CALIBRATION AND VALIDATION OF THE NEW WAVE$_{\mathrm{MATLAB}}$ VERSION IN A FALLOW FIELD PLOT

J.L. Gabriel[1]*, M. Quemada[2], J. Vanteenkiste[3], J. Diels[3] and M. Vanclooster[1]

[1]Earth and Life Institute (ELIE), Université Catholique de Louvain (UCL), Croix du Sud, 2 bte L7.05.02, B-1348 Louvain-la-Neuve, Belgium. e-mail: jose.gabriel@uclouvain.be
[2]Escuela Técnica Superior de Ingenieros Agrónomos, Universidad Politécnica de Madrid, Avd. Complutense s/n, 28040 Madrid. e-mail: miguel.quemada@upm.es
[3]Division Soil and Water Management, Department of Earth and Environmental Sciences, KU Leuven, Celestijnenlaan 200E – box 2411, B-3001 Leuven, Belgium. email: jan.diels@ees.kuleuven.be

RESUMEN. El lavado de nitratos disminuye su disponibilidad para los cultivos e incrementa la contaminación del agua. Pero la cuantificación del lixiviado por debajo de la zona de absorción radical es difícil sin alterar el suelo. Una versión en Matlab del modelo mecanístico WAVE para el balance de agua y nutrientes se ha aplicado para calcular el drenaje y el balance de N, comparándose con resultados previos.

El modelo mostro buena precisión en la estimación del balance de agua y temperatura del suelo, aunque ligeramente menor al estimar el ciclo del N. Sin embargo, las estimaciones concordaron con la dispersión observada en campo. Por tanto, aunque es necesario un mayor esfuerzo para mejorar el módulo del N, WAVE$_{\mathrm{Matlab}}$ es una herramienta muy útil para evaluaciones de diferentes técnicas agronómicas, para reducir pérdidas de fertilizantes y lixiviado de nitratos en la región mediterránea, donde la cantidad y distribución de precipitación es incierta.

ABSTRACT. Nitrate leaching decreases crop available N, increasing water contamination. But quantification of NO_3^- leaching below the root zone is difficult to measure without disturbing the soil in order to determine the contribution of each agricultural practice. A new Matlab version of the mechanistic nutrient and water balance model WAVE was applied in order to calculate drainage and N balance and compared with previous estimations.

The model showed the capacity for the estimation, with very high accuracy, the water balance and soil temperature. This accuracy was lightly reduced when the N cycle was estimated. However, estimations were in accordance with observed data dispersion. So, further research is necessary in the N module of this new Matlab version, but it can be a very interesting tool for evaluation of different agronomic techniques, reducing fertilizer losses and NO_3^- leaching in the Mediterranean regions, where the amount and precipitation timing are often very uncertain.

1.- Introduction

Agriculture in irrigated semiarid areas is often a source of groundwater contamination. Indeed the great yield potentials driven by extended frost-free periods and abundant solar radiation often results in large fertilization rates which are often unbalanced with the crop assimilation capacity (Vázquez et al., 2006). A good example of such a problematic cultivation system is maize cropping in the Mediterranean area (Díez et al., 1997; Causapé et al., 2004). Although adjustments of N applications to the maize crop requirements can reduce NO_3^- losses (Gehl et al., 2005), fertilizer recovered by the maize plants is usually less than 50% (Bundy and Andraski, 2005), leaving a large residue of mineral N (N_{min}) in the soil after harvesting that it is prone to leaching.

The quantification of NO_3^- leaching below the root zone allows determining the contribution of agricultural practices to the NO_3^- contamination of groundwater. Yet leaching is difficult to measure without disturbing the soil (Webster et al., 1993). Various methods have been used to collect water samples from the unsaturated zone: profile soil sampling (Lidon et al., 1999), tile drains (Strock et al., 2004), drainage from watersheds (Isidoro et al., 2006), pan and wick lysimeters (Feaga et al., 2010), and monolith lysimeters (Salmeron et al., 2010). All of these methods have advantages and disadvantages, but no single, direct method exists for soil solution sampling under most soil conditions (Gehl et al., 2005). Indirect methods based on a detailed knowledge of soil water dynamics combined with measuring soil water NO_3^- using ceramic cup samplers allows for the quantification of NO_3^- leaching with minimal soil disturbance and is practical for use in studies with multiple replications and treatments (Normand et al., 1997; Paramasivam et al., 2001; Vazquez et al., 2005). The calculation of drainage or water percolation below the root zone is one of the main factors determining NO_3^- leaching in indirect methods (Arregui and Quemada, 2006). Physically based numerical models for soil water movement are useful tools to quantify the different terms of the water and nutrient balances in agro-ecosystems (Muñoz-Carpena et al., 2008). However, the large number of parameters needs appropriate identification before such models can be used in a predictive mode (Simunek et al., 1999). Inverse calibration can help to identify the parameters by an iterative process. This procedure has the advantage of results that are based on variables monitored under field conditions (Ritter et al., 2003). The development of multisensor probes, allowing continuous monitoring of soil water content at different depths with minimum soil disturbance (Fares and Alva, 2000), and periodical measurements of the N_{min} concentration in the soil solution provide data sets over large time scales that can reduce the uncertainties in a model's predictions.

The main objective of this study was to evaluate the WAVE model as a useful tool in order to estimate the nitrate leaching and soil N_{min} accumulation during the intercrop period in an irrigated maize system.

2.- Materials and methods

2.1.- Experimental setup

The study was conducted on a monoculture of maize (*Zea maize* L., G-98 Pioneer) in an experimental field station located in Aranjuez (Madrid, Spain) in the Tajo river basin, from October 2006 to April 2010. The soil was a Typic Calcixerept (silty clay loam; Soil Survey Staff, 2003) and the site is characterized by a Mediterranean semi-arid climate (Papadakis, 1996). Temperature, humidity, wind speed, precipitation and solar radiation were recorded hourly with a Campbell Scientific CR23X micrologger (Logan, UT, USA) situated in the experimental field during the study period.

Although in this experiment only the fallow plots were considered, they were located inside a broader experiment with four cover crop treatments and four replications randomly distributed in sixteen plots (12 m x 12 m). The three other treatments were a barley treatment (*Hordeum vulgare* L., cv. Vanessa), a vetch treatment (*Vicia villosa* L., cv. Vereda) and a rapeseed treatment (*Brassica napus* L., cv. Licapo). All the plots, fallow included, were subjected to a shallow cultivator treatment after maize harvest and stubble removing, for covering hand broadcast cover crop seeds, on the following dates: 5/10/2006, 11/10/2007, 9/10/2008 and 5/10/2009. Maize was again sown on 17/04/2007, 16/04/2008, 03/04/2009 and 13/04/2010. During the maize period the plots were fertilized with 210 kg N ha^{-1} (ammonium nitrate). Irrigation was only applied during the maize session and was adjusted to the evapotranspiration, thereby trying to avoid drainage during these periods. A more detailed description of the experimental site and design can be found in Gabriel and Quemada (2011).

EnviroSCAN® capacitance probes (Sentek Pty Ltd, Stepney, Australia) were used for the daily monitoring of soil water content. Three probes were installed at three of the four fallow replications. Each probe consisted of six sensors placed every 20 cm from 10 to 110 cm depth. Every sensor was calibrated (Gabriel et al., 2010) and readings were registered every hour. Three ceramic suction cups were installed at 120 cm depth in the four plots in order to analyze soil solution, and were sampled every 15 days or when larger than 20 mm rainfall events occurred. Soil N_{min} was measured each 20 cm in the four plots at the beginning and at the end of each fallow period. The nitrate in the soil solution and in the soil samples was determined by spectrophotometry after reduction with a cadmium column (Keeney and Nelson, 1982), and ammonium was measured using the method of Solorzano (1969). A more detailed description of the direct measurements can be found in Gabriel et al. (2012).

2.2.- WAVE model use

The WAVE model (Vanclooster et al., 1996) solves the Richards equation parameterized with a conceptual model for the soil hydraulic properties (van Genuchten, 1980). A previous nitrate leaching estimation was obtained with the Fortran version of the WAVE model by Gabriel et al. (2012). In that case, only the soil water module of the WAVE model was inverted, using data from the first fallow period (calibration period: October 2006-April 2007), thereby comparing observed and simulated soil water content at different depths. The optimized parameters were soil water content at saturation, residual soil water content, saturated hydraulic conductivity and the van Genuchten constants n and α. After that, the model was validated for the rest of the fallow periods (October 2007-April 2008, October 2008-April 2009 and October 2009-April 2010), obtaining the different terms of the water balance. Final nitrate leaching was estimated by multiplying drainage volume obtained with WAVE with the nitrate concentration obtained in the suction cups.

In this study a new Matlab® (The MathWorks Inc., Natick, MA, USA) open source version of WAVE model has been used. This version presents improvements in the water module such as the introduction of an ET_o module, that is now directly calculated from energy balance considerations in the soil-crop continuum, following the dual crop coefficient described by Allen et al. (1998). This module implies that solar radiation, relative humidity and wind speed are now required as climatic data inputs. The N module remains similar to the Fortran version but the solute transport (including nitrate and ammonia) includes the immobile fraction concept, the possibility of solute application as defined concentration or known mass application and some changes in the time step after applications in order to maintain the balance. Moreover, the generic crop module has been changed by another with a continuous interaction between climate, photosynthesis and plant development stage, based on the Acock formula (Acock et al., 1978). A more detailed description of the Matlab® WAVE version can be found in Van Loon et al. (2011).

An automatic inversion was implemented for retrieving the soil hydraulic parameters from observations for the period October 2006-April 2007. The soil was divided in four homogeneous layers (0-20, 20-40, 40-80 and 80-120). The observed water content in the middle of each layer was obtained as the direct reading in the 10 and 30 cm depth sensors for the two upper layers and as the average of the 50-70 and the 90-110 cm depth readings for the two deeper ones. The predicted soil water content in the middle of the each layer was then compared with the soil water content observed as in Gabriel et al. (2012). Subsequently an inversion was implemented for retrieving the following N balance related parameters: hydrodynamic dispersivity, the ratio of the mobile - total water content, the decaying constant of NO_3^- and NH_4^+, the sorption constant for NO_3^- and NH_4^+, the *a* and *b* coefficients for the calculation of dispersion coefficient for NO_3^- and NH_4^+, the nitrification rate, the denitrification rate, the hydrolysis rate, the volatilization rate, the decaying rate for manure, litter and humus, the humification rate, the turn-over efficiency of the organic matter and the biomass C/N ratio of the organic matter. The objective function was the N_{min} concentration observed in the 12 suction cups installed in the four plots. For validation soil temperature at 5, 10 and 20 cm depth and final N_{min} in the soil profile were compared with observed data.

For the automatic inversion, WAVE was coupled to the Shuffled Complex Evolution Metropolis algorithm for optimization and uncertainty assessment of hydrological model parameters (SCEM-UA, Vrught et al., 2003). This global optimization algorithm is a Bayesian method based on the Markov chain Monte Carlo method (Gilks et al., 1998) that uses the Metropolis Hastings strategy (Metropolis et al., 1953) for population evolution, reaching within a single optimization run both the most likely parameter set and its underlying posterior probability distribution. The fit of the simulations to the observed data was evaluated by the coefficient of efficiency (C_{eff}; Nash and Sutcliffe, 1970) and the root mean squared error (RMSE), as Ritter and Muñoz-Carpena (2013) suggest for hydrological models.

3.- Results

The distribution and amount of rainfall and the winter temperatures varied greatly between years, affecting soil water content and drainage. This variability is very appropriate for testing the model under very different conditions. The results of both inverse calibrations for the two WAVE model versions showed an improvement in the Matlab version with respect to the Fortran one, not only during the calibration period but also during the validation period (Fig. 1 and 2). The C_{eff} was equal to 0.896 during the calibration period obtained for the Fortran version, and 0.933 for the Matlab version when the water content along the entire profile was considered. This improved the RMSE from 6.8 mm along the 1.2 m depth profile to 5.6 mm. When the four periods of simulation were compared, the C_{eff} improved from 0.776 with the Fortran version to 0.925 with the Matlab version, and also the RMSE from 8.6 mm in the 1.2 m profile to 8.3.

The optimal parameters set for both WAVE versions was very similar, but with some larger differences in the residual water content in the upper layers (Table 1) and in the *α* parameter in the bottom. In both cases the results were inside the ranges observed for this soil by Gabriel et al. (2012).

Table 1. Soil parameters obtained in the inverse calibration of both Matlab and Fortran versions of WAVE. θ_r was the residual water content, θ_s the saturated water content, α the inverse of the air entry value, n curve shape parameter of the water retention model described by Van Genuchten and K_s the saturated hydraulic conductivity

Depth	θ_r (cm^3 cm^{-3})		θ_s (cm^3 cm^{-3})		α (cm^{-1})		n		K_s (cm day^{-1})	
(m)	Fort.	Mat.	Fort.	Mat.	Fort.	Mat.	Fort.	Mat.	Fort.	Mat.
0-0.2	0.060	0.034	0.50	0.50	0.012	0.013	1.44	1.42	1009	1064
0.2-0.4	0.070	0.098	0.42	0.42	0.011	0.015	1.28	1.31	510	547
0.4-0.8	0.105	0.088	0.33	0.34	0.015	0.015	1.17	1.17	979	936
0.8-1.2	0.128	0.129	0.30	0.29	0.034	0.012	1.19	1.16	525	529

The new water balance obtained with the Matlab version (Table 2) suggested an increase of the evaporation with respect to the previous simulations (Gabriel et al., 2012), combined with a lightly reduction of the drainage during these fallow periods. Moreover, this increase in the evaporation was more in accordance with previous estimations made of the global evapotranspiration in these fallow plots using the dual method of the FAO for soils no completely covered, and considering soil water stress (Allen et al., 1998). The mass error in the water balance was for all periods smaller than 1 mm using both models.

Table 2. Rainfall measured and **w**ater balance obtained with WAVE Matlab version (mm)

Period	Rainfall	Evaporation	Drainage
2006/07	306.1	154.8	101.2
2007/08	155.3	189.4	18.0
2008/09	310.7	164.9	149.0
2009/10	498.5	195.7	267.7

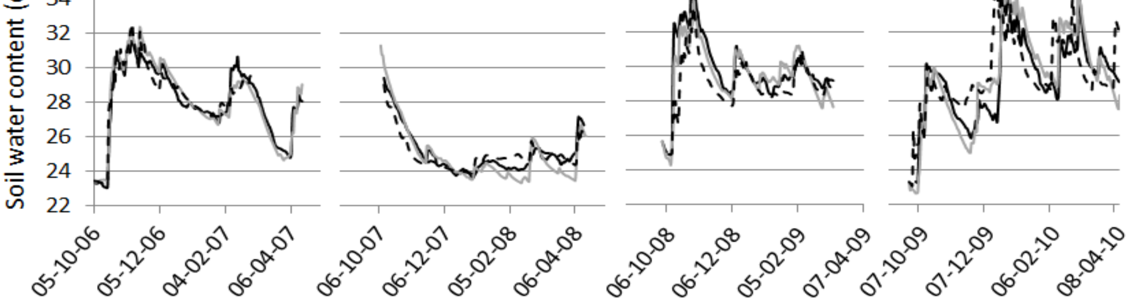

Fig. 1. The soil water content in the entire profile during the four fallow studied periods simulated using WAVE Fortran and Matlab versions versus the average soil water content observed using the capacitance sensors

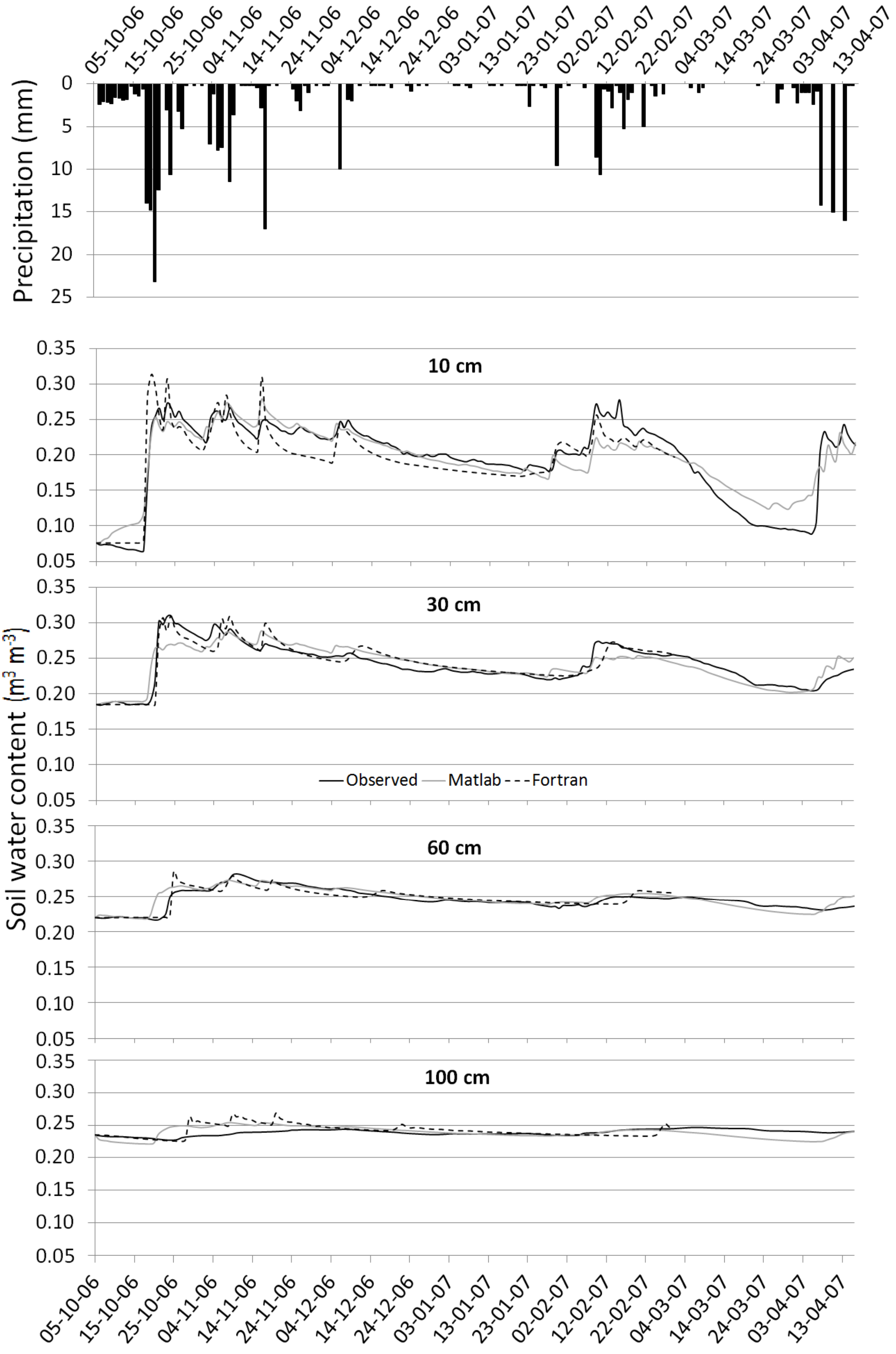

Fig. 2. Rainfall and soil water content at different depths during the calibration period simulated using WAVE Fortran and Matlab versions versus the average soil water content observed using the capacitance sensors during the calibration period

Soil temperature is an important variable for modeling soil biological processes. In this case, the WAVE Matlab version simulated well the temperature estimated at 5, 10 and 20 cm soil depth. The C_{eff} at each depth was 0.846, 0.480 and 0.792 for the 5, 10 and 20 cm depth respectively, with a RMSE equal to 3.2, 3.1 and 3.5°C.

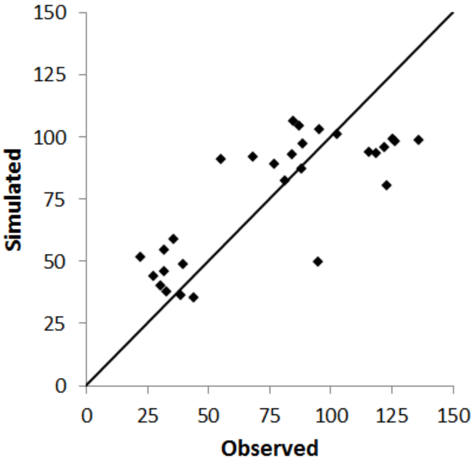

Fig. 3. The NO_3 concentration in the drainage in mg N L^{-1} measured during the four experimental periods with the suction cups versus the simulated with WAVE Matlab

Nitrate concentration in the drainage water was well adjusted to the measurements with a C_{eff} equal to 0.62 and a RMSE close to 22 mg N-NO_3^- L^{-1} (Fig. 3). The amount of NH_4^+ leached was negligible, with concentrations ranging from 0.006 to 1.1 mg N-NH_4^+ L^{-1}, which is similar to the observations in the suction cups, ranging from 0.0003 to 0.77. The validation made with the N_{min} observed at the end of each fallow period presented a loss in the accuracy, which is reflected in a global C_{eff} equal to 0.125 and a RMSE equal to 10.7 kg N ha^{-1} for the N_{min} amount during the whole studied period. However, some periods, like the first fallow, presented better simulations, reaching a C_{eff} adjustment close to 0.9, and in almost all the sampling dates the profiles simulated were within or very close to the observed range (Fig. 2). This reduction in the accuracy as compared to the water balance and the soil temperature was due to the N cycle complexity.

4.- Conclusions

The Matlab version of the physically based agrohydrological model WAVE was implemented for evaluating the field scale water balance, thermal balance and nutrient leaching during a fallow period. The Matlab version allowed easy data analysis, facilitated advanced modeling analysis (inverse modeling, sensitivity analysis, uncertainty propagation analysis). Although further research is needed with the new Matlab version of the model, it is a very interesting tool for evaluating the environmental performances of different agronomic techniques. The implementation of a more advanced crop module allows to increase the opportunities of application of the model, not only for water and nitrogen balance studies, but also for evaluating crop response processes. Other enhancements of this version are the possibility of running the model during more than a year and including rotations with more than one plant species.

The model showed an appropriate simulation of different terms of the water balance, not only during the calibration period but also during the validation period. The availability of observed nitrate concentrations in suction cups, combined with measured N_{min} along the profile at different moments, allowed a first approximation to the N turnover rates through inverse modeling and the quantification of the NO_3^- leaching. However, more improvements in the N modules are necessary in order to get better accuracy.

Acknowledgment. Financial support by Spain CICYT (ref. AGL 2011-24732), Comunidad de Madrid (project AGRISOST, S2009/AGR-1630), Belgium FSR 2012 (ref. SPER/DST/340-1120525) and Marie Curie actions. Special thanks to the technicians working with us at "La Chimenea" field station (IMIDRA).

5.- References

Allen, RG., L.S. Pereira, D. Raes, and M. Smith, 1998. FAO 56 Irrigation and drainage paper: crop evapotranspiration. Food and Agriculture Organization, Rome.

Acock, B., D.A. Charles-Edwards, D.J. Fitter, D.W. Hand, J. Ludwig, J. Warren Wilson, and A.C. Withers, 1978. The contribution of leaves from different levels within a tomato crop to canopy net photosynthesis: an experimental examination of two canopy models. *J. Exp. Bot. 29*, 815–827.

Arregui, L.M., and M. Quemada, 2006. Drainage and nitrate leaching in a crop rotation under different N-fertilizer strategies: application of capacitance probes. *Pl. Soil. 288*, 57-69.

Bundy, L.G., and T.W. Andraski, 2005. Recovery of fertilizer nitrogen in crop residues and cover crops on an irrigated sandy soil. *Soil Sci. Soc. Am. J. 69*, 640-648

Causapé, J., D. Quilez, and R. Aragues, 2004. Assessment of irrigation and environmental quality at the hydrological basin level - II. Salt and nitrate loads in irrigation return flows. *Agric. Water Manag. 70*, 211-228.

Díez, J.A., R. Roman, R. Caballero, and A. Caballero, 1997. Nitrate leaching from soils under a maize-wheat-maize sequence, two irrigation schedules and three types of fertilisers. *Agric. Ecosyst. Environ. 65*, 189-199.

Fares, A., and A.K. Alva, 2000. Evaluation of capacitance probes for optimal irrigation of citrus through soil moisture monitoring in an Entisol profile. *Irrig. Sci. 19,*57–64.

Feaga, J.B., J.S. Selker, R.P. Dick, and D.D. Hemphill, 2010. Long-term nitrate leaching under vegetable production with cover crops in the Pacific Northwest. *Soil Soc. Sci. Am. J. 74*, 186-195.

Gabriel, J.L., J.I. Lizaso, and M. Quemada, 2010. Laboratory versus field calibration of Capacitance Probes. *Soil Sci. Soc. Am. J. 74*, 593–601.

Gabriel, J.L., and M. Quemada, 2011. Replacing bare fallow with cover crops in a maize cropping system: Yield, N uptake and fertiliser fate. *Eur. J. Agron. 34*, 133-143.

Gabriel, J.L., R. Muñoz-Carpena, and M. Quemada, 2012. The role of cover crops in irrigated systems: water balance, nitrate leaching and soil mineral nitrogen accumulation. *Agric. Ecosyst. Environ. 155*, 50–61.

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

Gilks, W., G. Roberts, and S. Sahu, 1998. Adaptive Markov Chain Monte Carlo through regeneration*, J. Am. Statist. Assoc. 443*, 1045-1054.

Isidoro, D., D. Quílez, and R. Aragues, 2006. Environmental impact of irrigation in La Violada District (Spain): II. Nitrogen fertilization and nitrate export patterns in drainage water. *J. Environ. Qual. 35*, 776-785.

Keeney, D.R., and D.W. Nelson, 1982. Nitrogen - inorganic forms. En Page, A L. Methods of soil analysis. Part 2: chemical and microbiological properties. American Society of Agronomy, Soil Sci. Soc. Am., Madison, WI, USA. 643-698.

Lidon, A., C. Ramos, and A. Rodrigo, 1999. Comparison of drainage estimation methods in irrigated citrus orchards. *Irrig. Sci.* 19, 25-36.

Metropolis, N., A.W. Rosenbluth, M.N. Rosenbluth, A.H. Teller, and E. Teller, 1953. Equations of state calculations by fast computing machines. *J. Chem. Phys. 21*, 1087-1091.

Muñoz-Carpena, R., A. Ritter, D.D. Bosch, B. Schaffer, and T.L. Potter, 2008. Summer cover crop impacts on soil percolation nitrogen leaching from a winter corn field. *Agric. Water Manag. 95*, 633-644.

Nash, J.E., and J.V. Sutcliffe, 1970. River flow forecasting through conceptual models. Part 1. A discussion of principles. *J. Hydrol. 10*, 282–290.

Normand, B., S. Recous, G. Vachaud, L. Kengni, and B. Garino, 1997. Nitrogen-15 tracers combined with tension-neutronic method to estimate the nitrogen balance of irrigated maize. *Soil Sci. Soc. Am. J. 61*, 1508–1518.

Papadakis, J., 1966. Climates of the world and their agricultural potentialities. DAPCO, Rome, Italy.

Paramasivam, S., A.K. Alva, A. Fares, and K.S. Sajwan, 2001. Estimation of nitrate leaching in an entisol under optimum citrus production. *Soil Sci. Soc. Am. J. 65*, 914-921.

Ritter, A., F. Hupet, R. Muñoz-Carpena, S. Lambot, and M. Vanclooster, 2003 Using inverse methods for estimating soil hydraulic properties from field data as an alternative to direct methods. *Agric. Water Manage. 59*, 77-96.

Ritter, A., and R. Muñoz-Carpena, 2013 Performance evaluation of hydrological models: Statistical significance for reducing subjectivity in goodness-of-fit assessments. *J. Hydrol. 480*, 33-45.

Salmerón, M., J. Cavero, D. Quílez, y R. Isla, 2010. Winter cover crops affect monoculture maize yield and nitrogen leaching under irrigated Mediterranean conditions. *Agron. J. 102*, 33-42.

Simunek, J., O. Wendroth, and M.Th. van Genuchten, 1999. Soil hydraulic properties from laboratory evaporation experiments by parameter estimation, en: Ed. van Genuchten, M.Th., F.J. Leij, L. Wu, Proceedings of the International Workshop, Characterization and Measurement of the Hydraulic Properties of Unsaturated Porous Media. University of California, Riverside, CA, 713-724.

Soil Survey Staff, 2003. Keys to soil taxonomy. Ninth Edition. USDA, Natural Resources Conservation Service. Madison, WI, USA.

Solorzano, L., 1969. Determination of ammonia in natural waters by the phenolhypoclorite method. *Limnol. Oceanogr. 14*, 799-801.

Strock, J.S., P.M. Porter, and M.P. Russelle, 2004. Cover cropping to reduce nitrate loss through subsurface drainage in the northern US Corn Belt. *J. Environ. Qual. 33*, 1010-1016.

van Genutchen, M.T., 1980. A closed-form equation for predicting the hydraulic conductivity of soil. *Soil Sci. Soc. Am. J. 44*, 892-898.

Van Loon, J., J. Vansteenkiste, J. Diels, and E. Schrevens, 2011. Developing and testing a model for open field horticultural crops to enable use of a 'just-in-time' fertilization management. 19th International Congress on Modelling and Simulation, Perth, Australia. 1016-1022.

Vanclooster, M., P. Viaene, J. Diels, and K. Christiaens, 1996. WAVE: a mathematical model for simulating water and agrochemicals in the soil and vadose environment. In: Reference and user's manual (Release 2.0), Institute for Land and Water Management, Katholieke Universiteit Leuven, Belgium.

Vázquez, N., A. Pardo, M.L. Suso, and M. Quemada, 2006. Drainage and nitrate leaching under processing tomato growth with drip irrigation and plastic mulching. *Agric. Ecosyst. Environ. 112*, 313-323.

Vrugt, J.A., H.V. Gupta, W. Bouten, and S. Sorooshian, 2003. A Shuffled Complex Evolution Metropolis algorithm for optimization and uncertainty assessment of hydrologic model parameters. *Water Resour. Res*. 39, SWC11-SWC116.

Webster, C.P., M.A. Shepherd, K.W.T. Goulding, and E. Lord, 1993. Comparisons of methods for measuring the leaching of mineral nitrogen from arable land. *J. Soil Sci. 44*, 49–62.