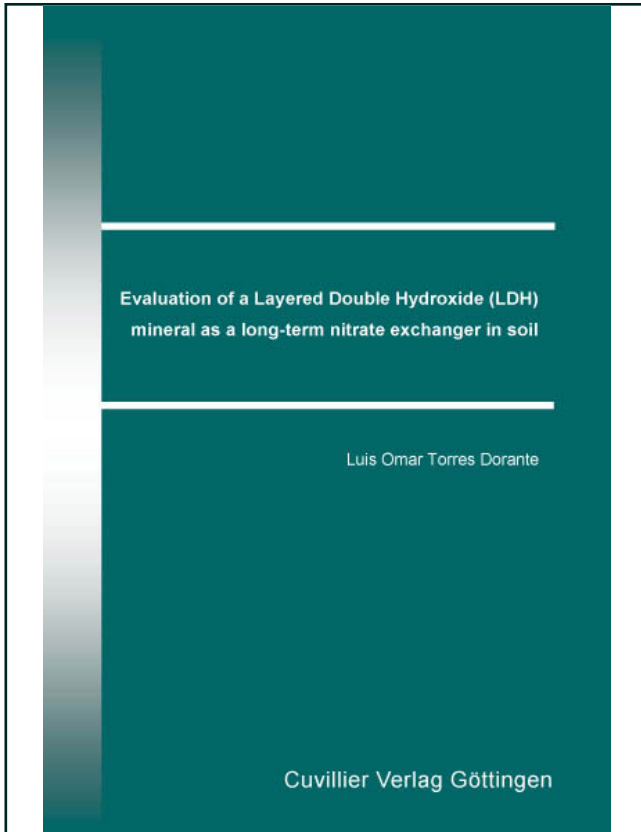




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**Evaluation of a Layered Double Hydroxide (LDH) mineral as a long-term nitrate exchanger in soil**



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## 1 Introduction

Crop production is affected by several pathways of losses of nitrogen mainly in the form of leaching, runoff/erosion or gas. The relative importance of each process depends on both, environmental and anthropogenic factors (*Legg and Meisinger, 1982; Hofman and van Cleemput, 2004*). The leaching of nitrate represents an important way of N losses in field crop production, especially in humid regions (*Addiscott et al., 1991; Schimming et al., 1995; Neeteson and Carton, 2001*). In irrigated agriculture and horticulture, the N losses due to leaching are similarly or even more important (*Keeney, 1982; Spalding et al., 2001; Thompson et al., 2004*). In most soils, nitrate as an anion is not adsorbed to the soil particles, thus it is mobile in the soil. Therefore the extent of N leaching losses depends on climate (e.g. rainfall), soil (e.g. water holding capacity, biological turnovers like extent of mineralization/immobilization), land use (e.g. cropping systems irrigation), and the management of organic and inorganic N sources (*Strebel et al. 1989; Shepherd and Lord, 2004*). The nitrate leaching losses must be reduced because they represent an economic loss since can not be taken up by crops, and at the same time it may reach ground and surface waters with the risk of causing eutrophication, and human health problems (*Keeney, 1982; Addiscott et al., 1991; Leifert et al., 1999*). The World health Organization (*WHO, 1993*), and the European Union via the Water Framework Directive (*EU, 2000*) set a limit value of  $50 \text{ mg NO}_3^- \text{ L}^{-1}$  ( $11.3 \text{ mg NO}_3^- \text{-N L}^{-1}$ ) in drinking water. In order to reduce and prevent nitrate pollution of potable water resources, the European Union also approved the Ground Water Directive (*EU, 2006*) which imposes the implementation of measures to reverse any upward trends in nitrate concentrations when the nitrate level in the ground water reaches  $37.5 \text{ mg NO}_3^- \text{ L}^{-1}$  (75 % of the legal threshold =  $50 \text{ mg NO}_3^- \text{ L}^{-1}$ ).

Several measures aiming to reduce nitrate leaching at field level are widely described in the literature (*Strebel et al., 1989; Baumgärtel and Scharpf, 2002; Shepherd and Lord, 2004; Stoy and Sattelmacher, 2004*). Nevertheless, nitrate leaching from field agricultural production is difficult to control because it does not only depend on the amount of residual soil inorganic N at crop harvest but also on the extent of N mineralization afterwards. To reduce residual inorganic N in the soil at harvest while maintaining a high yield, N fertilizer recommendations are carried out based on the  $N_{\text{min}}$  method according to *Wehrmann and Scharpf (1986)*. However, even at optimum

N supply, leaching of nitrate can still take place during winter. During this period, nitrate leaching depends on the soil water balance (amount of rain/water holding capacity of the soil), and on the extent of N mineralization after harvest, especially when N uptake of fallow crops is low (*Engels and Kuhlmann, 1993; Schimming et al., 1995; Richter et al., 1996; Trindade et al., 1997; Ryan et al., 2001*). To reduce the amounts of both, residual N as well as N mineralized during winter periods, cover or catch crops can be integrated into cropping systems. However, their success in reducing soil N depends on sowing date as well as on the type of crop (*Trindade et al., 1997; Francis et al., 1998; Köhler et al., 2006*).

In field vegetable production, the risks of nitrate leaching are even higher because of the higher residual N content in the soil at harvest, and the higher amount of crop residues, which can be mineralized during winter (*Krug et al., 2002; Riley, 2002*). In addition, the lower root density of many vegetables crops in deeper soil layers limits the further uptake of inorganic nitrogen (*Wehrmann and Scharpf, 1989*). The nitrate leaching losses during the period between autumn and winter in open field vegetable production in humid regions may reach up to 200 kg N ha<sup>-1</sup> (*Schrage, 1990; Neeteson and Carton, 2001*).

Reduced fertilizer N application below the optimum is often suggested to decrease nitrate leaching in open field agricultural production. However, several long-term field studies have shown only a poor correlation between the nitrate-N concentration in ground waters and level of N fertilization. *Strebel et al. (1989)* and *Köhler et al. (2006)* studied the relationship between nitrate leaching and N fertilization levels in arable farming on sandy soils, and found that even after strong reduction of fertilizer N applications, losses of N due to leaching still occur, but an important yield reduction was measured. *Stoichev et al. (1996)* found after a long-term field study that neither no fertilizer N application nor the fallow management were able to prevent the nitrate pollution of ground waters. The nitrate mineralization from organic soil sources during autumn until early spring was found to be the main cause of nitrate leaching losses from field crop production, despite of a reduced or optimum N supply (*Schimming et al., 1995; Trindade et al., 1997; Köhler et al., 2006*). Even the implementation of ecological farming practices may not always result in reductions of the nitrate concentrations in the leachate below the legal threshold, especially if farmyard manure is applied in autumn (*Knappe et al., 2002*).

Another attempt to reduce nitrate leaching during the cropping season is the application of slow release N fertilizers (SRF). However, their main disadvantage is that the N release pattern may not match timely with plant N demand, especially in fast growing crops (*Trenkel*, 1997). Also, the use of fertilizers mixed with nitrification inhibitors (e.g. stabilized ammonium products) is also suggested to avoid the formation of nitrate in soil. The performance of both SRF and nitrification inhibitors strongly depends on soil factors i.e. moisture, and biological activity (*Trenkel*, 1997; *McCarty*, 1999; *Werner*, 2006). Since nitrate leaching in open field production does not normally take place during the growth period but mainly after harvest, the use of these kinds of products has often only little success in reducing nitrate leaching.

The risks of nitrate leaching in irrigated crop production are also high. A study carried out by *Timmons* and *Dylla* (1981) showed that the annual N leaching losses in corn production with supplementary irrigation was up to 100 kg ha<sup>-1</sup>. *Spalding* et al. (2001) found after a 6-year field study that the nitrate concentration in the soil water percolation beneath irrigated-corn fields remained at a level higher than 11.3 mg NO<sub>3</sub><sup>-</sup>-N L<sup>-1</sup>. The nitrate leaching from an intensive vegetable production was estimated to be up to 200 kg NO<sub>3</sub><sup>-</sup>-N ha<sup>-1</sup> (*Thompson* et al., 2004). Improved irrigation techniques, and delivery of nutrients through fertigation systems can reduce N leaching losses. However, both measures require high levels of investments that might not be affordable for many farmers.

The N losses due to leaching in ornamental production, and particularly nursery crop production in containers can be important. To control the nitrate losses due to leaching in these systems, an efficient management of the water supply, and the use of slow-release fertilizers (SRF) are often recommended. However, high nitrate contents have been found in the soil beneath containerized nursery crops despite the use of SRF (*Colangelo* and *Brand*, 1997). *Colangelo* and *Brand* (2001) accounted in a nursery of rhododendron plants annual N leaching losses of up to 40 kg nitrate-N ha<sup>-1</sup> even with improved irrigation, and the use of SRF. *Bataglia* et al. (2005) found that nitrate-N leaching losses in a citrus nursery were significant even with the use of SRF. They estimated N losses up to about 50 kg N ha<sup>-1</sup>. In an olive nursery, the nitrate leaching was found to be in the same order of magnitude (*Fernández-Escobar* et al., 2004). If SRF are not used accordingly, the N leaching losses can be similar to that when using water-soluble products (*Brand* et al., 1993; *Cox*, 1993). This is

because of the frequent irrigation regimes, and the continuous fertilization requirements of crops growing in coarse-textured or peat-based mixtures with a low water retention capacity and no anion adsorption properties.

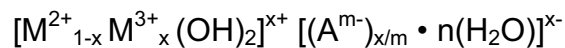
Most of the measures described above to reduce nitrate leaching focus on the management of the N inputs, and of the cropping systems. The results of the different studies reported clearly show that nitrate leaching occurs because most of the soils used for crop production do not have anion exchange properties. Therefore, nitrate as an anion remains mobile in the solution. An efficient way to reduce nitrate leaching would be the control of its movement in the soil by adsorbing it from soil solution in the same way as clay minerals i.e., vermiculites and smectites do with cations like potassium and ammonium (*Nommik and Vahtras, 1982; Borchardt, 1989; Douglas, 1989*) but most of the soils used for crop production normally do not have anion exchange capacity. For instance, acid soils with a high content of aluminium and iron hydroxides/oxides can loosely held nitrate. These soils are mainly found in the tropics and subtropics i.e., Oxisols and Ultisols (*Hsu, 1989; Adams, 1995; Amberger, 2006*). Also volcanic ash-derived soils containing allophane and imogolite minerals known as Andosols or Andepts, have anion exchange capacity of up to  $0.4 \text{ mol}_c \text{ kg}^{-1}$  (*Espinoza et al., 1975; Wada, 1989*). Allophane and imogolite minerals have also been found in soils derived from parent materials others than volcanic ash, particularly in soils derived from basalts, and in forest soils located in cool, humid and mountainous regions (*Wada, 1989*).

Anion exchangers may be suitable to control the movement of anions in soil. Synthetic organic ion exchangers i.e., resins, have already been used to exchange anions in soil. Nitrate-specific resins adsorbed nitrate from soil solution, and reduced nitrate leaching losses under laboratory conditions (*Wyland and Jackson, 1993; Lehmann, 2001*). The use of resins in crop production is limited because of their high costs, and in addition their decay by soil micro-organisms into undesired compounds may be a hazard to the environment.

An option to control the movement of nitrate in soil can be the use of a specific nitrate-adsorbing anionic clay mineral. The use of clay minerals for adsorbing ions in soil has been investigated. The addition of natural zeolites to a coarse-textured soil reduced the movement of ammonium (*Mackown and Tucker, 1985*). Natural zeolites minerals with cation exchange capacity have been investigated for its use in

agriculture i.e., as a soil amendment and slow-release potassium and ammonium fertilizer (Ming and Mumpton, 1989; Park and Komarneni, 1998; Kithome et al., 1998). Others have proposed the use of bentonite to deliver cations i.e. potassium, magnesium and calcium, especially in soils that do not have smectites clays (Gillman and Noble, 2005).

The hydrotalcite is a mineral with permanent anion exchange capacity, in contrast to the common soil clay minerals, which have cation exchange capacity. As with the other anionic clay minerals, the hydrotalcite mineral is not found in common agricultural used soils. Hydrotalcite belongs to the family of layered double hydroxides (LDH) or anionic clay minerals because of its lamellar or layered structure consisting of positively charged metal hydroxide layers with interlayers containing anions and water (de Roy et al., 2001; Kahn and O'Hare, 2002). A schematic representation of the LDH structural model is shown in the Annex 1. Hydrotalcite can be found in nature in the form of hydroxycarbonate of magnesium and aluminium (Allmann and Jepsen, 1969; Drits and Bookin, 2001; Trave et al., 2002) but a wide variety of LDHs can be synthesized at both, laboratory and industrial scales (Crepaldi et al., 2000; de Roy et al., 2001). The chemical composition of LDHs can be described by the general formula (de Roy et al., 2001; Kahn and O'Hare, 2002):



where:

$M^{2+}$  = are divalent cations =  $Mg^{2+}$ ,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ .

$M^{3+}$  = are trivalent cations  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Mn^{3+}$ ,  $Cr^{3+}$ ,  $Co^{3+}$ ,  $Ni^{3+}$ .

$A^{m-}$  = anions =  $NO_3^-$ ,  $CO_3^{2-}$ ,  $Cl^-$ ,  $OH^-$ ,  $SO_4^{2-}$ , and other inorganic and organic anions.

$x$  = cation isomorphous substitution ratio =  $[M^{3+}] / [M^{2+} + M^{3+}]$ , usually from 0.1 to 0.67.

Layered double hydroxide minerals are used in the polymer industry as co-stabilisers in PVC products (Crepaldi and Valim, 1998), and as catalysts in chemical reactions (Basile and Vaccari, 2001). They also have the potential to be used in medicinal chemistry (Constantino and Nocchetti, 2001; Ambrogi et al., 2002), for water decontamination (Ulibarri and Hermosín, 2001; Gillman, 2006), for adsorbing heavy metals in soils (Witzke and Pöllmann, 1998), and for microbial contaminant remediation (You et al., 2003).

The permanent anion exchange capacity of LDHs can also be used to exchange nitrate in soil. *Wada and Masuda (1995)* proposed the use of a LDH mineral to control the soil solution salt concentration in greenhouse soils. The nitrate release kinetics from a nitrate LDH under laboratory conditions for its potential use as a slow release nitrate fertilizer were studied by *Olanrewaju et al. (2000)*, *Komarneni et al. (2003)* and *Bull (2001)*. *Olfs and Torres-Dorante (2005)* and *Torres-Dorante et al. (2006)* explored the potential use of LDH as a nitrate fertilizer in pot trials. Moreover, *Gillman and Noble (2005)* proposed the combined use of bentonite and hydrotalcite-like minerals as soil amendments for providing cation and anion exchange capacity to soils aiming to decrease leaching problems. *Beavers (1999)* and *Bull (2001)* synthesized a high nitrate selective Mg-Al LDH with the formula:  $[\text{Mg}^{2+}_{0.83} \text{Al}^{3+}_{0.17} (\text{OH})_2]^{0.17+} [(\text{NO}_3^-)_{0.17} \cdot 0.5(\text{H}_2\text{O})]^{0.17-}$  with an  $\text{Al}^{3+}$  content of  $x = 0.17$  (Mg:Al ratio of 5:1), and evaluated its capacity to exchange nitrate in soil. The anion exchange capacity was  $2.1 \text{ mol}_c \text{ kg}^{-1}$  LDH, which is much higher than the anion exchange capacity of anionic clay minerals.

Up to now, the use of the LDH minerals to adsorb anions in soil has only been postulated based on studies carried out at laboratory conditions, mainly in aqueous solutions and/or within short time-frame periods. The functionality of the LDH under longer cropping conditions has not yet been shown. The successful application of the LDH mineral as a long-term soil exchanger to reduce N leaching losses finally depends on its permanent nitrate exchange capacity during periods with and without cultivation.

In principle, a LDH can be produced in a nitrate or chloride form. A nitrate form of the mineral can also be used to provide anion exchange to the soil, but the use of a nitrate form of the LDH would imply that its application rate is based on the crop N demand. Therefore the rate of application of a nitrate-LDH would be too low, and may provide low effective nitrate exchange capacity to the soil. The main objective of the present work was to evaluate the suitability of a LDH mineral as a long-term soil nitrate exchanger. The LDH mineral should adsorb nitrate if its concentration in soil solution is higher than needed for optimal plant growth and release it if the plant required it. The study was carried out with a chloride form of a Mg-Al LDH with the formula:  $[\text{Mg}^{2+}_{0.82} \text{Al}^{3+}_{0.18} (\text{OH})_2]^{0.18+} [(\text{Cl}^-)_{0.18} \cdot 0.5(\text{H}_2\text{O})]^{0.18-}$  with an  $\text{Al}^{3+}$  content of  $x = 0.18$  (measured Mg:Al ratio of 4.5:1). Moreover, this specific type of LDH also was

used because of its high selectivity for nitrate adsorption (*Bull*, 2001). The following studies were carried out:

1. Characterization of the nitrate adsorption and desorption properties of the LDH mineral in aqueous solutions and under soil conditions (section 3.1).
2. Evaluation of the nitrate adsorption and desorption capacity of the LDH during both, cultivation and fallow periods (section 3.2).
3. Study of the long-term stability of the LDH under non-cropped and cropped conditions (section 3.3).
4. Investigation of the structural changes of the LDH during cropping, and effects on the nitrate exchange capacity (section 3.4).