Journal of Environmental Biology
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September 2009, 30(5) 841-846 (2009)
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Increased eutrophication and nutrient imbalances in the agricultural soil of NE Catalonia, Spain

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(Received: June 23, 2008; Revised received: September 25, 2008; Accepted: October 11, 2008)

Abstract: *The soil C, N, P and K content of agricultural soil were measured over the last 4 decades in NE Catalonia (NE Spain). Plant-available P and K increased by ca 109 and 105% respectively and total N decreased by 30%. The increases in plant-available P content are in accordance with the increasingly used pig slurry being very rich in P, and with P tendency to be retained in soils, since it is less mobile than N. The total soil N (N_{tot}) decrease occurred in the first decade (by 41%). The uptake and withdrawal of mineral N by crops and the leaching of mineral N into groundwater and rivers after torrential rainfalls were the two likely major pathways of N-loss from the soil. After the first decade, there has been no further decrease of N_{tot} as a result of the increasing fertilization of these fields, including the increasing applications of pig slurry. These results show an increasing P eutrophication in Mediterranean agricultural soils and will have several consequences for the next decades with (i) an increasing unbalance between N and P (and K) in soils that might affect crop productivity, (ii) an increasing leaching of N as nitrate to continental waters, both ground and surface waters, and (iii) a consequent need for the establishment of another fertilization strategy based on lowering the use of pig slurry and on increasing the use of fertilizers of slow mineralization that increase soil organic matter, and stabilise the soil N and P contents.*

Key words: *Fertilization, Girona, K, Nitrogen, P, Pig slurry, Soil*
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Introduction

Eutrophication, understood as the increase of nutrients, e.g. compounds containing N or P, in aquatic and terrestrial ecosystems, is one of the main drivers of global change (Vitousek *et al*., 1997). Increased foliar concentrations of N, P, K and other nutrients have been reported in terrestrial plants of the Mediterranean Basin collected in herbaria throughout the last 20th century (Penuelas and Filella, 2001). Eutrophication may also occur in some crop soils in the Mediterranean basin, where significant effects of mineral and pig slurry fertilization on soil chemical properties have been reported (Arcara *et al*., 1999; Dauden and Quilez, 2004; Abad *et al*., 2005; Angas *et al*., 2006; Torrent *et al*., 2007). However, as far as we know, there are no studies on the long term effects of the progressive increase of mineral and pig slurry fertilization in the last decades in this Mediterranean basin area.

During the last decades, the agricultural soils of most Mediterranean regions have been increasingly over-fertilized, not only by mineral fertilization but also by N deposition and pig slurry fertilization. Total atmospheric deposition is calculated to reach up to 15-22 kg ha^{-1} $year^{-1}$ in several areas of this region (Roda *et al*., 2002) and there is an excessive use of pig slurry as fertilizer (Babot *et al*., 2004). In Catalonia there has been a continuous increase in the number of pigs on farms over the last decades (from 4642000 in the 1980s to the current 6348000 pigs). This has generated increased amounts of pig slurry (*ca.* $15x10^6$ m^3 y^{-1} in 2006) with the consequent increasing need for their disposal. The 97% of this pig slurry is applied to agricultural fields (CADS, 2008; Babot *et al*., 2004; Dauden and Quilez, 2004). Pig slurry has a high N concentration (5.8-7.6%, dry wt.) which enhances nitrification and thus leads to groundwater nitrate enrichment. Application of doses of 16-32 m^3 ha^{-1} of pig slurry in croplands can be considered normal in pig slurry management (Brechin and McDonald, 1994). This means a dose of 96-182 kg N ha^{-1} in a single application, which is often repeated several times through the year. In the Girona province (north east Catalonia), the annual pig slurry production is equivalent to 150-400 kg N ha^{-1} of crop soil (CADS, 2008). Thus, the use of the 97% of this pig slurry N is greater than the recommended values 45-240 kg N ha^{-1} for N fertilization of the common crop types of this area Vivancos (1984). This excess of pig slurry is applied in several regions, generating an excess of macronutrients that can result on increased concentration of the less mobile P, or increased lixiviation to continental waters of the more mobile N. In this sense the increase of nitrate concentration has increasingly reached values over 50 mg l^{-1} in underground waters in the last decades in several Catalonian areas, including the one studied here (Ninerola *et al.,* 2006). This effect has been observed to be mostly due to the use of pig slurry in field experiments (Boixadera, 1998). Moreover, the use of inorganic N-fertilizers that

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Fig. 1: Geographic situation of the studied area: Girona province, NE Catalonia (Spain)

are also added to crop soils in this area may have additionally contributed to nitrate leaching to continental waters as observed in several experiments in other sites (Saraswathy and Singaram, 2005; Saraswathy *et al*., 2007). But pig slurry also has high contents of other nutrients such as P (2.0-2.9%, dry wt.) and K (2.1-3.1%, dry wt.), which represents 33-48 kg P ha^{-1} and 35-51 kg K ha^{-1} with the usual application doses (Brechin and McDonald, 1994). One of the effects of this field management is the increasing concentration of nitrate in the ground waters, which in most cases have reached the threshold values for human health established by the EU legislation (50 mg l^{-1}). Phosphate is less water soluble than nitrate and ammonium salts, and, consequently, P tends to be retained in soil more than N. The great amounts of pig slurry dispersed on the fields may increase the P eutrophication of soils unless it is totally withdrawn by crop biomass (DeSmet *et al*., 1996). Several studies of agricultural soil throughout the time have reported increases of plant-available P during the first decades due to the great retention of the P added by fertilization (Li *et al*., 2005; Bunemann *et al*., 2006). This increasing fertilization of soils may have also contributed to the increasing presence of P in the rivers and groundwater (water eutrophication) observed in this Mediterranean region in the 1990s (DeSmet *et al*., 1996; Chardon *et al*., 1997; Hodgkinson *et al*., 2002).

We hypothesized an increase specially of P and likely of N and K in soil as a result of the frequent use of mineral and pig slurry fertilization in the Catalan agricultural soils. We expected a less clear result for N, given its greater uptake and withdrawal by crops and its higher mobility towards ground and surface waters. To test these hypotheses, we analyzed the evolution of C, N, P and K throughout the last four decades in NE Catalonian agricultural soils.

Materials and Methods

We used the results obtained in 274 soil analyses conducted over the last four decades (1970s, 1980s, 1990, 2000s) by the Girona Association of Agronomists in the top 20-25 cm depth soil layer of 136 sites corresponding to fruit tree, olive-vine, cereal and forage crop fields randomly spread through the Girona Province, NE Catalonia, Spain (Fig. 1). The studied zone has an area of approximately 469250 ha, the agriculture fields representing 31% of the total area. The total number of pigs in this zone was 630000 in 2007 according to Catalan Government data.

Although their properties differ depending on the source area of the parent material, almost all the agricultural soils analysed in this study are developed on sedimentary rocks. Three broad zones can be distinguished: a south one dominated by soils formed from sandy granitic-derived materials (mostly *Fluventic Haploxerepts* or *Typic Xerofluvents*; Soil Survey Staff, 1998) a central one constituted by calcareous sediments, fine textured (mostly *Aquic* and *Typic Xerofluvents*, *Typic Calcixerepts*, *Calcic Haploxerepts*, *Petrocalcic Palexeralfs* and *Calcic Haploxeralfs)*; and a north one, more heterogeneous constituted by a complex glacis and alluvial fans coming from the southern basin of the Pyrenees mountains (mostly *Haploxerepts* and *Xerorthents*).

The Walkley-Black method (1934) was used for the determination of oxidable soil organic C (SOC). N_{tot} was determined by the Kjeldhal method, using a distillation method to collect ammonium from the Kjeldhal digest process that transforms soil N into ammonium, and then the ammonium was determined by a colorimetric procedure (Bradstreet, 1965). To measure the plant-available P_i in soil, an extraction with 0.5 M $NaHCO_3$ (Olsen-P) was conducted (Watanabe and Olsen, 1965). Plant-available K was determined in filtered (f<0.2 mm) soil extracts (1:10, soil:1M Ammonium Acetate, W/W) by optic emission spectrophotometry.

We analyzed the data by one-way ANOVA using the values of soil properties observed in each decade as dependent variables and the different decades as independent variables. We also used ANCOVA tests with crop type as independent categorical variable, the decade of the analysis as continuous variable and the soil traits as dependent variables. All analyses were performed with the *Statview* software package (Abacus Concepts Inc., Cary, North Carolina) and the *Statistical* software package (StatSoft Inc. Tulsa, Oklahoma).

Results and Discussion

In the last four decades the available P (Olsen-P_i) and K increased by 109% and 105% respectively whereas N_{tot} decreased by 30% (Fig. 2). The increase in P content has been persistent since the 1980s and the increase in K content since the 1970s (Fig. 2). The decrease in N content occurred in the 1980s (by 41% relative to the 1970s) and thereafter the N soil concentrations showed no significant change (Fig. 2). No significant changes of SOC were either observed in this period (Fig 2).

The results show a progressive increase in the plant-available P. P is much less mobile than N, and tends to be retained throughout time in crop soils (Li *et al*., 2005) and during soil formation (Carreira and Lajtha, 1997; Lilienfein *et al*., 2004). The increased plant-available P is in accordance with the general trend observed in other soil chronosequences, mainly in crop soils where P has been added by fertilization (Lemenih *et al*., 2005; Li *et al*., 2005). Ulen and Snall (2007) have observed in southwest Sweden that the continuous application of pig slurry increases the soil P content in different soil types. The increased soil available K observed in these Catalan soils has also been observed in other studies of crop soils throughout time (Lemenih *et al*., 2005) and is probably a result of the high K fertilization. In accordance with the observations in these Catalonian soils, there are several studies of crop soils throughout time that have found no significant changes in SOC (Desjardins *et al*., 2006). However, others have reported increases (Manlay *et al*., 2002) and others have reported decreases (Han *et al*., 2006).

Conversely, these results indicate that in spite of the considerable fertilization inputs, there is now less total N in these soils than four decades ago. The apparent contradiction between the increasing inputs of N in fertilization and the loss of N in soils is a likely result of the increased use of pig slurry as fertilizer. A 73% of the total N content of pig slurry is NH_4^+ (CADS, 2008), very soluble and easily leached by water. On the other hand, in the soils of this region, mostly of neutral or basic pH, organic forms of N mineralize rapidly. Mineral N is a very mobile nutrient that has already been reported to decrease in other crop soils throughout the time (Lemenih *et al*., 2005). The overall soil N losses were related with the increase in nitrate contents detected in the continental waters, both in the surface and ground waters in Catalonia in the last decades (Teixidó *et al*., 2001). The use of pig slurry produces greater N losses by denitrification than those produced using other fertilizer types such as the mineral ones (Rochette *et al*., 2000). The high P content in pig slurry can contribute to increase N losses by increasing denitrification specially when applied together with mineral fertilizers (Arcara *et al*., 1999). Denitrification usually increases after increased nitrification, *e.g.* in an experiment under Mediterranean climate conditions the nitrous oxide (N_2O) emissions in plots fertilized with pig manures increased with respect to non fertilized plots (Lopez-Fernandez *et al*., 2007). Thus, the increases on nitrification after pig slurry application (Aita *et al*., 2007) allow N losses by both,

Table - 1: Significance level (*P*) of the categorical factor (crop type), the continuous covariable (decade) and their interaction for the soil chemical traits (ANCOVA), and the means + S.E. of each variable in the different crop types and decades (different letters stand for significant differences in the post-hoc ANOVA test)

	Soil chemical variable						
Statistical factor	**Total N (%, dry wt.)**	**Available-P_i (mg P kg^{-1})**	**Total N / Available-P_i**	**SOC (%, dry wt.)**	**C/N**	**Available K (mg P kg^{-1})**	**Available (K/P)**
Crop type	0.327	0.080*	0.151	0.590	0.293	0.100*	**0.031**
Decade	**0.012**	**0.024**	**0.038**	0.203	0.228	0.127	0.610
Crop type x decade	0.327	0.077*	0.153	0.591	0.591	0.099*	0.743
Crop type							
Vegetables	0.134 ± 0.017	42 ± 6^{a}	56 ± 15	1.03 ± 0.12	7.7 ± 0.4^{b}	238 ± 29^{a}	6.9 ± 1.2^{b}
Olive and vine	0.158 ± 0.047	32 ± 4^{ab}	256 ± 209	0.85 ± 0.12	7.4 ± 0.5^{b}	158 ± 14^{b}	7.1 ± 0.9^{b}
Cereals	0.127 ± 0.04	25.5 ± 32^{ab}	62 ± 6	1.25 ± 0.12	9.6 ± 0.6^{a}	186 ± 16^{b}	9.2 ± 1.0^{ab}
Fruit trees	0.171 ± 0.013	19.4 ± 2.4^{ba}	308 ± 270	1.23 ± 0.09	7.4 ± 0.3^{b}	165 ± 19^{b}	11.7 ± 1.7^{a}
Decade							
1968-1979	0.192 ± 0.013^{a}	16.1 ± 3.3^{b}	275 ± 40^{a}	0.82 ± 0.09	6.5 ± 0.1^{b}	107 ± 30^{cb}	10.1 ± 2.6
1980-1989	0.100 ± 0.019^{b}	15.9 ± 8.7^{b}	141 ± 37^{b}	2.05 ± 1.14	8.1 ± 0.4^{a}	138 ± 51^{b}	12.5 ± 2.1
1990-1999	0.125 ± 0.004^{b}	23.0 ± 12.0^{b}	80 ± 8^{b}	1.08 ± 0.07	8.8 ± 0.3^{b}	184 ± 15^{ab}	9.7 ± 0.8
2000-2006	0.131 ± 0.013^{b}	33.5 ± 2.4^{a}	52.8 ± 6.1^{b}	1.08 ± 0.07	8.5 ± 0.3^{b}	197 ± 12^{a}	8.2 ± 0.7

Bold type means significant differences at p < 0.05, * = Marginally significant differences at p < 0.1

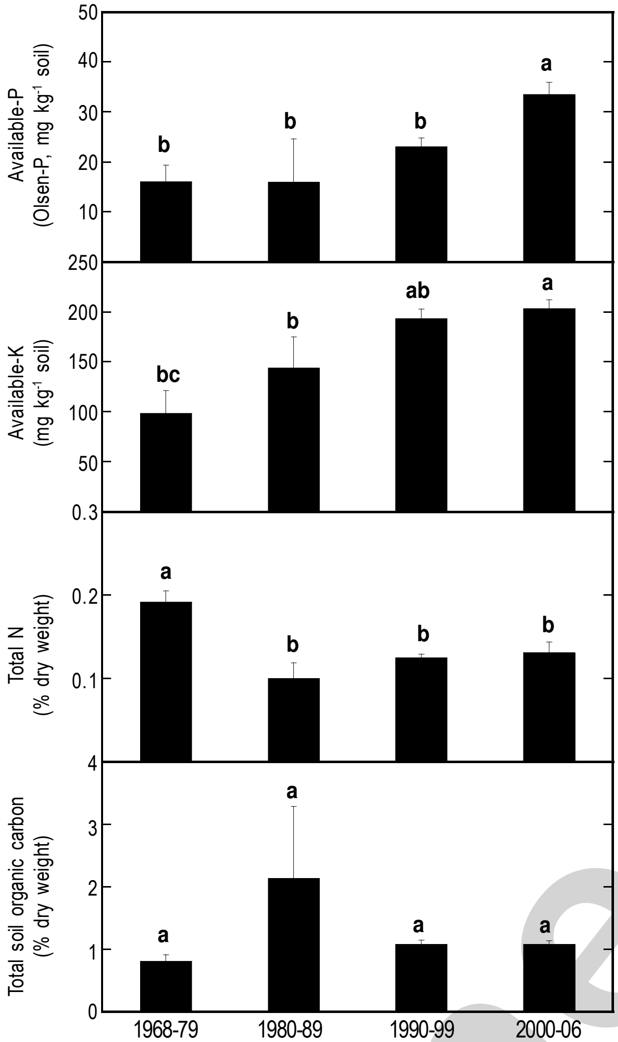

Fig. 2: Changes in plant-available P_i (Olsen -P), total N, available K contents and total soil organic carbon in the crop soil. Different letters indicate significant differences between decades ($p < 0.05$, Fisher post-hoc test)

leaching and denitrification (Arcara *et al*., 1999; Abbasi and Adams, 2000). The early increases in the number of pigs and in the use of pig slurry and the early increases of mineral fertilization increased the N losses in the first decades, but the continuous increase of pig slurry fertilization has probably allowed to reach an equilibrium between losses and inputs, remaining the total N concentration in soils more or less stable since the 1980s.

The crop soils in the study area have low to moderate amounts of SOC (0.5-1.8% in most cases). The SOC has not changed significantly after 4 decades of soil tillage and fertilization management, what calls for a reconsideration of the management practices, since crop yield can be increased by increasing SOC pool in the root zone (Lal, 2006; Soon *et al*., 2007). The lower organic C content of pig slurry than other traditional manures such as crop residues (Al-kaisi *et al*., 2005; Wright *et al*., 2007), and its faster mineralization account for the absence of increase in SOC in spite of the great amounts of pig slurry used as fertilizer during this period.

The reduction of N in soil was especially evident in olive and vine crops, whereas the increase in plant-available Pi was mainly evident in fruit tree crops (Table 1, Fig. 3). The increases of available K were also slightly affected by the crop type in a similar way to plant-available P_i (Table 1). Olive crops and vineyards frequently occur on slopes, have low percentage of plant cover, and usually grow on soil with a sandy or stony texture. This makes these crops more vulnerable to nutrient losses by leaching and erosion than other crops such as cereals or fruit trees growing on soils without slopes and less likely to suffer leaching. Moreover, olive-vine crops are much less fertilized than the other crop types, specially regarding to N and P. The usual doses in the area for olive-vine crops are 45-80 and 13-22 (kg ha^{-1} $year^{-1}$) for N and P, respectively, whereas the corresponding values for cereal, vegetables and fruit crops are 120 and 35, 240 and 48 and 160 and 33, respectively. In contrast, Olsen-P_i increased mainly in forage and fruit tree crops which occupy low slope positions and are frequently more intensely fertilized.

As a result of these changes, in the last four decades the N/Available-P_i ratio decreased by 71% and the N/K ratio by 95%. The C/N ratio increased by 25% in the 1980s and remained without change later (Fig. 4). The fact that N/P ratios are lower in pig dejection (4.0-6.2) (Van Delden *et al*., 2003) compared with those reported in soils (2-20) (Aerts *et al*., 2003: Hobara *et al*., 2005), in litter (8-60) (Gusewell and Verhoeven, 2006) and in plant tissues (6-30) (Bakker *et al*., 2005; Niklas and Cobb, 2006) and the fact that the biomass collected by farmers (fruits, leaves or the full plant) has a greater N/P ratio than the pig slurry additionally contributes to the decreasing N/P ratio in these agricultural soils.

These results constitute another indication of the overfertilization and eutrophication of terrestrial soils. The increases in P and K are not necessarily negative by themselves, since these two elements are linked to water use efficiency, which needs to be maximized in this area prone to drought problems. However, the current evolution of the soil chemistry may lead to nutrient imbalances between N, P, and K now and in the immediate future.

The recommended K/P ratios in fertilizers in this region are approximately 2.1 for cereal crops, 1.9 for vegetable crops, 3.8 for fruit tree crops and 3.8-6.0 for olive and vine crops (Vivancos, 1984). The ratio of available-(K/P) ratio in the soils of all crops types (6.9-11.9) (Table 1) is greater than the recommended values in fertilizer (1.9-6.0). The observed trend to decrease of this ratio from 12 in the 1980-1989 decade to 8.2 in the period 2000-2006 (Table 2) indicates a greater soil accumulation of P than of K, coinciding with the lower solubility of P than of K and in this case may represent a positive change for crops. However, the increasing probability of N, P and K losses to continental waters constitute an environmental problem. Ceretta *et al*. (2005) observed a great increase of N and P in leaches in successive months after pig slurry application in different soil types. Moreover, in Mediterranean soils there is a significant increase of

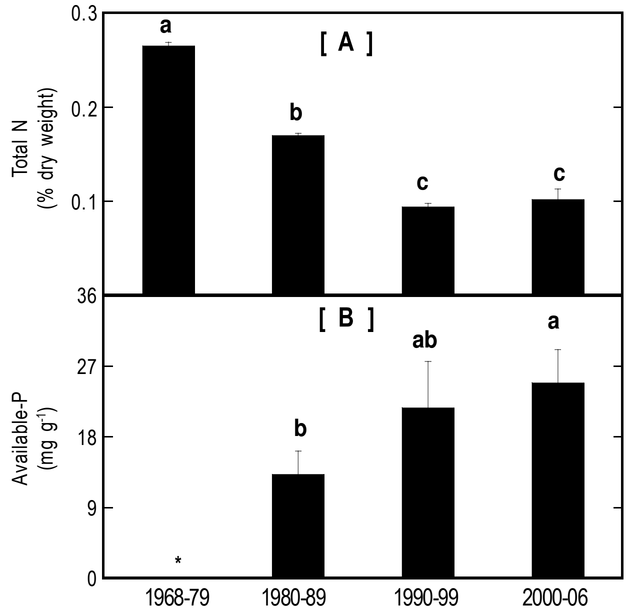

Fig. 3: Changes in total N and plant available-P_i (Olsen-P) content in (A) soils of olive vine crops and (B) soils of fruit tree crops. Different letters indicate significant differences between decades (p < 0.05, Fisher post-hoc test), * = Data not available

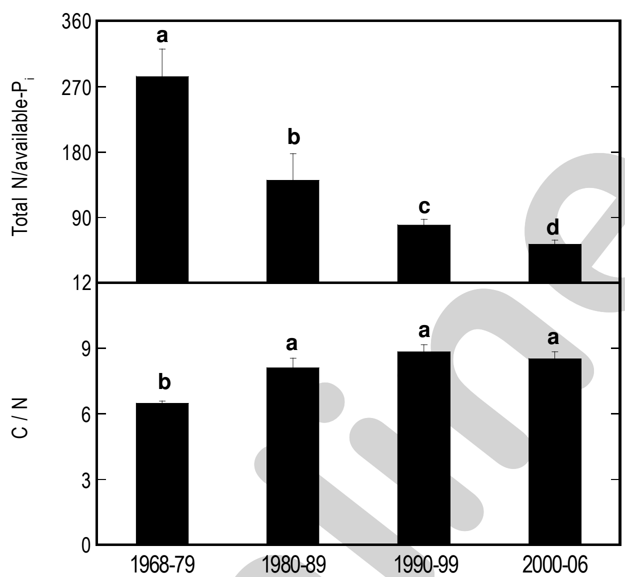

Fig. 4: Changes in N/plant-available P_i (Olsen-P) and C/N ratios in crop soils. Different letters indicate significant differences between decades (p < 0.05, Fisher post-hoc test)

nitrates after pig slurry application (Berenguer *et al*., 2008). These results thus show that a new fertilization management strategy is needed, mainly because of the problem of water nitrate enrichment and eutrophication in a geographic area where the problems of water availability are increasing because of climate change and rising population. The use of other manures such as crop residues would suppose a nutrient and carbon source with slow mineralization rates that would liberate nutrients slowly, allowing a greater plant uptake and decreasing the soil N losses. On the other hand, the slower mineralization would allow a greater accumulation of SOC in these soils. If pig slurry has to be used, it should be accompanied by nitrification inhibitors and other pig slurry treatments such as its digestion or it's composting (Vallejo *et al*., 2006).

We can conclude that the increasing use of pig slurry as fertilizer in North East Catalonia associated to the continuous increase in the number of pigs on Catalan farms over the last decades has increased the availability of P in crop soils as a consequence of the great concentration of P in pig slurry and the great soil capacity to retain P. In these last 40 years the SOC has not changed significantly in spite of continuous tilling and fertilization, and in spite of the low SOC contents of these soils. The increasing presence of nitrates and eutrophication in the rivers and groundwater of this area in the last decades has coincided with the increasing use of mineral and pig slurry fertilizers. These data show that the current fertilization system based on pig slurry plus inorganic fertilizers should be reconsidered.

Acknowledgments

This research was supported by European project NEU NITROEUROPE (GOCE017841), by the Spanish Government project CGL2006-04025/BOS, the Catalan Government grant SGR 2005-00312, the European ALARM (Contract 506675) project, and a *Fundación* BBVA 2004 grant.

References

Abad, A., A. Michelena and J. Lloveras: Effects of nitrogen supply on wheat and on soil nitrate. *Agro. Sust. Develop.*, **25**, 439-446 (2005).

Abbasi, M.K. and W.A. Adams: Gaseous N emission during simultaneous nitrification-denitrification associated with mineral N fertilization to a grassland soil under field conditions. *Soil Biol. Biochem.*, **32**, 1251-1259 (2000).

Aerts, R., H. de Caluwe and B. Beltman: Is the relation between nutrient supply and biodiversity co-determined by type of nutrient limitation?. *Oikos*, **101**, 489-498 (2003).

Aita, C., S.J. Giacomini and A.P. Hubner: Nitrification of ammoniacal nitrogen from pig slurry in soil under no-tillage. *Pes. Agro. Brasil*, **42**, 95-102 (2007).

Al-Kaisi, M.M., X.M. Yin and M.A. Licht: Soil carbon and nitrogen changes as affected by tillage system and crop biomass in a corn-soybean rotation. *Appl. Soil Ecol.*, **30**, 174-191 (2005).

Angas, P., J. Lampurianes and C. Cantero-Martinez: Tillage and N fertilization – Effects on N dynamics and barley yield under semiarid Mediterranean conditions. *Soil Tillage Res.*, **87**, 59-71 (2006).

Arcara, P.G., C. Gamba, D. Bidini and R. Marchetti: The effect of urea and pig slurry fertilization on denitrification, direct nitrous oxide emission, volatile fatty acids, water-soluble carbon and anthrone-reactive carbon in maize-cropped soil from the Po plain (Modena, Italy). *Biol. Fert. Soil*, **29**, 270-276 (1999).

Babot, D., N. Andres, L. de la Pena and E.R. Chavez: Techniques of environmental managing in pork production. TRAMA (LIFE) Project. Edicion de la fundacion Catalana de Coooperacion (2004).

Bakker, C., J. Rodenburg and P.M. van Bodegom: Effects of Ca- and Fe-rich seepage on P availability and plant performance in calcareous dune soils. *Plant Soil*, **275**, 111-122 (2005).

Berenguer, P., F. Santiveri, J. Boixadera and J. Lloveras: Fertilization of irrigated maize with pig slurry combined with mineral nitrogen. *Europ. J. Agro.*, **28**, 635-645 (2008).

Boixadera, J.: The code for good agricultural practices: Nitrate, an example of improved agricultural practices. Agriculture service of the Catalan Government. *Quaderns Agraris,* **22**, 67-70 (1998).

Bradstreet, R.B.: The Kjeldahl Method for Organic Nitrogen. Academic Press. New York (1965).

Brechin, J. and G.K. McDonald: Effect of form and rate of pig manure on the growth, nutrient-uptake and yield of barley (CV Galleon). *Aust. J. Exp. Agric*., **34**, 505-510 (1994).

Bunemann, E.K., D.P. Heenan, P. Marschner and A.M. McNeill: Long-term effects of crop rotation, stubble management and tillage on soil phosphorus dynamics. *Aus. J. Soil Res*., **44**, 611-618 (2006).

CADS: REport for the improvement of pig slurry management in Catalonia. Committee for the Sustainable Development of the Catalan Government. Barcelona (2008).

Carreira, J.A. and K. Lajtha: Factors affecting phosphate sorption along a Mediterranean, dolomitic soil and vegetation chronosequence. *Eur. J. Soil Sci*., **48**, 139-149 (1997).

Cerretta, C.A., C.J. Basso, F.C. Beber Vieira, M.G. Herbes, I.C. Lopez Moreira and A.L. Berwanger: Pig slurry: Nitrogen and phosphorus loses on solutions applied on soil surfaces. *Ciencia Rural*, **35**, 1296-1304 (2005).

Chardon, W.J., O. Oenema, P. del Castilho, R. Vriesema, J. Japenga and D. Blaauw: Organic phosphorus in solutions and leachates from soils treated with animal slurries. *J. Environ. Qual*., **26**, 372-378 (1997).

Dauden, A. and D. Quilez: Pig slurry versus mineral fertilization on corn yield and nitrate leaching in a Mediterranean irrigated environment. *Eur. J. Agric*., **21**, 7-19 (2004).

Desjardins, T., P.J. Folgarait, A. Pando-Bahuon, C. Grirardiu and P. Lavelle: Soil organic matter dynamics along a rice chronosequence in north-eastern Argentina: Evidence from natural C-13 abundance and particle size fractionation. *Soil Biol. Biochem*., **38**, 2753-2761 (2006).

DeSmet, J., G. Hofman, J. Vanderdeelen, M. VanMeirvenne and L. Baert: Phosphate enrichment in the sandy soils of West-Flanders, Belgium. *Fert. Res.*, **43**, 209-215 (1996).

Gusewell, S. and J.T.A. Verhoeven: Litter N:P ratios indicate whether N or P limits the decomposability of graminoid leaf litter. *Plant Soil*, **287**, 131-143 (2006).

Han, X.Z., S.Y. Wang, P.L.M. Veneman and B. Xing: Change of organic carbon content and its fractions in black soil under long-term application of chemical fertilizers and recycled organic manure. *Com. Soil Sci. Plant Anal.,* **37**, 1127-1137 (2006).

Hobara, S., K. Koba, T. Osono, N. Tokuchi, A. Ishida and K. Kameda: Nitrogen and phosphorus enrichment and balance in forest colonized by cormorants: Implications of influence of soil adsorption. *Plant Soil*, **268**, 89-101 (2005).

Hodgkinson, R.A., B.J. Chambers, P.J.A. Withers and R. Cross: Phosphorus losses to surface waters following organic manure applications to a drained clay soil. *Agric. Water Manage*., **57**, 155-173 (2002).

Lal, R.: Enhancing crop yields in the developing countries through restoration of the organic carbon pool in agricultural lands. *Land Degrad. Develop*., **17**, 197-209 (2006).

Lemenih, M., E. Karitun and M. Olsson: Assessing chemical and physical property responses to deforestation and subsequent cultivation in smallholders farming system in Ethiopia. *Agric. Ecosyst. Environ*., **105**, 373-386 (2005).

Li, Z.P., T.L. Zhang, D.C. Li, B. Veide and F.X. Han: Changes in soil properties of paddy fields across a cultivation chronosequence in subtropical China. *Pedosphere*, **15**, 110-119 (2005).

Lilienfein, J., R.G. Qualis, S.M. Uselman and S.D. Bridgham: Adsorption of dissolved organic and inorganic phosphorus in soils of a weathering chronosequence. *Soil Sci. Soc. America J*., **68**, 620-628 (2004).

Lopez-Fernandez, S., J.A. Diez, P. Hernaiz, A. Arce, L. Garcia-Torres and A. Vallejo: Effects of fertilizer type and the presence or absence of plants on nitrous oxide emissions from irrigated soils. *Nutr. Cycl. Agroecosyst*., **78**, 279-289 (2007).

Manlay, R.J., D. Masse, J.C. Chotte, J.Y. Laurent and C. Feller: Carbon, nitrogen and phosphorus allocation in agro-ecosystems of a West African savanna. II. The soil component under semi-permanent cultivation. *Agric. Ecosyst. Environ*., **88**, 233-248 (2002).

Niklas, K.J. and E.D. Cobb: Biomass partitioning and leaf N, P – stoichiometry: comparisons between tree and herbaceous current-year shorts. *Plant Cell. Environ*., **29**, 2030-2042 (2006).

Ninerola, J.M., M. Iglesias, J. Fraile, E. Florla and T. Garrido: Evolotion and status of groundwater in catalonia as a result of nitrate pollution. Agencia Catalana de l'Aigua. Department de Medi Ambient I Habitatge. Generalitat de Catalunya. http://www.Mediambient.gencat.net/aca/documents/ca/agenda/nitrates.pdf. (2006).

Penuelas, J. and I. Filella: Herbaria century record of increasing eutrophication in Spanish terrestrial ecosystems. *Global Change Biol*., **7**, 427-433. (2001).

Rochette, P., E. van Bochove, D. Prévost, D.A. Angers, D. Cote and N. Bertrand: Soil carbon and nitrogen dynamics following application of pig slurry for the 19th consecutive year: II. Nitrous oxide fluxes and mineral nitrogen. *Soil Sci. Soc. Am. J*., **64**, 1396-1403 (2000).

Roda, F., A. Avila and A. Rodrigo: Nitrogen deposition in Mediterranean forests. *Environ. Pollut*., **118**, 205-213 (2002).

Saraswathy, R. and P. Singaram: Nitrogen losses throuhgt leacheate and its distribution. *J. Environ. Biol*., **26**, 355-362 (2005).

Saraswathy, R., S. Suganya and P. Singaram: Environmental impact of nitrogen fertilization in tea ecosystem. *J. Environ. Biol*., **28**, 779-789 (2007).

Soil Survey Staff: Keys to Soil Taxonomy, 18th Edn., USDA Natural Resources Conservation Service, Washington DC (1998).

Soon, Y.K, M.A. Arshad, A. Haq and N. Lupwayi: The influence of 12 years of tillage and crop rotation on total and labile organic carbon in a sandy loam soil. *Soil Till. Res*., **95**, 38-46 (2007).

Teixido, E., L. Olivella, M. Figueras, A. Ginebreda and R. Tauler: Multivariate exploratory analysis of the organic micropollutants found in the Llobregat River (Catalonia, Spain). *Inter. J. Environ. Anal. Chem*., **81**, 295-313. (2001).

Torrent, J., E. Barberis and F. Gil-Sotres: Agriculture as a source of phosphorus for eutrophication in southern Europe. *Soil Use Manag*., **23**, 25-35 (2007).

Ulen, B. and S. Snall: Forms and retention of phosphorus in an illite-clay soil profile with a history of fertilization with pig manure and mineral fertilizers. *Geoderma*, **137**, 455-465 (2007).

Vallejo, A., U.M. Skiba, L. García-Torres, A. Acre, S. Lopez-Fernández and L. Sanchez: Nitrogen oxides emission from soils bearing a potato crop as influenced by fertilization with treated pig slurries and compost. *Soil Biol. Biochem*., **38**, 2782-2793 (2006).

Van Delden. A., J.J. Schröder, M.J. Kropff, C. Grashoff and R. Booij: Simulated potato yield, and crop and soil nitrogen dynamics under different organic nitrogen management strategies in The Netherlands. *Agric. Ecosyst. Environ*., **42**, 9-26 (2003).

Vitousek, P.M., J.D. Aber, R.W. Howarth, G.E. Likens, P.A. Matson, D.W. Schlinder, WH Schlesinger and D.G. Tilman: Human alteration of the global nitrogen cycle: Sources and consequences. *Ecol. Appl*., **7**, 737-750 (1997).

Vivancos, D.: Tratado de Fertilization. Mundi Prensa, Madrid (1984).

Walkley, A. and I.A. Black: An examination of Degtjareff Method for determination soil organic matter and a proponed modification of the chromic acid titration method. *Soil Sci*., **37**, 29-37 (1934).

Watanabe, F.S. and S.R. Olsen: Test of an ascorbic acid method for determining phosphorus in water and $NaHCO_3$ extracts from soil. *Soil Sci. Soc. Am. J*., **29**, 677-678 (1965).

Wright, A.L., F.G. Dou and F.M. Hons: Crop species and tillage effects on carbon sequestration in subsurface soil. *Soil Sci*., **172**, 124-131 (2007).