are needed to assess the reliability of the model used.

4.4.3 Soil physical properties

Most sites showed increasing sand content until 50 cm depth, and then decreasing sand content until 100 cm depth (Table 2.2 in Chapter 2). An exception was found in SC soil, where sand content showed a regular decrease with depth. The position in terraces and fans of alluvial origin promotes a natural soil stratification in both basins, which can be seen through the variations in horizon morphological properties (Fuentes *et al*., 2013).

Soil organic matter (SOM) displayed similar behaviour to sand content, related to organic debris deposited on the surface and its oxidation. There was an increase in SOM at 100 cm depth, related to texture; in fact, clay content showed a direct significant relationship with SOM (p<0.01). Compensation for oxidation processes under conventionally tilled soils by slurry applications explains the absence of significant differences in SOM between sites with and without amendments (see Chapter 2).

Although repeated slurry applications favour high SOM accumulation, bulk density (*Bd*) was higher under conventional tillage (CT) than in the control sites due to the external loads induced by machinery traffic. The exception occurred in SC soil (control), where the experimental plots were established in untilled soils adjacent to a track, which led to higher *Bd* until 25 cm depth (Horn, 1988; Horn, 2003).

Pore size distribution, characterised through pF curves, is presented and complemented with textural and structural porosity values (*TP* and *SP*, respectively) in Table 2.3 in Chapter 2. Most *SP* decreased with depth, where at present exogenous pedogenic factors are almost non-active, but might have promoted soil genesis in buried horizons. Such could be the case of San Pedro soils, for the horizon at 100 cm depth. *TP* was always considerably higher than *SP*.

In general the total porosity (*Ptotal*) was higher in Pichidegua than in San Pedro soils, and only significantly higher in PC compared with PS. However, soils in both basins had a drainage porosity that favoured plant development due to good air-water relations (Pagliai and Vignozzi, 2002).

There were small but significant differences in drainage and available water porosity values between managements (see Table 2.3 in Chapter 2) when compared against permanent wilting point porosity. However, in every case pore size distribution was mainly correlated with soil particle size, SOM content and bulk density (see Table 2.4 in Chapter 2), the last associated with soil structure development.

4.4.4 Hydraulic conductivity and air permeability in soil

Hydraulic conductivity and air permeability both showed high statistical dispersion, with standard deviation even exceeding the mean values (see Table 2.5 in Chapter 2) despite the spatial proximity, a variability which must be interpreted as inherent to soil heterogeneity. Saturated hydraulic conductivity (*Ks*) in general tended to decrease with time at almost all depths, but after 24 h tended to stabilise. Similarly, Ellies *et al*. (1997), found a decrease in aggregate stability by water flow through the soil, which collapses the pore system and decreases *Ks*.

The large variation in *Ks* at different depths reflected the anisotrophic nature of soil pedons, governed by sedimentation and horizon genesis (Kutilek and Nielsen, 1994; Hillel, 1998; Domenico and Shwartz, 1998). Nevertheless, soil management can be important in explaining *Ks* variations in terms of short-term temporal and spatial variability, as reported by Alarcón *et al*. (2010) and Dörner *et al*. (2010a). In the present study, several relationships between soil physical properties and *Ks*, were found using the mean values to reduce spatial variability, but most were associated with soil particle diameter (sand and silt content) and soil porosity (clod bulk density and total porosity) as shown in Figure 2.5 in Chapter 2.

Saturated hydraulic conductivity depends mainly on textural and structural properties determined by the soil skeleton and the fabric or arrangement of the skeleton. This also promotes the development of a complex interconnected network of voids or pores between soil particles (Berry and Reid, 1993), which confers to the soil its system functionality

(Dörner *et al*., 2010b). Textural properties in the soils studied here (Figure 2.5 in Chapter 2) related to sand and silt contents and *TP*, while *clBd*, fast draining pores, available water pores and total porosity could be considered as depending simultaneously on structural and textural properties.

Air conductivity (*Ka*) did not show a clear relationship with soil depth, air-filled porosity or soil matric tension, but some significant correlations ($p<0.05$) between *Ka*33 and *Ks* were observed (data not shown. For details see Chapter 2).

4.4.5 Soil structural and dynamic properties

As previously explained, high mean diameter variation (MDV) values denote low soil macroaggregate stability, while microaggregate stability is inversely related to dispersion ratio (DR) values.

Macroaggregate stability, assessed from MDV, tended to decrease with depth in both soils, with some exceptions such as PC and SS at 50 cm depth (Table 2.6 in Chapter 2), which showed low cohesion and similar mechanical behaviour in wet and dry sieving. The tendency for MDV to increase with depth is explained by the absence of exogenous conditions such as the wetting and drying cycles and organic matter accumulation and decomposition which occur at the surface, promoting structure development from surface to C horizons without pedogenetic processes acting upon them (Van Breemen and Buurman, 2003; Schaetzl and Anderson, 2005).

In macroaggregate stability, more labile organic matter compounds play a major role through roots, fungal hyphae and polysaccharides excreted by microorganisms that promote bonding between soil particles, improving structural stability (Chaney and Swift, 1986; Waters and Oades, 1991; Kay and Angers, 2002). In the present case, this resulted in lower MDV (higher macroaggregate stability) to PS above 25 cm depth compared with PC.

Dispersion ratio (DR), as microaggregate stability index, showed different behaviour to MDV, being considerably higher in San Pedro pedons. This was associated with lower soil development or was due to soil particle type, particularly sand particles, which in the absence of cementing agents and SOM conferred low adhesion and cohesion, and consequently low aggregate stability.

Recalcitrant organic matter compounds fill micropores and mesopores, resulting in higher structural stability of microaggregates compared with macroaggregates and lower values of DR in PC (Kay and Angers, 2002). Several authors (Mbagwu and Ekwealor, 1990; Mbah and Onweremadu, 2009) have reported that microaggregate stability does not increase with addition of organic amendments, in contrast to macroaggregate stability. Furthermore, organic matter compounds under natural conditions are translocated through pedoturbation, whilst under tillage such translocation occurs inside the first 30 cm of soil.

In San Pedro soils there were no significant differences between different soil management regimes, but there was a tendency for higher macroaggregate stability (lower MDV) and lower microaggregate stability (higher DR) in SC, except at 50 and 100 cm depth. In this case, and in both basins, the size of soil particles and their nature (mineral and organic) affected their structural development (see Figure 2.8 in Chapter 2).

4.4.6 Preferential flow and stained path width patterns

The distribution of stained areas and stained path width classifications are shown in Table 3.3 in Chapter 3 for different sampling depths. The percentage values of stained path width (SPW) are with respect to stained pixels and the pixel range corresponds to 10 cm according to the size of samples and depends on picture scale.

The pattern distribution showed a regular decrease in stained coverage with depth, especially in PC and SC. There was a marked decrease in SPW_{200}, but this was compensated for by a sharp increase in SPW_{20} at depth, except in SS. In general, $SPW_{20\text{-}200}$ values increased between 25 and 50 cm soil depth.

The SPW vertical patterns are presented in the Figure 3.5 in Chapter 3. In Pichidegua the two SPW profiles showed considerable similarities, with SPW_{200} being more homogeneous and deeper in the arable top layer of PS, whilst $SPW_{20\text{-}200}$ and SPW_{20} showed a common distribution pattern in the two soil profiles, but with a higher proportion of $SPW_{20\text{-}200}$ in PS. The SPW distributions in San Pedro showed clear differences between soil conditions. Areas with SPW_{200} were widespread through the entire SS vertical profile, although higher in the arable soil top layer, whilst in SC they were confined to the top layer.

Flow classification was carried out according to the SPW distribution, based on Weiler and Flühler (2004) (see Figure 3.6 in Chapter 3). In all profiles homogeneous matrix flow occurred in the upper horizons, but was deeper in San Pedro than in Pichidegua soils. This was followed by heterogeneous matrix flow and solution-matrix macropore flow with different degrees of interaction. The exception was SS, in which the homogeneous matrix flow was extended through the entire soil profile, but intercalated by zones of matrix heterogeneous flow. The factors inducing such matrix flow through the first 50 cm of soil are associated with tillage in the topsoil, greater soil aggregation and coarse textural classes (Addiscott, 1996; Ogawa *et al*., 2002; Jarvis *et al*., 2012). Hence, soil aggregation plays a major role in controlling flow type through soils and attention must be paid to studying their impact in the leaching of solutes and pollutants.

4.4.7 Pedotransfer functions (PTF) for nitrate leaching

Through a backward stepwise procedure and a least square fit model, some pedotransfer functions relating NL to some basic physical soil properties were obtained:

$$NL_{budget} = -67.2 + 77.0\,SDP + 131.0\,TP + 1.6\mathrm{MDV} + 1.5\,[\mathrm{NO_3^-}] + 0.2LogKa33$$

p<0.0001; R^2=0.89; RMSE=13.289 (Eq. 4)

$$NL_{model} = -1.7 - 473.7\,WPP + 148.8\,TP + 1.2\,[\mathrm{NO_3^-}]$$

p<0.0001; R^2=0.84; RMSE=13.953 (Eq. 5)

where NL is expressed in kg ha^{-1}, *SDP* corresponds to slow draining porosity ($cm^3\ cm^{-3}$), *WPP* is wilting point porosity ($cm^3\ cm^{-3}$), *TP* is textural porosity (%), MDV is mean diameter variation (%) as a macroaggregate stability parameter, [NO_3^-] is nitrate concentration (ppm) and *Ka33* corresponds to air conductivity at 33 kPa of water tension (m d^{-1}). All data obtained from different depths in all soils assessed were used.

According to the above equations, NL is directly and intimately associated with *TP*. Indeed, elevated *TP* values indicate poor soil aggregate development, which leads to a high NL from sandy soils. On the other hand, *SDP* and *WPP*, which were directly and inversely associated with NL, respectively, clearly denote the particular functionality of soil pores by size. The same applies for *Ka*33, because a higher diameter and connectivity of pores enhances the flow capacity, which consequently drives higher solute movement and elevates NL. The direct relationship between MDV and NL indicates that elevated macroaggregate stability (low MDV values) in the study soils reduces NL due to fine soil particles that infill the pore space left between sand particles. Finally, there was the expected direct relationship between NO_3^- concentration and NL (Kleber *et al*., 2000; Thomsen, 2005)

Applying a Gauss Newton artificial neural network (ANN) with 58-fold cross-validation (n = 64) to improve the relations obtained through the least square fit model gave some better adjustment of parameters due to non-linearity of the data (Figure 4.3). The hidden nodes applied to obtain the model were denoted H1, H2 and H3.

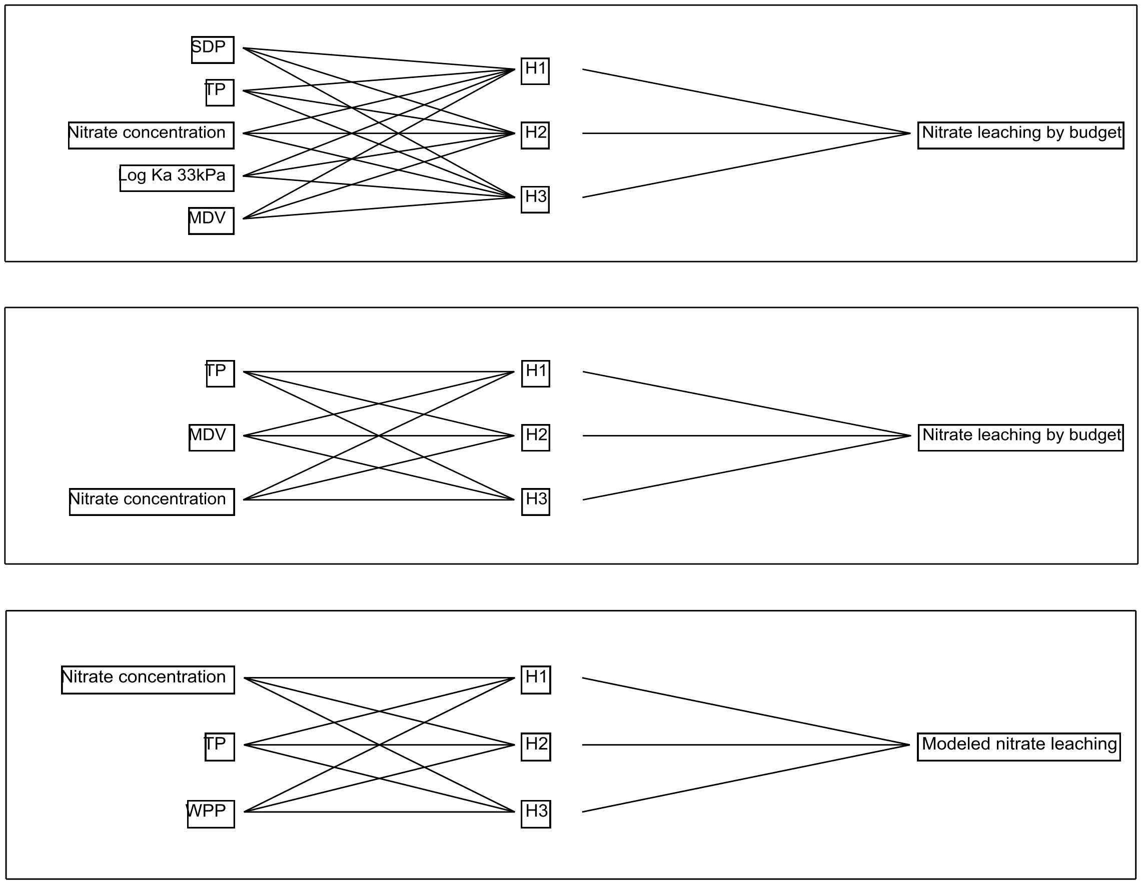


Figure 4.3. Artificial neural network diagrams to predict budget and modelled nitrate leaching (NL) with three hidden nodes. Above: NL_{budget} with SSE scaled: 2.49, RMSE scaled: 0.200 and R^2: 0.96. Middle: NL_{budget} with SSE scaled: 4.83, RMSE scaled: 0.284 and R^2: 0.92. Below: NL_{model} with SSE scaled: 4.44, RMSE scaled: 0.270 and R^2: 0.93.

By assessing mean values of NL at a same depth of measurement for each site, other PTF were obtained, correlating porosity distribution and stained path width to NO_3^- leaching:

$$NL_{budget} = \mathit{8.8} + \mathit{1.5}\ [NO_3^-] - \mathit{0.2}\ SPW_{200}$$
$$p<0.0001;\ R^2=0.93;\ RMSE=10 \qquad \text{(Eq. 6)}$$

$$NL_{model} = \mathit{157.0} - \mathit{1208.7\ WPP} + \mathit{0.7}\ [NO_3^-] - \mathit{0.4}\ SPW_{200}$$
$$p<0.0001;\ R^2=0.86;\ RMSE=14.136 \qquad \text{(Eq. 7)}$$

where SPW_{200} corresponds to stained path width >200 mm (%).

Again, using ANN with a 14-fold cross-validation (n = 16), the Gauss Newton method improved the model assessed previously due to its non-linearity (Figure 4.4).

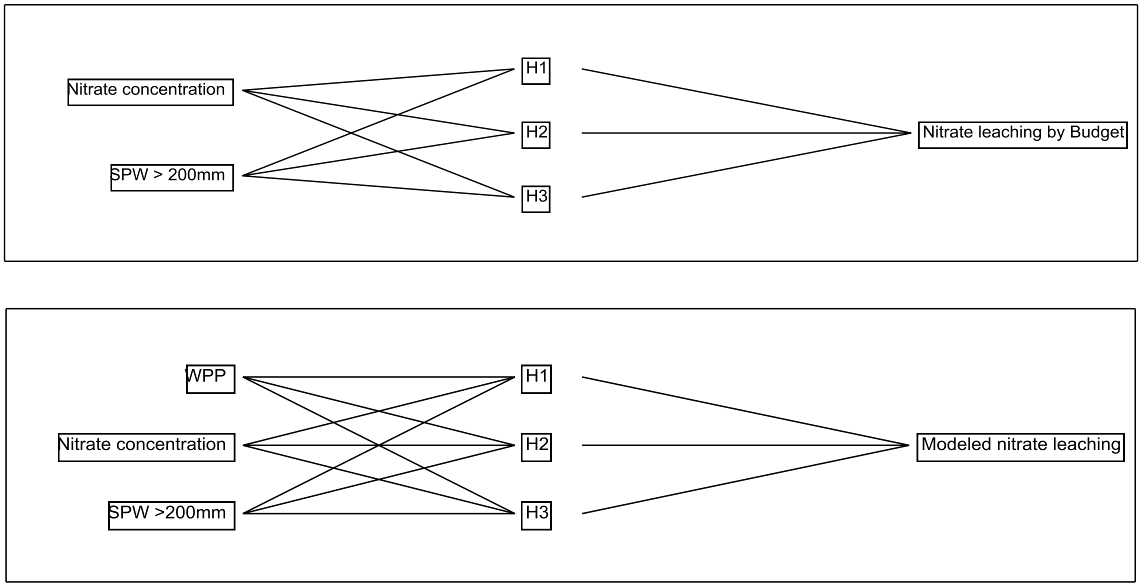


Figure 4.4. Artificial neural network diagrams to predict budget and modelled nitrate leaching (NL) with three hidden nodes. Above: NL_{budget} with SSE scaled: 0.22, RMSE scaled: 0.136 and R^2: 0.99. Below: NL_{model} with SSE scaled: 0.22, RMSE scaled: 0.140 and R^2: 0.99.

The SPW_{200} value is related to matrix flow type, which allows the soil solution to interact greatly with the soil matrix, inducing an inverse relationship with NL. The same inverse relationship applies for *WPP*, where higher distributions of pores with a narrow diameter retain water at higher tensions, inducing lower water movement through the soil profile and retaining solutes present in solution, such as nitrate.

The above models allowed the levels of NL to be predicted accurately, even through two or three variables, which thus served as soil physical indices to assess the susceptibility of soils to cause groundwater pollution by NL. Although the selected variables, especially SPW_{200}, hinder the model application in field conditions, the present study generated new information of the soil matrix interaction and the NL risk, having projections to be used at sub basin level with contrasting soils. Thus, further studies must be carried out at basin or even greater scale and should also comprise geomorphological and geological factors, to obtain a better understanding of the relationships between soil properties and pollute leaching associated with slurry applications and to obtain a general model for predicting NL, thus advancing hydropedological field studies.

4.5 CONCLUSIONS

In addition to N inputs as artificial fertilisers or manures, NO_3^- leaching (NL) is associated with several soil properties. Soil structure and particle size distribution are fundamental to understanding those complex water flow processes that lead to solute movement through pedons. Hence, many physical and hydraulic soil properties can be used to predict or model NL.

Dye tracer (Brilliant Blue) tests can reveal soil physical and hydraulic properties and provide a better understanding of water flow types and solute movement patterns through soils.

To obtain an index of NL based on soil physical properties, pedotransfer functions were obtained here using stepwise and least square fit models. These showed that textural porosity, macroaggregate stability, amount of slow draining pores, macropore continuity (evaluated as air permeability at 33 kPa water tension) and NO_3^- soil concentration were positively related to NL. Wilting point porosity and dye stained path width > 200 mm were negatively related to NL in the study soils.

Artificial neural network analysis proved to be a better method than stepwise and least square fit models, giving a higher degree of adjustment and smaller errors in the prediction due to the non-linearity of such adjustment.

The models assessed allowed the levels of NL to be predicted accurately, using only two or three variables as soil physical indices to assess soil susceptibility to cause groundwater pollution by NL. However, the selected variables are difficult to apply and are not usually determined in conventional soil survey and characterisation. Thus, more studies are needed at basin or even greater scale to identify easily determined variables and create a general model for accurately predicting NL in the field.

4.6 REFERENCES

Addiscott, T.M. 1996. Fertilizers and nitrate leaching. pp: 1-26. *In*: Hester, R.E., Harrison, R.M. (Eds.). Agricultural chemicals and the environment. Issues in Environmental Science and Technology N° 5. The Royal Society of Chemistry, Cambridge. 126 p.

Alaoui, A., Goetz, B., 2008. Dye tracers and infiltration experiments to investigate macropore flow. Geoderma 144, 279-286.

Alarcón, C., Dörner, J., Dec, D., Balocchi, O., López, O. 2010. Efecto de dos intensidades de pastoreo sobre las propiedades hidráulicas de un Andisol (Duric Hapludand). Agro Sur 38, 30-41.

Alfaro, M., Salazar, F., Endress, D., Dumont, J., Valdebenito, A. 2006. Nitrogen leaching losses on a volcanic ash soil as affected by the source of fertilizer. Revista de la Ciencia del Suelo y Nutrición Vegetal 6, 54-63.

Allaire, S., Roulier, S., Cessna, A. 2009. Quantifying flow in soils: A review of different techniques. Journal of Hydrology 378, 179-204.

Allen, R.G., Pereira, L.S., Raes, D., Smith, M., 1998. Crop Evapotranspiration - Guidelines for Computing Crop Water Requirements. Irrigation and Drainage Paper 56, FAO. Rome. 300 p.

Arumi, J., Oyarzún, R., Sandoval, M. 2005. Natural protection against groundwater pollution by nitrates in the Central Valley of Chile. Hydrological Sciences Journal 50(2), 331-340.

Beckwith, C.P., Cooper, J., Smith, K.A., Shepherd, M.A. 1998. Nitrate leaching loss following application of organic manures to sandy soils in arable cropping. I. Effects of application time, manure type, overwinter crop cover and nitrification inhibition. Soil Use and Management 14, 123-130.

Benjamin, N. 2005 Nitrate and Health. pp: 145-162. *In*: Addiscott, T.M. (Ed). Nitrate, Agriculture and the Environment. CABI Publishing. 279 p.

Berry, P., Reid, D. 1993. Mecánica de suelos. Caicedo, B., Arrieta, A. (Trad.). McGraw-Hill. Bogotá, Colombia. 415 p.

Berryman, C., Davies, D., Evans, C., Harrod, M., Hughes, A., Skinner, R., Swain, R., Soane, D. 1982. Techniques for Measuring Soil Physical Properties. Formerly Advisory Paper Nº18. Reference Book 441. Ministry of Agriculture, Fisheries and Food, Sweden, 116 p.

Bohn, H.L., McNeal, B.L., O'Connor, G.A. 2001. Soil Chemistry, 3rd ed.; John Wiley & Sons, New York. 320 p.

Bryan, N., Loscalzo, J. 2011. Nitrite and Nitrate in Human Health and Disease. Bendich, A. (Ed). Humana Press - Springer Science Business Media. New York, USA. 306 p.

Bryan, N., van Grinsven, H. 2013. The role of nitrate in human health. Advances in Agronomy 119, 153-182.

Buczko, U., Kuchenbuch, R., Lennartz, B. 2010. Assessment of the predictive quality of simple indicator approaches for nitrate leaching from agricultural fields. Journal of Environmental Management 91, 1305-1315.

Chaney, K., Swift, R.S. 1986. Studies on aggregate stability: II. The effect of humic substances on the stability of reformed soil aggregates. Journal of Soil Science 37, 337-343.

CIREN. 1996a. Estudio Agrológico VI Región. Descripción de suelos materiales y símbolos. Centro de Información de Recursos Naturales. Publicación Nº 114, 483 p.

CIREN. 1996b. Estudio Agrológico Región Metropolitana. Descripción de suelos materiales y símbolos. Centro de Información de Recursos Naturales. Publicación Nº 115, 430 p.

Claret, M., Urrutia, R., Ortega, R., Best, S., Valderrama, N. 2011. Quantifying nitrate leaching in irrigated wheat with different nitrogen fertilization strategies in an Alfisol. Chilean Journal of Agricultural Research 71, 148-156.

Dane, J.H., Topp, G.C., 2002. Methods of Soil Analysis. Part 4: Physical Methods. Soil Science Society of America, Inc., Madison, WI, USA, 1692 p.

Daudén, A., Quílez, D., Vera, M.V. 2004. Pig slurry applications and irrigation effects on nitrate leaching in Mediterranean soil lysimeters. Journal of Environmental Quality 33, 2290-2295.

De Paz, J., Delgado, J., Ramos, C., Shaffer, M., Barbarick, K. 2009. Use of a new GIS nitrogen index assessment tool for evaluation of nitrate leaching across a Mediterranean region. Journal of Hydrology 365, 183-194.

Dinnes, D.L., Karlen, D.L., Jaynes, D.B., Kaspar, T.C., Hatfield, J.L., Colvin, T.S., Cambardella, C.A. 2002. Nitrogen management strategies to reduce nitrate leaching in tile-drained Midwestern soils. Agronomy Journal 94, 153-171.

Domenico, P.A., Schwartz, F.W., 1998, Physical and Chemical Hydrogeology, 2nd ed.; John Wiley and Sons Inc., NY, 506 p.

Dörner, J., Dec, D., Peng, X., Horn, R. 2010a. Effect of land use change on the dynamic behaviour of structural properties of an Andisol in southern Chile under saturated and unsaturated hydraulic conditions. Geoderma 159, 189-197.

Dörner, J., Sandoval, P., Dec, D. 2010b. The role of soil structure on the pore functionality of an Ultisol. Journal of Soil Science and Plant Nutrition 10(4), 495-508.

Ellies, A., Grez, R., Ramírez, C. 1997. La conductividad hidráulica en fase saturada como herramienta para el diagnóstico de la estructura del suelo. Agro Sur 25, 51-56.

EPA. 1987. Agricultural Chemicals in Ground Water: Proposed Strategy. Environmental Protection Agency. Office of Pesticides and Toxic Substances, U.S.A., Washington, D.C., 150 p.

Flury, M., Flühler, H. 1995. Tracer characteristics of brilliant blue FCF. Soil Science Society of America Journal 59, 22-27.

Fuentes, I., Casanova, M., Salazar, O., Seguel, O. 2013. Morphological, physical and hydraulic soil properties related to nitrate dynamics under pig slurries addition. Unpublished.

Gehl, R.J., Schmidt, J.P., Stone, L.R., Schlegel, A.J. Clark, G.A. 2005. *In situ* measurements of nitrate leaching implicate poor nitrogen and irrigation management on sandy soils. Journal of Environmental Quality 34, 2243-2254.

George, G., Järvinen, M., Nõges, T., Blenckner, T., Moore, K. 2010. The Impact of the Changing Climate on the Supply and Recycling of Nitrate. pp: 161-178. *In*: George, D. (Ed.). The Impact of Climate Change on European Lakes. Aquatic Ecology Series 4. Springer Science Business Media. New York, USA. 507 p.

Hartge, K.H., Horn, R. 1992. Die physikalische Untersuchung von Boden. Ferdinand Enke Verlag, 3. Auflage, Stuttgart, Germany. 177 p.

Harter, T., Davis, H., Mathews, M., Meyer, R. 2002. Shallow groundwater quality on dairy farms with irrigated forage crops. Journal of Contaminant Hydrology 55, 287-315.

Havlin, J.L., Tisdale, S.L., Nelson, W.L., Beaton, J.D. 2005. Soil Fertility and Fertilizers. An Introduction to Nutrient Management. 7th ed.; Pearson Education Inc.-Prentice All. 528 p.

Hemmat, A., Aghilinategh, N., Rezainejad, Y., Sadeghi, M. 2010. Long-term impacts of municipal solid waste compost, sewage sludge and farmyard manure application on organic carbon, bulk density and consistency limits of a calcareous soil in central Iran. Soil and Tillage Research 108, 43-50.

Hillel, D., 1998. Environmental Soil Physics. Academic Press. Boston, USA. 771 p.

Horn, R. 1988. Compressibility of Arable Land. pp: 53-71. *In*: Drescher, J., Horn, R., de Boodt M. (Eds). Impact of Water and External Forces on Soil Structure. Catena Supplement 11. Catena Verlag, Reiskirchen, Germany. 171 p.

Horn, R. 2003. Stress – strain effects in structured unsaturated soils on coupled mechanical and hydraulic processes. Geoderma 116, 77-88.

INN. 1984. Norma Chilena Oficial para Agua Potable, NCh 409. Instituto Nacional de Normalización, Chile, 15 p.

Iriarte, A. 2007. Evaluación espacial de la lixiviación potencial de nitratos en suelos de la subcuenca del río Cachapoal bajo. Memoria para optar al Título Profesional de Geógrafo. Universidad de Chile, Santiago. 124 p.

Jarvis, N., Moeys, J., Koestel, J., Hollis, J. 2012. Preferential Flow in a Pedological Perspective. pp: 75-120. *In*: Lin, H. (Ed.) Hydropedology. Synergistic Integration of Soil Science and Hydrology. Academic Press, USA. 858 p.

Jensen, M.B., Olsen, T.B., Hansen, H.C.B., Magid, J. 2000. Dissolved and particulate phosphorus in leachate from structured soil amended with fresh cattle faeces. Nutrient Cycling in Agroecosystem 56, 253-261.

Kay, B.D., Angers, D.A. 2002. Soil Structure. pp: 249-283. *In*: Warrick, A.W (Ed). Soil Physics Companion. CRC Press. Boca Raton, Florida, USA. 389 p.

Kleber, M., Nikolaus, P., Kuzyakov, Y., Stahr, K. 2000. Formation of mineral N (NH_4^+, NO_3^-) during mineralization of organic matter from coal refuse material and municipal sludge. Journal of Plant Nutrition and Soil Science 163, 73-80.

Kolberg, R.L., Rouppet, B., Westfall, D.G., Peterson, G.A. 1997. Evaluation of an in situ net soil nitrogen mineralization in dryland agroecosystems. Soil Science Society of America Journal 61, 504-508.

Kutilek, M., Nielsen, R. 1994. Soil Hydrology. Catena Verlag, Cremlingen - Destedt, Germany, 370 p.

Laudone, G.M, Matthews, G.P., Bird, N.R.A., Whalley, W.R., Cardenas, L.M., Gregory, A.S. 2011. A model to predict the effects of soil structure on denitrification and N_2O emission. Journal of Hydrology 409, 283-290.

Mantovi, P., Baldoni, G., Toderi, G. 2005. Reuse of liquid, dewatered and composted sewage sludge on agricultural land: effects of long-term application on soil and crop. Water Research 39, 289-296.

Mantovi, P., Fumagalli, L., Beretta, G., Guermandi, M. 2006. Nitrate leaching through the unsaturated zone following pig slurry applications. Journal of Hydrology 316, 195-212.

Matus, F.J., Rodríguez, J. 1994. A simple model for estimating the contribution of nitrogen mineralization to the nitrogen supply of crops from a stabilized pool of soil organic matter and recent organic input. Plant and Soil 162, 259-271.

Mbagwu, J.S., Ekwealor, G.C. 1990. Agronomic potential of brewer’s spent grain. Biological Wastes 34, 335-347.

Mbah, C.N., Onweremadu, E. 2009. Effect of organic and mineral fertilizer inputs on soil and maize grain yield in an acid ultisol in Abakaliki-South Eastern Nigeria. American Eurasia Journal of Agronomy 2(1), 7-12.

Mellek, J. Diecko, J., da Silva, V., Favaretto, N., Pauletti, V., Machado, F., Moretti, J. 2010. Dairy liquid manure and no-tillage: Physical and hydraulic properties and carbon stocks in a Cambisol of Southern Brazil. Soil and Tillage Research 110, 69-76.

Miller, J.J., Sweetland, N.J., Chang, C. 2002. Hydrological properties of a clay loam soil after long-term cattle manure application. Journal of Environmental Quality 31, 989-996.

Nájera, F. 2013. Soil nitrogen balance in two soils with pig slurry application during autumn - winter period in the mediterranean zone of central Chile. Unpublished.

Nájera, F., Salazar, O., Casanova, M. 2013. *In situ* soil nitrogen mineralization rate after pig slurry application in the Mediterranean zone of central Chile. Unpublished.

Nielsen, M., Styczen, M., Ernstsen, V., Petersen, C., Hansen, S. 2010. Field study of preferential flow pathways in and between drain trenches. Vadose Zone Journal 9, 1073-1079.

Ogawa, S., Baveye, P., Parlange, J., Steenhuis, T. 2002. Preferential flow in the field soils. Forma 17(1), 31-53.

Oviattt, C.A., Gold, A.J. 2005. Nitrate in Coastal Waters. pp: 127-144. *In*: Addiscott, T.M. (Ed). Nitrate, Agriculture and the Environment. CABI Publishing. 279 p.

Pachepsky, Y.A., Rawls, W.J. 2004. Development of Pedotransfer Functions in Soil Hydrology. Elsevier, Amsterdam. 542 p.

Pagliai, M., Vignozzi, N. 2002. The Soil Pore Systems as an Indicator of Soil Quality. pp: 71-82. *In*: Pagliai, M., Jones, R. (Eds.). Sustainable Land Management - Environmental Protection. A Soil Physical Approach. IUSS – UISS – IBU, Reiskirchen, Germany. 588 p.

Peth, S. 2004. Bodenphysikalische Untersuchungen zur Trittbelastung von Bóden bei der Rentierweidewirtschaft an borealen Wald- und subarktisch-alpinen Tundrenstandorten. Dissertation in Agrarwissenschaften, Universität Christian Albrechts, Kiel, Nr. 64. 160 p.

Powlson, D., Addiscott, T., Benjamin, N., Caassman, K., de Kok, T., van Grinsven, H., L'hirondel, J., Avery, A., van Kessel, C. 2008. When does nitrate become a risk for humans? Journal of Environmental Quality 37 (2), 291-295.

Radcliffe, D., Rasmussen, T. 2002. Soil Water Movement. pp: 85-126. *In*: Warrick, A.W. (Ed.) Soil Physics Companion. CRC Press. Boca Raton, Florida, USA. 373 p.

Ramos, C., Kücke M. 1999. Revisión Crítica de los Métodos de Medida de la Lixiviación de Nitrato en Suelos Agrícolas. pp: 25-32. *In*: Muñoz-Carpena, R., Ritter, A., Tascón, C. (Eds.). Estudios de la Zona No Saturada del Suelo. ICIA: Tenerife. España. 193 p.

Sadzawka, M.A., Carrasco, M.A., Grez, R., Mora, M.L., Flores, H., Neaman, A. 2006. Métodos de análisis de suelos recomendados para los suelos de Chile. Revisión 2006. Instituto de Investigaciones Agropecuarias, Serie Actas INIA Nº 34, Santiago, Chile, 164 p.

Sadzawka M.A., Carrasco, M.A., Demanet, R., Flores, H., Grez, R., Mora, M.L., Neaman, A. 2007. Métodos de análisis de tejidos vegetales. 2ª Ed. Instituto de Investigaciones Agropecuarias. Serie Actas INIA Nº 40. Santiago, Chile. 140 p.

Salazar, F., Alfaro, M., Misselbrook, T., Lagos, J. 2010. Nitrogen Leaching Following a High Rate of Dairy Slurry Application on a Ryegrass Sward of a Volcanic Soil in Southern Chile. pp: 48-55. *In*: Losses on Application and Storage. Environmental, Nutrient Losses, Impact of Storage and Spreading operations. Proceedings of the 14th RAMIRAN International Conferences, Lisboa, Portugal. CD.

Santibáñez, F., Uribe, J.M., 1990. Atlas Agroclimático de Chile: regiones Metropolitana y Quinta. Ministerio de Agricultura. Fondo de Innovación Agraria. Corporación de Fomento de la Producción. Santiago de Chile. 66 p.

Santibáñez, F., Uribe, J.M., 1993. Atlas Agroclimático de Chile: regiones Sexta, Séptima, Octava y Novena. Ministerio de Agricultura. Fondo de Innovación Agraria. Corporación de Fomento de la Producción. Santiago de Chile. 99 p.

Schaetzl, R.J., Anderson, S. 2005. Soils: Genesis and Geomorphology. Cambridge University Press, 832 p.

Scheffer, B., Ortseifen, U. 1997. Zur Abschatzung des Nitrataustrags in die Gewasser am Beispiel der Boden Niedersachsens. pp: 61-70. *In*: Brunswick Groundwater Colloquium 1997. Environmentally Friendly Management of Groundwater and Soil.184 p.

Shein, E.V., Arkhangel'skaya, T. A. 2006. Pedotransfer functions: state of the art, problems, and outlooks. Eurasian Soil Science 39, 1089-1099.

Sparks, D. L. 2003. Environmental Soil Chemistry. Academic Press, USA. 352 p.

Studart, R., White, R.E., Weatherley, A.J. 2005. Modelling the risk of nitrate leaching from two soils amended with five different biosolids. Revista Brasileira de Ciencia do Solo 29, 619-626.

Thomas, M. 2007. Soil conditions and early crop growth after repeated manure applications. Dissertation Degree of Master Science. University of Saskatchewan, Canada. 139 p.

Thomsen, I. 2005. Nitrate leaching under spring barley is influenced by the presence of a ryegrass catch crop: results from a lysimeter experiment. Agriculture, Ecosystems and Environment 111, 21-29.

Vahtera, E., Conley, D., Gustafsson, B., Kuosa, H. 2007. Internal ecosystem feedbacks enhance nitrogen fixing cyanobacteria blooms and complicate management in the Baltic Sea. Ambio 36, 186-194.

van Breemen, N., Buurman, P., 2003. Soil Formation. 2nd ed.; Kluwer Academic Publishers, 415 p.

Waters, A.G., Oades, J.M. 1991. Organic Matter in Water-stable Aggregates, pp: 163–174. *In*: Wilson, W.S (Ed.). Advances in Soil Organic Matter Research. The Impact on Agriculture and the Environment. Royal Society of Chemistry, Cambridge, UK. 400 p.

Weiler, M., Flühler, H. 2004. Inferring flow types from dye patterns in macroporous soils. Geoderma 120, 137-153.

Zebarth, B.J., Paul, J.W., Schmidt, O., McDougall, R. 1996. Influence of the time and rate of liquid–manure application on yield and nitrogen utilization of silage corn in South Coastal British Columbia. Canadian Journal of Soil Science 76, 153-164.

4.7 APPENDIX

Table A1. Water budget through autumn-winter season in two soils of central Chile, with volumes of deep percolation beyond 100 cm depth (see Eq. 1).

Soil	Time interval	Δθ	ETc	Rainfall	Irrigation	Percolation/Capillary rise
				(mm)		
PC	5/26/2011 - 6/7/2011	-1.64	0.00	5.20	0.00	6.84
PC	6/8/2011 - 6/21/2011	25.05	0.00	48.00	0.00	22.95
PC	6/22/2011 - 7/5/2011	-7.63	0.00	15.40	0.00	23.03
PC	7/6/2011 - 7/18/2011	9.64	0.00	39.90	0.00	30.26
PC	7/19/2011 - 8/16/2011	83.28	2.64	54.70	0.00	-31.22
PC	8/17/2011 - 8/30/2011	12.76	2.58	36.70	0.00	21.36
PC	8/31/2011 - 9/20/2011	-46.68	5.38	9.30	0.00	50.59
PC	**Period**	**74.78**	**10.6**	**209.2**	**0.00**	**123.81**
PS	5/26/2011 - 6/7/2011	26.20	0.00	5.20	0.00	-21.00
PS	6/8/2011 - 6/21/2011	51.92	0.00	48.00	0.00	-3.92
PS	6/22/2011 - 7/5/2011	1.65	0.00	15.40	0.00	13.75
PS	7/6/2011 - 7/18/2011	51.79	0.00	39.90	50.00	38.11
PS	7/19/2011 - 8/16/2011	14.03	0.13	54.70	50.00	90.54
PS	8/17/2011 - 8/30/2011	12.73	1.29	36.70	0.00	22.68
PS	8/31/2011 - 9/20/2011	6.68	3.71	9.30	0.00	-1.09
PS	**Period**	**165.00**	**5.13**	**209.20**	**100.00**	**139.07**
SC	6/2/2011 - 6/14/2011	0.62	0.00	6.00	0.00	5.38
SC	6/15/2011 - 6/20/2011	41.51	0.00	66.60	0.00	25.09
SC	6/21/2011 - 6/28/2011	4.08	0.00	1.40	0.00	-2.68
SC	6/29/2011 - 7/13/2011	22.94	0.00	12.00	0.00	-10.94
SC	7/14/2011 - 7/26/2011	57.23	0.00	52.80	0.00	-4.43
SC	7/27/2011 - 8/10/2011	19.77	1.21	12.00	0.00	-8.97
SC	8/11/2011 - 8/23/2011	10.64	1.89	56.50	0.00	43.97
SC	8/24/2011 - 9/6/2011	-6.95	5.14	30.00	0.00	31.81
SC	9/7/2011 - 9/14/2011	-4.56	5.68	0.00	0.00	-1.12
SC	**Period**	**145.28**	**13.92**	**237.3**	**0.00**	**78.11**
SS	6/2/2011 - 6/14/2011	8.83	0.00	6.00	0.00	-2.83
SS	6/15/2011 - 6/20/2011	56.00	0.00	66.60	0.00	10.60
SS	6/21/2011 - 6/28/2011	45.81	0.00	1.40	0.00	-44.41
SS	6/29/2011 - 7/13/2011	17.44	0.00	12.00	0.00	-5.44
SS	7/14/2011 - 7/26/2011	14.74	1.50	52.80	0.00	36.56
SS	7/27/2011 - 8/10/2011	1.13	5.35	12.00	0.00	5.52
SS	8/11/2011 - 8/23/2011	9.36	11.36	56.50	0.00	35.78
SS	8/24/2011 - 9/6/2011	22.21	21.76	30.00	0.00	-13.97
SS	9/7/2011 - 9/14/2011	-40.51	18.92	0.00	0.00	21.59
SS	**Period**	**135.01**	**58.89**	**237.30**	**0.00**	**43.40**