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Nitrogen deposition in Spain: modeled patterns and potential implications for conservation

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Abstract

Evidences of an ongoing nitrogen enrichment of Spanish terrestrial ecosystems have been recently recorded. Atmospheric chemical transport models are valuable tools to identify those areas where these effects of atmospheric nitrogen deposition could be occurring. This study documents the performance of two chemical transport models (EMEP and CHIMERE) in predicting annual values of wet deposition of nitrogen and describes its main patterns for the period 2005-2008 in Spain. Wet nitrogen deposition was acceptably predicted by both models, showing better results for oxidized than for reduced nitrogen, particularly using the CHIMERE model. Dry nitrogen deposition may be underestimated, particularly by the EMEP model. Both models estimated higher wet deposition values in Northern and Northeastern Spain, decreasing along a NE-SW axis and ranging 1.2-13.3 and 1.0-8.7 kgN ha^{-1} $y^{-1}$for

EMEP and CHIMERE model, respectively. Total nitrogen deposition (wet plus dry) in 2008 was used to calculate Critical Load exceedances within the Spanish Natura 2000 network (188,856.9 km^2). Threatened areas of 4521.4 and 1657 km^2 were predicted by CHIMERE and EMEP models, respectively. Grassland habitats proved to be the most threatened group, particularly in the Alpine Bio-geographical Region, pointing out that biodiversity conservation in these protected areas could be endangered.

1. Introduction

The global biogeochemical cycle of nitrogen (N) has been deeply altered (Sutton et al., 2011), to the extent that the boundary within which humankind can operate safely has long been crossed (Rockström et al., 2009). Anthropogenic reactive nitrogen (N_r) circulates across different compartments (atmosphere, hydrosphere and terrestrial ecosystems) inducing a cascade of environmental effects, such as tropospheric ozone formation, ecosystem acidification and eutrophication (Bobbink et al., 2010; Galloway et al., 2008; Sutton et al., 2011) . Particularly, eutrophication is still a widespread problem that affects most European ecosystems (EEA, 2013). Increased atmospheric N deposition can directly damage vegetation, alter nutrient ratios in soil and vegetation, and increase plant susceptibility to other stressors, resulting in changes of community composition, loss of biodiversity and invasions of new species (Dise et al., 2011; EEA, 2013).

The Mediterranean Basin presents an extraordinary biological richness recognized as one of the first 25 Global Biodiversity Hotspots for conservation priorities (Myers et al., 2000). Dentener *et al.*, (2006) indicated that central Europe and circum-Mediterranean countries are one of the planet hotspots experiencing high N deposition rates. Nonetheless, scarce information is available on the threat that air pollution and in particular reactive N, can pose to biodiversity in the Mediterranean area (Bleeker et al., 2011; Ochoa-Hueso et al., 2011, 2013).

The implemented Gothenburg Protocol of the Convention on Long-Range Trans-boundary Air Pollution (CLRTAP) under the UNECE framework and the related European policies have resulted in substantial reductions of the emissions of N compounds to the atmosphere in the period 1990-2009 in Europe (EEA, 2011). During the same period, Spanish emission of NH_3 increased 12.8% and NOx emissions decreased 17%, but only after that a continuous increase stopped in 2007 (MAGRAMA, 2013). Increments in NO_3^- deposition in Catalonia

(NE of Spain) during period 1983-2007 have been related with the increase in Spanish NOx emissions (Àvila et al., 2010; Àvila and Rodà, 2012). Moreover, similar trends in N deposition have been detected in mountain areas of the Pyrenees in the period 1997-2007 (Camarero and Catalán, 2012). Total annual atmospheric N deposition loads in eastern Spain have been estimated in 15-30 kg N ha^{-1} yr^{-1}, with dry deposition representing about 40-70% of total N deposition (Àvila and Rodà, 2012; Rodà et al., 2002; Sanz et al., 2002). Regardless of that, atmospheric N deposition in Spain is lower than values recorded in central Europe, from both measured (Lorenz and Becher, 2012) and modeled data (Simpson et al., 2011). However, since changes in species composition occur early in the sequence of N saturation (Emmet, 2007), N deposition effects could be occurring in Spanish natural ecosystems.

Some evidences of N enrichment already occurring in Spanish terrestrial ecosystems have been reported. A continuous increase of nitrophilous plants has been detected in the Iberian Peninsula for the period 1900-2008 using the Global Biodiversity Information facility (GBIF) database (Ariño et al., 2011). Also an increase in the N content in bryophytes, but not in vascular plants, has been observed in herbarium specimens collected in Spain throughout the last century (Peñuelas and Filella, 2001). Rising nitrate concentration in headwater streams detected in areas of NE Spain have been considered a sign of the onset of eutrophication is (Àvila and Rodà, 2012; Camarero and Aniz, 2010).

Suitable N deposition data are needed to identify those areas where effects of N deposition could be occurring in natural ecosystems. Since the deployment of air quality networks is still limited in rural areas, air quality models constitute a valuable tool to quantify air pollution over broad geographical areas. The European Monitoring and Evaluation Program developed the EMEP MSC-W chemical transport model, which estimates regional atmospheric dispersion and deposition of acidifying and eutrophying compounds (S, N), ground level ozone and particulate matter all over Europe. This model plays a key role in the development of emission control strategies for Europe within the framework of the CLRTAP/UNECE and the European Union policies. Similarly, the CHIMERE chemical transport model has been extensively applied to simulate the evolution and spatial distribution of concentration of several pollutants such as ozone and its precursors, aerosols, etc. along with estimates of pollutant deposition (Bessagnet et al. 2004; Vivanco et al. 2008, 2009). The successive developments of this model were recently reviewed on the basis of published investigations by Menut et al. (2013).

Critical loads (CL) are effect thresholds for N deposition, defined under the CLRTAP for the protection of the ecosystems. CL are defined as a quantitative estimate of pollutant deposition below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge (UBA, 2004). Different approaches have been adopted in the Convention to define N critical loads involving either modeling or field evidences. Empirical N critical loads have been defined for specific ecosystems based on observed changes in the structure and function of the ecosystems, primarily in species abundance, composition and/or diversity (Bobbink et al., 2010; Bobbink and Hettelingh, 2011). Exceedance of empirical critical loads has been used in Europe since 1990s to assess impacts on biodiversity in natural systems and, in this way, its use is recommended in the EC Habitats Directive (EC, 2010) to inform whether nitrogen deposition should be recorded as a "threat to future prospects" (Whitfield et al, 2011). However, the definition and application of N empirical critical loads in Mediterranean areas is still very limited and further research is being required (Bobbink et al., 2010; Ochoa-Hueso et al., 2011).

The objectives of this work were 1) to document the performance of atmospheric N deposition values predicted with EMEP and CHIMERE models under Mediterranean environmental conditions; 2) to analyze the distribution of atmospheric N deposition in the Iberian Peninsula; and 3) to assess the possible effects of atmospheric N deposition for biodiversity preservation in the Spanish Natura 2000 network (more than 30% of the Spanish territory). For this analysis, wet deposition of nitrate (NO_3^-) and ammonium (NH_4^+) modeled by EMEP (v 3.8.1) and CHIMERE (v V200603par-rc1 and V2008) models were compared with measured data for the period 2005-2008 obtained from different monitoring networks in Spain: ICP Forests Level II plots, EMEP monitoring network and the Air Quality Network of the Regional Catalan Government. Modeled deposition values were used to calculate exceedances of empirical critical loads in the Natura 2000 network for a preliminary assessment of the possible threat posed by N in these areas.

2. Material and Methods

2.1. Measurements

2.1.1. *ICP Forests Level II network*

The ICP Forest is a biomonitoring program launched in 1985 under the CLRTAP with the aim of providing comprehensive information on forest condition in Europe and the possible relationships to anthropogenic and natural stress factors, in particular air pollution (http://icp-forests.net/). This Program includes Level II plots as intensive monitoring sites offering the possibility of understanding complex ecosystem processes. At these sites, bulk deposition is measured in open areas in the neighbourhood of the forest plots and deposition under canopy is derived from throughfall measurements following standard protocols (http://icp-forests.net/). Measured bulk deposition data of 13 ICP Forest Level II plots located in Spain (Figure 1) were considered for the period 2005-2008. Fortnightly collected data were used to calculate annual accumulated deposition rates (in some occasions data were collected monthly). Contaminated or unrealistic values were removed from the data set. Only those years and plots with maxima 30 days (2 fortnightly periods) of missing measurements per year were considered. Valid data used for the analysis represented 80% of the total dataset. Missing values were filled in with the monthly mean value for that site estimated from data available for the other years. Annual deposition was calculated adding the product of concentration and precipitation for each measuring period. The Spanish Level II plots are located in a range of 50-1650 m.a.s.l, with 421-1787 mm average annual precipitation and 7.1-17.2 ºC average annual temperature.

2.1.2. *EMEP measurement network*

The EMEP program (www.emep.int) of the CLRTAP includes a network for monitoring air pollutant concentration and deposition following standard methodologies and adequate quality assurance procedures (http://www.nilu.no/projects/ccc/manual/index.html). The EMEP network has focused on air pollutants in rural and background areas. These measurements are combined with emissions and modeling data, allowing the assessment of concentration and deposition of air pollutants, the significance of transboundary fluxes and the related exceedances to critical levels and loads. The network needs to ensure an adequate spatial coverage and sufficient temporal resolution to test the effectiveness of the Convention's protocols. In Spain, the current network has 10 monitoring stations located from sea level to 1360 m.a.s.l. (http://www.aemet.es/es/idi/medio_ambiente/vigilancia; Figure 1). Daily samples of precipitation chemistry are collected with wet-only samplers in 9 of the monitoring stations. Measured deposition data accumulated throughout the year following EMEP protocols (www.emep.int) were considered for the period 2005-2008.

- *Catalan Air Quality sites*

Precipitation samples were obtained in four station of the Catalan Air Quality Network (*Xarxa de Vigilància y Prevenció de la Contaminació Atmosfèrica* of the Generalitat de Catalunya) in NE Spain (Figure 1). Weekly precipitation was sampled with wet-only collectors (MCV®, CPH-004, Spain) at 4 sites ranging 198-685 m.a.s.l elevation. All the sites were located in the outskirts of small towns with less that 9000 inhabitants (further information of the sites provided in Àvila et al., 2010). Additionally, weekly wet-only precipitation was also collected at La Castanya experimental site in the Montseny Mountains at 720 m.a.s.l (Figure 1). All samples were analyzed by CREAF laboratory following a protocols published elsewhere (Àvila and Rodà, 2002). Participation in the AQUACON project for "Acid Rain" (Mosello et al., 1998) provided an interlaboratory check for analytical quality. Concentrations were weighted by volume to give annual volume weighted mean (VWM) concentrations and deposition was calculated as the product of annual VWM by annual precipitation.

2.2. Air quality models

2.2.1. EMEP MSC-W chemical transport model

The EMEP programme relies on the collection of emission data from the European countries and the measurements of air and precipitation quality from the EMEP stations to model regional atmospheric dispersion and deposition of air pollutants all over Europe with the EMEP MSC-W model. The model currently uses 20 vertical layers and considers about 140 reactions among 70 species. A detailed description of the model is provided in Simpson et al. (2012). For this study, monthly atmospheric nitrogen deposition data estimated for the period 2005-2008 with the EMEP model rv3.8.1 over Europe using a grid size of 50 km × 50 km were used (Fagerli et al., 2011). Meteorological data were obtained from ECMWF-IFS Cycle36r1 (http://www.ecmwf.int/research/ifsdocs/) and emissions from 2011_CEIP_tends (Fagerli et al., 2011).

2.2.2. CHIMERE regional air quality model

CHIMERE computing modelling was performed using the regional V200603par-rc1 version for the 2005-2007 simulations and the V2008b version for 2008 simulations. More information and detailed description of the model can be found in http://www.lmd.polytechnique.fr/chimere/ and in Menut et al. (2013). The simulations were performed as at a 0.2º- horizontal resolution for the period 2005-2007 and at a 0.1º-horizontal resolution for 2008, covering the Iberian Peninsula and Balearic Islands. A further description of the model setup for the 2005-2007 simulations is described in Vivanco et al. (2009). For 2008 a different set-up was used. For the same territory extension resolutions for the coarser and finer domains were 0.2 and 0.1º respectively. On the other hand, in 2008 the WRF model was used to obtain the meteorological fields. Regarding emissions, they were derived from the annual totals of the EMEP database (Vestreng et al., 2005). Spatial emission distribution was performed and NMVOC speciation was also estimated as indicated in Vivanco et al. (2009).

2.3. Comparison of measured and modelled data

The location of the monitoring sites of the different networks was matched with the corresponding EMEP and CHIMERE grid cells using ARCGIS version 9.3 (ESRI, Redlands CA, USA). Annual bulk deposition of NO_3^- and NH_4^+ measured in the ICP Forest plots and wet-only deposition measured in EMEP network and Catalan Air Quality sites were compared with modelled wet deposition data obtained with EMEP and CHIMERE models. Traditional metrics commonly used in model evaluation (Chang and Hanna, 2004; Yu et al., 2006), such as index of agreement (IOA), mean normalized bias (MNB), mean normalized absolute error (MNAE) and root mean square error (RMSE) were calculated as shown in Table 1 for nitrate wet deposition (WDON), ammonium wet deposition (WDRN) and total N wet deposition (WDTN). Also scatterplots, Pearson's correlation coefficients and linear regression were used to study the relationships between modelled and measured values. All the analysis were performed using Statistica version 11 (StatSoft, Inc. Tule, OK, USA). Alpha was set at 0.05.

2.4. Risk assessment of atmospheric N deposition in the Natura 2000 network

Total atmospheric N deposition, including wet and dry deposition, estimated with EMEP and CHIMERE models for 2008 was used to evaluate the risk for vegetation in the areas included in the Spanish Natura 2000 designated areas. Only the Habitat Types of Community Interest described in the Annex I of the Habitats Directive (EC, 2010) and included in the Natura 2000 network were considered. These habitats covered 34% of the 188,856.9 km^2 included in the Spanish Natura 2000 network. Empirical critical loads (CL) of N deposition recently revised by Bobbink et al. (2010) were used for estimating N exceedances, calculated as deposition minus CL (positive exceedance is taken to be undesirable). Aquatic and some other habitats were excluded of the analysis: coastal and halophytic habitats, freshwater habitats, rocky habitats and caves, and wetlands. Consequently, the area used for estimating N exceedances occupied an extension of 57,675.7 km^2. The CL assigned to each habitat type was defined as the average of the range of CL reported by Bobbink and Hettelingh (2011) for habitat type. When a N empirical CL was not defined for a habitat, the CL of similar or equivalent habitats were used (these cases represented about 35% of the surface analyzed). Table 2 shows the sub-groups of habitats included in the analysis and the corresponding N empirical CL. Annex I includes the details of the N empirical CL applied to each vegetation type. The scientific background supporting the empirical CL of nitrogen is described in detail in Bobbink and Hettelingh (2011). The exceedance values and the area where the CL is exceeded were estimated for each vegetation type. Similarly, for each habitat sub-group CL exceedances were estimated weighting exceedances by the corresponding area.

3. Results and discussion

3.1. Comparison of measured and modelled data

Some metrics (Table 3) and scatterplots (Figure 2) were performed to compare the observed values of annual N wet deposition with those estimated by the EMEP and CHIMERE air quality models. A more detailed evaluation is currently being developed considering monthly values (Vivanco et al., unpublished results).

In general, CHIMERE model seems to perform better for WDON than EMEP, since the former obtained a better correlation and IOA and a lower error metrics (RMSE, MNB and MNAE). Besides, scatterplots of model results vs. observations showed similar slope and interception. In the case of WDRN, the CHIMERE model seems to provide worse estimates than the EMEP model as deduced from the lower correlation and IOA, higher MNB and MNAE (Table 3), and the regression functions and scatterplots (Figure 2). CHIMERE clearly underestimates WDRN (with a MNB of -46%). Meanwhile, EMEP estimates showed a satisfactory MNB, but MNAE was poor, not showing a clear trend to under- or overprediction. For total wet deposition (WDTN), the correlation for the CHIMERE results is better, while the EMEP model provides a higher IOA. However, CHIMERE clearly subpredicts WDTN (with a MNB of -26%), mostly due to the strong underprediction of

WDRN. The values of RMSE y MNAE are very similar for both models. The RMSE metrics indicated that the average difference between both model estimations for WDTN was about 0.2 kgN ha^{-1} y^{-1}.

Correlation coefficients of wet deposition values were 0.40 and 0.37 with EMEP, and 0.67 and 0.32 with CHIMERE, for WDON and WDRN, respectively. In general, the scatterplots of modelled vs. measured values of N deposition (Figure 2) showed y-interception values (‘a’) clearly above 0 kgN/ha and relatively low slopes (‘b’; 0.20-0.60) indicating that both CHIMERE and EMEP models generally underestimate the high and overestimate the low N deposition values.

Interestingly, annual precipitation estimates used by both models correlated better with measured values than wet deposition. EMEP and CHIMERE models showed similar error indices with some scattering and underestimation of high precipitation, but all the evaluation metrics indicated an adequate model performance (high IOA values and relatively low values of MNB and MNAE). When analysing the precipitation results for each measurement network independently, the correlation and IOA was higher when comparing models estimates with ICP Forest data than when considering the EMEP monitoring network or Catalan sites. However the error expressed as RMSE was higher for the ICP Forest data since both models underestimated the high precipitation values recorded in this network.

Both estimates of precipitation performed better for Spanish ICP Forest dataset than values reported in a previous comparison with EMEP model for other European ICP Forest data excluding Mediterranean area (Simpson et al., 2006a).This result could be explained by the homogeneity of precipitation collectors used in Spain, compared to the variety of collectors used by the different countries at the time when previous comparisons were performed (Erisman et al., 2003).

Nitrogen wet deposition estimations were also compared with observed values for each measurement network independently. Modelling N wet deposition in EMEP sites obtained the best results, especially when using the EMEP model (Table 3), with correlation coefficients in a range (0.60-0.76) similar to those reported for other European areas (Simpson et al., 2006b). For the Spanish EMEP sites, EMEP model generally slightly overestimated the WDTN observed values (MNB equal to 5%) while CHIMERE underestimated them (MNB equal to 16%). Evaluation of EMEP model performance is regularly assessed in EMEP reports (http://www.emep.int/) through comparing model estimations with values measured in the EMEP monitoring network. A recent review reported that EMEP model performance for the Mediterranean area was comparable to the one found for other parts in Europe (Aas et al., 2010).

Model estimates of N wet deposition for the ICP Forest sites were similar or slightly worse than for EMEP sites. In this case, both EMEP and CHIMERE underestimated wet N deposition values of reduced and oxidized forms (Table 3). These underestimations can be partially explained by the bulk samplers used by the ICP Forest network to collect wet deposition, since some influence of dry deposition onto the funnels cannot be disregarded. The proportion of dry deposition collected in the funnels depends on location, climate, sampler aerodynamic characteristics and chemical component (Erisman et al., 2003). On the other hand, wet-only samplers used in the EMEP sites might underestimate wet deposition due to the delayed opening of the lid at the onset of precipitation, when the concentration of compounds may be highest, and also because of the different aerodynamic characteristics of the samplers (Erisman et al., 2003; Thimonier, 1998).

Model performance was quite poor when comparing with measurements obtained in the 5 monitoring Catalan sites. Correlations between modelled and measured deposition were not significant and the IOA metrics were always below 0.50 for both model approaches, even if precipitation estimations were acceptable (Table 3). While EMEP overestimated N wet deposition in this area, and especially WDRN, CHIMERE underestimated the deposition showing smaller errors than EMEP. Some variability is always expected when comparing values modelled for an entire grid cell with measurements performed at single sites. The lack of correlation in the Catalan region could be due to the small range of deposition values. The complex topography of this region and the influence of local emissions might also explain the poor model performance at small regional scale, as it is argued in previous studies for similar regions (e.g. Simpson et al., 2006a).

Evaluation metrics and scatterplots indicate that estimations of total N wet deposition of both models are within acceptable ranges of performance although results should be applied with caution, especially at small regional scale. The higher resolution used with CHIMERE for 2008 estimations (10x10 km compared to 20x20 km resolution used for 2005-2007) did not improve the overall estimation of wet deposition and all the evaluation metrics considered were within the ranges of values observed for previous years (data not shown). Some studies, such as Cuvelier et al. (2013) and Vivanco et al. (2008), showed that an increase in model resolution did not lead to an improvement of model performance at rural sites for air concentration. Similarly, different EMEP model runs with finer resolution found small improvements in the estimations of air concentration of most acidifying and eutrophying compounds, but similar performance for wet deposition and concentration in precipitation in rural areas (Nyíri and Gauss, 2010). Increasing model resolution and a finer placement of emission sources are expected to have more remarkable improvements in polluted than in rural areas (Cuvelier et al., 2013; Hirst and Storvik, 2002; Nyíri and Gauss, 2010).

3.2. Atmospheric nitrogen deposition in Spain

Annual values of N wet deposition measured in the monitoring sites for the period 2005-2008 ranged 0.3-7.7 kgN ha^{-1} y^{-1} of WDRN, 0.4-9.6 kgN ha^{-1} y^{-1} of WDON, and 0.7-13.3 kgN ha^{-1} y^{-1} of WDTN. Unfortunately, none of the monitoring sites included in this analysis were located in the Canary or Balearic Islands, thus the reported values of Spanish N wet deposition represent only the peninsular territory.

For each monitoring station, interannual variability of measured wet deposition represented about 25-30% of the average value. Similar interannual variability was observed in wet deposition values estimated with CHIMERE in the cells corresponding to the experimental sites while EMEP model presented lower interannual variability (13-14%). Despite this lower interannual variability observed in the EMEP results, both models provided acceptable predictions of wet deposition values as discussed in the previous section. It is interesting that the noticeable reduction of oxidized N emissions in 2008 with respect to the previous year (-14%) was not reflected in measured nor in modeled WDON (Figure 3). This result is probably related to the higher precipitation rate registered in 2008 compared to 2007 and highlights the importance of considering precipitation variability in order to evaluate the effects of changing emission in deposition trends. In fact, total N wet deposition (WDTN) was significantly correlated with precipitation ($r=0.61$; $p<0.05$). In this sense, maximum deposition was mainly located in the Northern area of Spain where the highest precipitations occur.

Similarly to measured values, total N wet deposition predicted by the models for the monitoring sites for the period 2005-2008 ranged 1.2-13.3 kgN ha^{-1} $y^{-1}$for EMEP and 1.0-8.7 kgN ha^{-1} y^{-1} for CHIMERE. Considering all the Spanish territory included in model grids (i.e. excluding the Canary Islands), WDTN estimated in 2008 were within the range 1.5-13.4 kgN ha^{-1} y^{-1} when using EMEP and 0.9-16.1 kgN ha^{-1} y^{-1} when using CHIMERE. Both models showed that N wet deposition distribution in Spain decreased along a NE-SW axis, with higher deposition in the northern and eastern coastal regions than inland and southern areas (Figure 4). EMEP model showed similar distribution patterns of oxidized and reduced N deposition, with the highest values in NE of Spain (reaching 6.5 and 7.7 kgN ha^{-1} y^{-1}, respectively). CHIMERE estimated values higher than EMEP for WDRN in the Pyrenees along the border with France, with values up to 12.1 kgN ha^{-1} y^{-1}. On the other hand, oxidized N estimated with CHIMERE showed maxima values throughout the northern coast and in the south of Spain close to the Strait of Gibraltar, and also higher WDON and WDTN than EMEP model in Northwestern Spain (Galicia Region).

This distribution pattern of N wet deposition across the Spanish territory clearly responds to the spatial distribution of the expected three main drivers: regional emissions, precipitation distribution and transboundary contribution. In fact, the areas withstanding the highest loads of N deposition, mainly located in the north and NE regions, enclose some highly populated and industrialized areas and present high precipitation rates. Moreover, according to EMEP reports (e.g. Nyíri et al., 2010), transboundary pollution can represent an important contribution for N wet deposition in Northern Spain regions like Pyrenees mountain range (up to 60-70% in 2008 in some areas).

Average measured wet deposition of oxidized N (WDON) was about 12% higher than reduced N (WDRN) for the period analysed (2005-2008); although many of the inland sites located far from the coast and from the main industrial areas showed slightly higher WDRN than WDON. This composition of measured wet deposition seems to reflect national emissions, since average values for the period 2005-2008 of oxidized N were 26% higher than emissions of reduced N (1315 kTon of NOxvs 387 kTon of NH_3 respectively; MAGRAMA, 2013). However, modeled deposition of oxidized and reduced N in these monitoring sites showed an averaged ratio WDON/WDRN slightly lower than expected in the case of EMEP model (0.96) and clearly higher for CHIMERE model (2.67).

Chemical transport models also provide estimations of N dry deposition. When considering both dry and wet N deposition, total N deposition in 2008 in Spain reached maxima values of 19.5 kgN ha^{-1} y^{-1} and 22.9 kgN ha^{-1} y^{-1} for EMEP and CHIMERE, respectively. Distribution of total N deposition followed patterns similar to those observed for wet deposition, with higher values in the north and NE of the country and close to the strait of Gibraltar in the south (Figure 4).

Dry deposition estimated with EMEP in 2008 represented 14-59% of total N deposition with an average value of 40 %. In the case of CHIMERE estimations, dry deposition represented 11-83% of total N deposition with an average value of 54 %. Previous studies performed in Spain have calculated that dry deposition represented 62-67% of total N deposition in *Quercus ilex* forests (Rodá et al., 2002) and 40-75% in *Pinus halepensis* forests (Sanz et al., 2002) in NE and eastern Spain respectively. Values estimated by the models on those cells of the grid where monitoring plots are located in *Q. ilex* or *P. halepensis* forests, showed that 39% with EMEP and 54% with CHIMERE of N total deposition was associated to dry deposition. Although data from different years are compared, these results might suggest that the importance of dry deposition could be underestimated, particularly by the EMEP model, for the Mediterranean area. However little information is available and more detailed studies are needed to characterize dry deposition in Spanish ecosystems under typically Mediterranean climate conditions.

3.3.- Risk assessment of atmospheric N deposition in the Natura 2000 network

Total N deposition (including wet and dry deposition) estimated with EMEP and CHIMERE models for 2008 was used to assess the risk of N enrichment in terrestrial Habitat Types of Community Interest. Exceedances of empirical N critical load and the area affected were calculated for the different vegetation types (Table 2 and Annex I). The CHIMERE model predicted an area at risk twice as large as the one foreseen with EMEP model (4521.4 and 1657 km^2 respectively, Table 2). The threatened areas were mainly distributed in high N deposition regions (Figures 4 and 5) and empirical CL of 10 kgN ha^{-1} y^{-1} or lower had been ascribed to more than 70% of them. Thus, both high deposition rates and relatively low CL were the parameters determining the areas at risk.

Both models predicted exceedances of CL mainly in NE Spain. According to EMEP, the highest exceedance (up to 12.0 kgN/ha) occurred in NE Catalonia, close to Barcelona, in areas covered with scrub and grassland habitats. On the other hand, the highest exceedance predicted with CHIMERE (up to 13.3 kgN/ha) was registered in Central Pyrenees, mainly in grassland habitats. Both models highlighted that the highest number of threatened areas occurred in the Pyrenees, where 9.1% and 18.4% of the Spanish Alpine Bio-geographical Region could be withstanding a CL exceedance according to EMEP and CHIMERE models respectively. Interestingly, an increase in bulk N deposition and nitrate concentration in headwater streams has been detected for the period 1997-2007 in the *Aigüestortes i Estany de Sant Maurici* National Park in the Central Pyrenees (2236 m.a.s.l.; Camarero and Catalán, 2012),suggesting a possible N saturation in these high altitude catchments Although other climate factors should be taken into account as potential drivers of nitrate leaching (Baron et al., 2009), the N saturation of alpine catchments in Central Pyrenees seems to be a generalized process and it could be widespread in the Pyrenees System (Camarero and Aniz, 2010). The CHIMERE model also pointed out other areas spread through the Spanish territory where exceedances of N empirical CL could be occurring, such as mountain areas north of Madrid region and Eastern Coast, on the Cantabrian Range and near the Strait of Gibraltar. The higher resolution used in CHIMERE simulation could partially explain the detection of more areas at risk of N enrichment.

'Natural and semi-natural grasslands' is the habitat group most threatened by N deposition, since an average from 9.1 to 15.5% (depending on the model approach) of the assessed surface is at risk and presents some subgroups such as 'natural grasslands' with up to 42-71% of the area affected (Table 2). Moreover, the 'siliceous Pyrenean *Festuca eskia* grasslands' within this sub-group is the habitat type at highest risk within Spanish Natura 2000 network, with a threatened surface from 76 to 100% of the total assessed (Annex I). For 'natural and semi-natural grasslands' the CHIMERE model predicts an averaged CL exceedance above 7 kgN ha^{-1}. The habitats in this group were assigned relatively low CL, but most of them were ascribed to its specific habitat type and had a good reliability (#), according to Bobbink and Hettelingh (2011) (Annex 1). The major uncertainty regarding the potential threat to Pyrenean grasslands, and other grasslands located in mountain areas, is that no monitoring site was able to test the performance of the models in this alpine region. Although both models obtained acceptable approximations (data not shown) to N wet deposition in the closest monitoring sites to Pyrenean grasslands (Figure 1), these monitoring sites are located at altitudes below threatened habitats. Moreover, other habitat sub-groups typical of mountains areas (Table 2) like 'temperate mountainous coniferous forest' (e.g. *Pinus uncinata* or *Abies pinsapo* forests) and habitat types like 'Luzulo-Fagetum beech forests' (Annex I) presented a high percentage of their surface area at risk. Thus, further deployment of air quality monitoring networks should be planned in Spanish mountain areas for assessing the risk of air pollution to these particularly rich and valuable ecosystems.

The EMEP model also predicted an averaged exceedance of the N empirical CL above 4 kgN ha^{-1} in 'Mediterranean sclerophyllous forests' (Table 2), although the area affected was only around 5%. Those sclerophyllous forests experiencing N exceedances are mainly located in the NE Spain, close to Barcelona, where high N atmospheric deposition has been reported (Rodà et al., 2002). Increases of NO_3^- concentration in streamwaters in undisturbed catchments in this area have been detected, being considered a sign of the onset of eutrophication (Àvila and Rodà, 2012). However, these ecosystems are considered still far from N saturation because most of the deposited N is retained within the ecosystem (Àvila and Rodà, 2012). An empirical CL of 15 kgN ha^{-1} y^{-1} was ascribed to these sclerophyllous forests for prevention of nitrate leaching from the ecosystem following expert criteria (Bobbink and Hettelingh, 2011), but more information is needed to define CL for the protection of changes in vegetation or other effects that could appear before N saturation (Emmet, 2007). In this sense, an empirical CL of 5.5 kgN ha^{-1} y^{-1}has been proposed for the protection of epiphytic lichens in a similar ecosystem in California (Fenn et al., 2010).

This analysis represents the first approach to assess the risk of N enrichment for Spanish ecosystems. Although further investigation is urgently needed to confirm the suitability of N empirical critical loads used, this study points out that effects of N enrichment could be already occurring in some natural ecosystems, particularly in grasslands and forest of mountain areas located in the north (Pyrenees, Cantabrian Range) and other habitats located close to high emission sources such as big cities (Barcelona, Madrid), industrial areas located in the east coast or the Strait of Gibraltar. Interestingly, exceedances of N critical loads were related with high WDON more often than with high WDRN or dry deposition rates.

4. Conclusions

This performance of the EMEP and CHIMERE air quality models to estimate N wet deposition in Spain showed that both models provided acceptable estimates, particularly for oxidized N, although results should be applied with caution especially at small regional scale. This result is especially relevant in a country like Spain where several mountains ranges cross the territory. Nitrogen wet deposition in Spain reached maxima measured values up to 13.3 kgN ha^{-1} y^{-1} for the period 2005-2008. Both models estimated higher N wet deposition in the north and NE Spain. While measured oxidized N wet deposition was on average 12% higher than reduced N, CHIMERE model overestimated the ratio between oxidized and reduced N wet deposition. Adding dry deposition, total N deposition in 2008 in Spain reached maxima values of 19.5 kgN ha^{-1} y^{-1} and 22.9 kgN ha^{-1} y^{-1} calculated with EMEP and CHIMERE respectively. Distribution of total N deposition followed similar patterns observed for wet deposition. Total atmospheric N deposition exceeded empirical critical loads proposed for the protection of terrestrial Habitat Types of Community Interest included in the Natura 2000 net. The habitats presenting higher risk of N effects were the natural and semi-natural grasslands and forest of mountain areas located in the north (Pyrenees, Cantabrian Range). This result highlights the need to extend air quality networks and include some monitoring stations in mountains areas. Other habitats showing exceedances of N empirical critical loads were some forests and grasslands located close to high emission sources such as big cities (Barcelona, Madrid), industrial areas located in the east coast or the Strait of Gibraltar. This preliminary analysis indicates that atmospheric N deposition should be considered as a factor that could be affecting the biodiversity and health of the natural ecosystems in Spain. More detailed investigations should be carried out to quantify these effects and to explore possible management practices that might ameliorate these effects.

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References

1. Aas W, Solberg S, Gauss M, Simpson D. (2010). The Mediterranean Region. In: *Transboundary Acidification, Eutrophication and Ground Level Ozone in Europe in 2008. EMEP Status Report 2010*. The Norwegian Meteorological Institute, Oslo, Norway, pp. 99-104

2. Ariño AH, Gimeno BS, Pérez de Zabalza A, Ibáñez R, Ederra A, Santamaría JM (2011) Influence of nitrogen deposition on plant biodiversity at Natura 2000 sites in Spain. In: *Nitrogen Deposition and Natura 2000. Science & practice in determining environmental impacts*. pp. 140-146

3. Àvila A, Rodà F (2002)Assessing decadal changes in rainwater alkalinity at a rural Mediterranean site in the Montseny Mountains (NE Spain). *Atmospheric Environment* **36**: 2881–2890

4. Àvila A, Rodà F (2012) Changes in atmospheric deposition and streamwater chemistry over 25 years in undisturbed catchments in a Mediterranean mountain environment. *Science of the Total Environment* **434**: 18–27

5. Àvila A, Molowny-Horas R, Gimeno BS, Peñuelas J (2010) Analysis of decadal time series in wet N concentrations at five rural sites in NE Spain. *Water, Air and Soil Pollution* **207** (1-4): 123-138

6. Baron JS, Schmidt TM, Hartman MD (2009) Climate-induced changes in high elevation stream nitrate dynamics. *Global Change Biology* **15**: 1777-1789

7. Bessagnet B, Hodzic A, Vautard R, Beekmann M, Rouil L, Rosset R (2004) Aerosol modelling with CHIMERE – first evaluation at continental scale. *Atmospheric Environment* 38(18): 2803–2817

8. Bleeker A, Hicks WK, Dentener E, Galloway J, Erisman JW (2011) N deposition as a threat to the World's protected areas under the Convention on Biological Diversity. *Environmental Pollution* **159**(10): 2280-2288

9. Bobbink R, Hettelingh JP (eds.) (2011) Review and revision of empirical critical loads and dose-response relationships, Coordination Centre for Effects, National Institute for Public Health and the Environment (RIVM), www.rivm.nl/cce. 244 pp.

10. Bobbink R, Hicks K, Galloway J, Spranger T, Alkemade R, Ashmore M, Bustamante M, Cinderby S, Davidson E, Dentener F, Emmett B, Erisman JW, Fenn M, Gilliam F, Nordin A,

Pardo L, de Vries W (2010) Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. *Ecological Applications* **20**(1): 30-59

11. Camarero L, Aniz M (2010) Surface waters monitoring in the LTER-Aigüestortes node: trends and indicators of the impacts of N and S atmospheric deposition. *Ecosistemas* **19**(2): 24-41 (in spanish)

12. Camarero L, Catalan J (2012) Atmospheric phosphorus deposition may cause lakes to revert from phosphorus limitation back to nitrogen limitation. *Nature Communications* **3**(1118)

13. Chang JC, Hanna SR (2004) Air quality model performance evaluation. *Meteorology and Atmospheric Physics* **87**: 167-196

14. Cuvelier C, Thunis P, Karam D, Schaap M, Hendriks C, Kranenburg R, Fagerli H, Nyiri A, Simpson D, Wind P, Schulz M, Bessagnet B, Colette A, Terrenoire E, Rouïl L, Stern R, Graff A, Baldasano JM, Pay MT (2013) ScaleDep: Performance of European chemistry-transport models as function of horizontal special resolution. EMEP Technical report 1/2013. 63 pp.

15. Dentener F, Drevet J, Lamarque JF, Bey I, Eickhout B, Fiore AM, Hauglustaine D, Horowitz LW, Krol M, Kulshrestha UC, Lawrence M, Galy-Lacaux C, Rast S, Shindell D, Stevenson D, Van Noije T, Atherton C, Bell N, Bergman D, Butler T, Cofala J, Collins B, Doherty R, Ellingsen K, Galloway J, Gauss M, Montanaro V,.Muller JF, Pitari G, Rodriguez J, Sanderson M, Solmon F, Strahan S, Schultz M, Sudo K, Szopa S, Wild O (2006) Nitrogen and sulfur deposition on regional and global scales: A multi-model evaluation. *Global Biogeochemical Cycles* **20**(4): GB4003

16. Dise NB, Ashmore M, Belyazid S, Bleeker A, Bobbink B, de Vries W, Erisman JW, Spranger T, Stevens CJ, van den Berg L (2011) Nitrogen as a threat to European terrestrial biodiversity. En: Sutton MA et al. (eds). *The European Nitrogen Assessment*. Sources, effects and Polcy Perspectives, Cambridge University Press, pp. 463-494

17. EEA (2011) Air quality in Europe – 2011 Report. European Environment Agency Technical Report 12/2011. Available on-line at http://www.eea.europa.eu

18. EEA (2013) Air quality in Europe – 2013 Report. European Environment Agency Technical Report No 9/2013. Available on-line at http://www.eea.europa.eu

19. Emmett AB (2007) Nitrogen saturation of terrestrial ecosystems: Some recent findings and their implications for our conceptual framework. *Water, Soil and Air Pollution: Focus* **7**: 99-109

20. Erisman JW, Mols H, Fonteijn P, Geusebroek M, Draaijers G, Bleeker A, van der Veen D (2003) Field intercomparison of precipitation measurements performed within the framework of the Pan European Intensive Monitoring Program of EU/ICP Forest. *Environmental Pollution* **125**: 139–155

21. Fagerli H, Gauss M, Benedictow A, Griesfeller J, Jonson JE, Nyiri A, Schulz M, Simpson D, Steensen BM, Tsyro S, Valdebenito A, Wind P, Aas W, Hjellbrekke AG, Mareckova K, Wankmüller R, Iversen T, Kirkevag A, Seland O, Vieno M (2011) *Transboundary acidification, eutrophication and ground level ozone in Europe in 2009. EMEP Status Report 1/2011*. Norwegian Meteorological Institute, Oslo. 127 pp.

22. Fenn ME, Allen EB, Weiss SB, Jovan S, Geiser LH, Tonnesen GS, Johnson RF, Rao LE, Gimeno BS, Yuani F, Meixner T, Bytnerowicz A (2010) Nitrogen critical loads and management alternatives for N-impacted ecosystems in California. *Journal of Environmental Management* **91**: 2404-2423

23. Galloway JN, Townsend AR, Erisman JW, Bekunda M, Cai ZC, Freney JR, Martinelli LA, Seitzinger SP, Sutton MA (2008) Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions. *Science* **320**(5878): 889-892

24. Hirst D, Storvik G (2003) Estimating critical load exceedance by combining the EMEP model with data from measurement stations. *Science of the Total Environment* **310**:163–170

25. EC (2010). Council Directive 92/43/EEC of 21 May 1992 on the conservation of natural habitats and of wild fauna and flora. European Commission. Consolidated version 1.1. 2007.

26. Lorenz M, Becher G (eds.) (2012) Forest Condition in Europe, 2012. Technical Report of ICP Forests. Work Report of the Thünen Institute for World Forestry 2012/1. ICP Forests, Hamburg. 165 pp.

27. MAGRAMA (2013). Inventario de Emisiones a la Atmósfera de España. Edición 2013 (serie 1990-2011). Sumario de resultados de acidificadores, eutrofizadores y precursores del ozono. Available on-line at www.magrama.gob.es

28. Menut L, Bessagnet B, Khvorostyanov D, Beekmann M, Blond N, Colette A, Coll I, Curci G, Foret G, Hodzic A, Mailler S, Meleux F, Monge J-L, Pison I, Siour G, Turquety S, Valari M, Vautard R, Vivanco MG (2013) CHIMERE 2013: a model for regional atmospheric composition modeling. *Geoscientific Model Development* **6**(4): 981-1028

29. Mosello R, Bianchi m, Geiss H, Marchetto A, Serrini G, Serrini Lanza G, Tartari GA, Muntau H (1998) AQUACON-MedBas Subproject No. 6. Acid rain analysis. Intercomparison 1/97. Joint Res. Centre European Commission, Rep. EUR 18135 EN, 65 pp.

30. Myers N, Mittermeier RA, Mittermeier CG, da Fonseca GA, Kent J (2000) Biodiversity hotspots for conservation priorities. *Nature* **403**(6772): 853-858

31. Nyíri Á, Gauss M (2010) Improved resolution in the EMEP model. In: *Transboundary Acidification, Eutrophication and Ground Level Ozone in Europe in 2008. EMEP Status Report 2010*. The Norwegian Meteorological Institute, Oslo, Norway, pp. 99-104

32. Nyíri Á, Gauss M, Klein H (2010) Transboundary air pollution by main pollutants (S, N, O3) and PM in 2010. Spain. MSC-W Data Note 1/2010. ISSN 1890-0003. 24 pp.

33. Ochoa-Hueso R, Allen EB, Branquinho C, Cruz C, Dias T, Fenn ME, Manrique E, Pérez-Corona ME., Sheppard LJ, Stock WD (2011) Nitrogen deposition effects on Mediterranean-type ecosystems: An ecological assessment. *Environmental Pollution* **159(**10): 2265-2279

34. Ochoa-Hueso R, Stevens CJ, Ortiz-Llorente MJ, Manrique E (2013) Soil chemistry and fertility alterations in response to N application in a semiarid Mediterranean shrubland. *Science of the Total Environment* **452-453:**78-86

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

36. Rockström J, Steffen W, Noone K, Persson Å, Chapin FS, Lambin EF,Lenton TM, Scheffer M, Folke C, Schellnhuber HJ, Nykvist B, de Wit CA, Hughes T, van der Leeuw S, Rodhe H, Sörlin S, Snyder PK, Costanza R, Svedin U, Falkenmark M, Karlberg L, Corell RW, Fabry VJ, Hansen J, Walker B, Liverman D, Richardson K, Crutzen P, Foley JA (2009). A safe operating space for humanity. *Nature*, **461**(7263), 472-475.

37. Rodà F, Àvila A, Rodrigo A (2002) Nitrogen deposition in Mediterranean forests. *Environmental Pollution* **118**: 205-213

38. Sanz MJ, Carratalá A, Gimeno C, Millán MM (2002) Atmospheric nitrogen deposition on the east coast of Spain: relevance of dry deposition in semi-arid Mediterranean regions. *Environmental Pollution* **118**: 259-272

39. Simpson D, Fagerli H, Hellsten S, Knulst JC, Westling O (2006a) Comparison of modelled and monitored deposition fluxes of sulphur and nitrogen to ICP-forest sites in Europe. *Biogeosciences* **3**: 337-355

40. Simpson D, Butterbach-Bahl K, Fagerl, H, Kesik M, Skiba U, Tang S. (2006b) Deposition and emissions of reactive nitrogen over European forests: a modelling study. *Atmospheric Environment* 40(29): 5712-5726

41. Simpson et al., 2011 (modeled data for Spain are lower than European values)

42. Simpson, D, Benedictow, A, Berge, H, Bergstrom, R, Emberson, LD; Fagerli, H; Flechard, CR; Hayman, GD; Gauss, M ; Jonson, JE; Jenkin, ME; Nyiri, A; Richter, ; Semeena, VS; Tsyro, S; Tuovinen, JP; Valdebenito, A; Wind, P. (2012). The EMEP MSC-W chemical transport model - technical description. *Atmospheric Chemistry and Physics* 12(16): 7825-7865

43. Sutton MA, Billen G, Bleeker A, Erisman JW, Grennfelt P, van Grinsven H, Grizzetti B, Howard CM, Leip A (2011) The European nitrogen Assessment. Technical Summary. En: Sutton MA et al. (eds). The European Nitrogen Assessment. Sources, effects and Polcy Perspectives, Cambridge University Press, 2011, pp. xxxv-li

44. Thimonier A. (1998) Measurement of atmospheric deposition under forest canopies: some recommendations for equipment and sampling design. *Environmental Monitoring and Assessment* 52: 353–387

45. UBA (2004). Manual on methodologies and criteria for modelling and mapping of critical loads and levels and air pollution effects, risks and trends. Umweltbundesamt, Dessau, Germany. Available on-line at http://www.icpmapping.org

46. Vestreng V, Breivik K, Adams M, Wagener A, Goodwin J, Rozovskkaya O, Pacyna JM (2005) Inventory Review 2005, Emission Data Reported to LRTAP Convention and NEC Directive, Initial review of HMs and POPs, Technical Report MSC-W 1/2005.

47. Vivanco MG, Correa M, Azula O, Palomino I, Martín F (2008). Influence of model resolution on ozone predictions over Madrid area (Spain) The 2008 International Conference on Computational Science and Applications (ICCSA 2008). Perugia (Italy) Lecture Notes in Computing Science LNCS 5072. Vol. I, Pp. 165-178, Editorial: Springer ISBN-10: 3-540-69838-8 Germany.

48. Vivanco MG, Palomino I, Vautard R, Bessagnet B, Martín F, Menut L, Jiménez S (2009) Multi-year assessment of photochemical air quality simulation over Spain. *Environmental Modelling & Software* **24**: 63-73

49. Whitfield C, Strachan I, Aherne J, Dirnböck T, Dise N, Franzaring J, Hall J, Hens M, van Hinsberg A, Mansat A, Martins-Louçao MA, Mohaupt-Jahr B, Nielsen KE, Pesch R, Rowe E, Santamaría JM (2011) Assessing Nitrogen Deposition Impacts on Conservation Status. In Hicks, et al. (eds.) *Nitrogen Deposition and Natura 2000: Science and practice in determining environmental impacts*. COST729/Nine/ESF/CCW/JNCC/SEI Workshop proceedings. COST. xxx pp.

50. Yu S, Eder B, Dennis R, Schwartz SH (2006) New unbiased symmetric metrics for evaluation of air quality models. *Atmospheric Science Letters* **7**: 26-34

Table 1. Definition of the metrics used for evaluating model performance. N: pairs of modelled (*Mi)* and observed (*Oi)* depositions . $\overline{O}$ corresponds to the arithmetic mean of observed values. The index *i* is over time series and over all the locations in the domain.

Index of agreement	$IOA = 1 - \frac{\sum (M_i - O_i)^2}{\sum \left(\lvert P_i - \overline{O} \rvert + \lvert O_i - \overline{O} \rvert \right)^2}$
Mean normalized bias	$MNB = \frac{1}{N} \sum \left(\frac{M_i - O_i}{O_i} \right) = \left(\frac{1}{N} \sum \frac{M_i}{O_i} - 1 \right)$
Mean normalized absolute error	$MNAE = \frac{1}{N} \sum \left(\frac{\lvert M_i - O_i \rvert}{O_i} \right)$
Root mean square error	$RMSE = \left[\frac{1}{N} \sum (M_i - O_i)^2 \right]^{\frac{1}{2}}$

Table 2. Surface area of habitat sub-groups from Annex 1 of Habitats Directive assessed for exceedance of empirical critical loads (CL_{exc}) and results, according EMEP and CHIMERE modelizations.

Sub-groups from Annex I of Habitats Directive	Area assessed (km^2)	CL (kgN ha^{-1} y^{-1})	EMEP CL_{exc} area (km^2 (%))	CHIMERE CL_{exc}area (km^2 (%))	EMEP CL_{exc} Avg. (kg/ha)	CHIMERE CL_{exc}Avg. (kg/ha)
21. Sea dunes of the Atlantic coast	21.8	11.5 – 15.0	n.e.	0.04 (0.2)	n.e.	4.21
22. Sea dunes of the Mediterranean coast	259.4	9.0 – 11.5	6.1 (2.3)	10.4 (4.0)	2.01	2.14
4. Temperateheath and scrub	23 870.9	10.0 – 15.0	280.8 (1.2)	2204.3 (9.2)	2.49	1.92
51. Sub-Med. and temperate sclerophyllous scrub	1555.9	10.0 – 25.0	1.9 (0.1)	242.4 (15.6)	2.36	1.30
52. Mediterraneanarborescent matorral	3857.0	25.0	n.e.	n.e.	n.e.	n.e.
53. Thermo-Mediterranean and pre-steppe brush	5547.6	25.0	n.e.	n.e.	n.e.	n.e.
54. Phryganascrub	0.2	15.0	n.e.	n.e.	n.e.	n.e.
61. Natural grasslands	1920.9	7.5 – 20.0	807.6 (42.0)	1373.3 (71.5)	1.73	4.24
62. Semi-natural dry grasslands and scrubland	4809.0	12.5 – 20.0	n.e.	23.3 (0.5)	n.e.	1.04
63. Sclerophillous grazed forests (*dehesas*)	2336.2	20.0	n.e.	n.e.	n.e.	n.e.
64. Semi-natural tall-herb humid meadows	477.6	7.5 – 20.0	77.62 (16.3)	113.0 (23.7)	3.43	5.30
65. Mesophile grasslands	125.3	25.0	n.e.	n.e.	n.e.	n.e.
71. Sphagnum acid bog	0.001	12.5	n.e.	0.001 (92.1)	n.e.	1.75
72. Calcareous fens	76.5	22.5	n.e.	n.e.	n.e.	n.e.
91. Forest of temperate Europe	1757.6	15.0 – 17.5	79.7 (4.5)	117.4 (6.7)	3.82	1.00
92. Med. deciduous forests	2770.2	15.0 – 25.0	35.7 (1.3)	30.3 (1.1)	3.86	1.43
93. Mediterranean sclerophyllous forests	5303.3	15.0 – 17.5	290.2 (5.5)	241.5 (4.6)	4.04	2.59
94. Temperate mountainous coniferous forests	119.0	10.0	50.9 (42.8)	107.1 (90.0)	3.48	2.96
95. Med. and Macaron. mountainous coniferous	1339.7	9.0 – 15.0	26.5 (2.0)	58.3 (4.4)	1.56	0.69
TOTAL AREA	57675.7	7.5 – 25.0	1657.0 (2.9)	4521.4 (7.8)		

CL_{exc} area (km^2 (%)): Sum of areas with exceedance of CL expressed in total area (km^2) and in percentage (%) of area assessed for each sub-group.
n.e.: None exceedance was found within this sub-group.

Table 3.Correlation results and comparison metrics. Values are given for the entire dataset and, below, by network subset.

		CHIMERE MODEL				EMEP MODEL			
		ON	**RN**	**TN**	**PRECIP**	**ON**	**RN**	**TN**	**PRECIP**
n	**ALL**	**97**	**95**	**95**	**97**	**97**	**95**	**95**	**97**
	CAT	20	20	20	20	20	20	20	20
	EMEP	35	35	35	35	35	35	35	35
	ICP-F	42	40	40	42	42	40	40	42
r	**ALL**	**0.67**	**0.32**	**0.55**	**0.63**	**0.40**	**0.37**	**0.47**	**0.73**
	CAT	-0.14$^{n.s.}$	-0.15$^{n.s.}$	0.04$^{n.s.}$	0.48	-0.27$^{n.s.}$	0.32$^{n.s.}$	0.27$^{n.s.}$	0.70
	EMEP	0.77	0.49	0.79	0.54	0.76	0.60	0.76	0.66
	ICP-F	0.81	0.64	0.67	0.66	0.43	0.79	0.72	0.90
a	**ALL**	**1.13**	**0.62**	**1.47**	**355.7**	**1.17**	**1.30**	**1.64**	**343.6**
	CAT	3.33	2.35	4.14	229.6	6.32	2.85	4.33	323.1
	EMEP	1.23	0.48	1.40	315.0	0.74	0.62	1.05	213.3
	ICP-F	0.79	0.22	1.14	385.0	1.17	0.51	1.33	225.0
b	**ALL**	**0.42**	**0.20**	**0.37**	**0.38**	**0.40**	**0.44**	**0.60**	**0.50**
	CAT	0.20	0.21	0.07	0.71	0.73	0.60	0.72	0.73
	EMEP	0.34	0.20	0.36	0.36	0.52	0.72	0.69	0.86
	ICP-F	0.51	0.27	0.36	0.36	0.17	0.44	0.39	0.53
IOA	**ALL**	**0.74**	**0.48**	**0.60**	**0.72**	**0.62**	**0.60**	**0.66**	**0.82**
	CAT	0.24	0.31	0.37	0.65	0.19	0.40	0.34	0.71
	EMEP	0.73	0.49	0.68	0.68	0.82	0.75	0.86	0.74
	ICP-F	0.81	0.51	0.58	0.70	0.50	0.69	0.64	0.85
RMSE	**ALL**	**1.14**	**1.78**	**2.47**	**395.1**	**1.63**	**1.52**	**2.66**	**341.2**
	CAT	1.30	1.69	2.44	245.3	2.25	2.38	4.05	222.4
	EMEP	1.17	1.16	1.83	251.6	1.08	0.74	1.42	320.0
	ICP-F	1.02	2.23	2.92	529.3	1.66	1.47	2.60	402.4
MNB	**ALL**	**0%**	**-46%**	**-26%**	**4%**	**-5%**	**13%**	**0%**	**16%**
	CAT	-8%	-8%	-17%	16%	39%	95%	53%	36%
	EMEP	19%	-46%	-16%	5%	-1%	17%	5%	30%
	ICP-F	-11%	-65%	-40%	-5%	-29%	-33%	-31%	-7%
MNAE	**ALL**	**32%**	**62%**	**36%**	**35%**	**39%**	**51%**	**39%**	**35%**
	CAT	35%	75%	37%	31%	64%	98%	56%	37%
	EMEP	38%	51%	31%	35%	28%	41%	32%	42%
	ICP-F	27%	65%	40%	39%	36%	36%	35%	30%

n: number of pairs of data compared; r: correlation coefficient; a: y-axis intercept of the regression equation; b: slope of the regression equation

Figure 1 Monitoring sites with observed wet deposition of nitrogen included in this study.

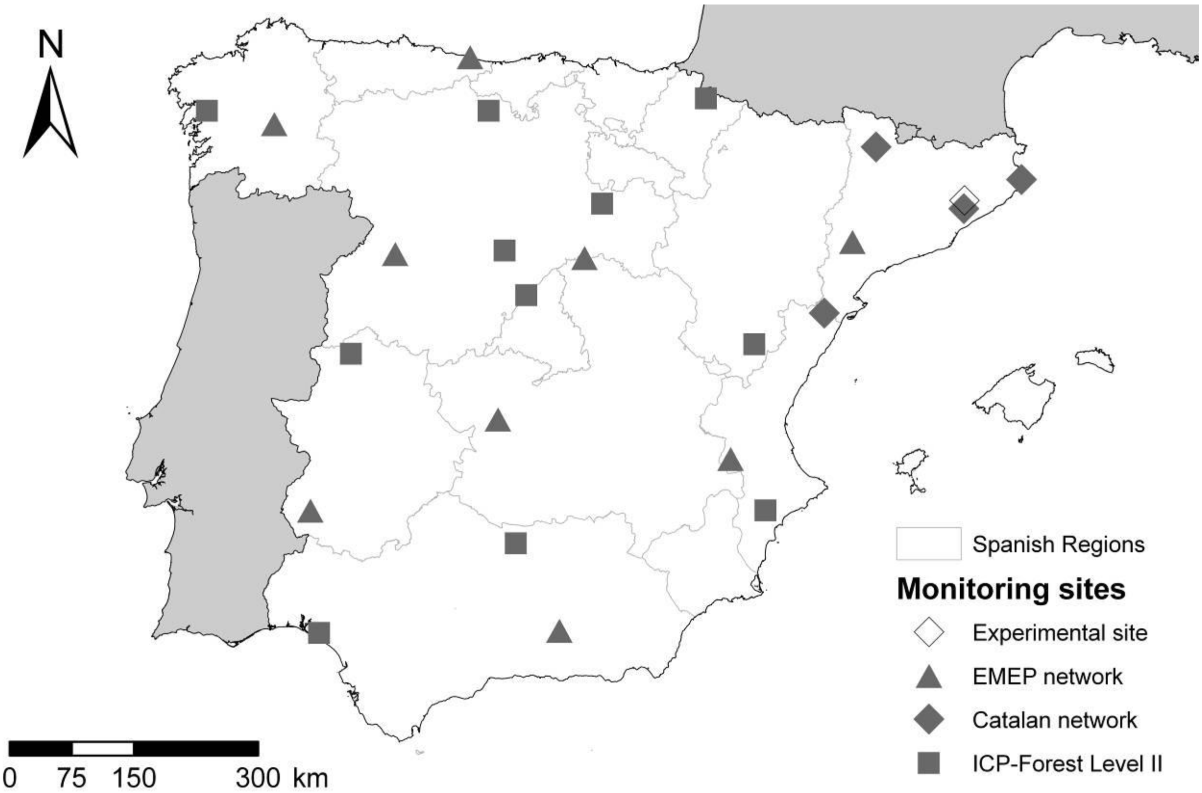
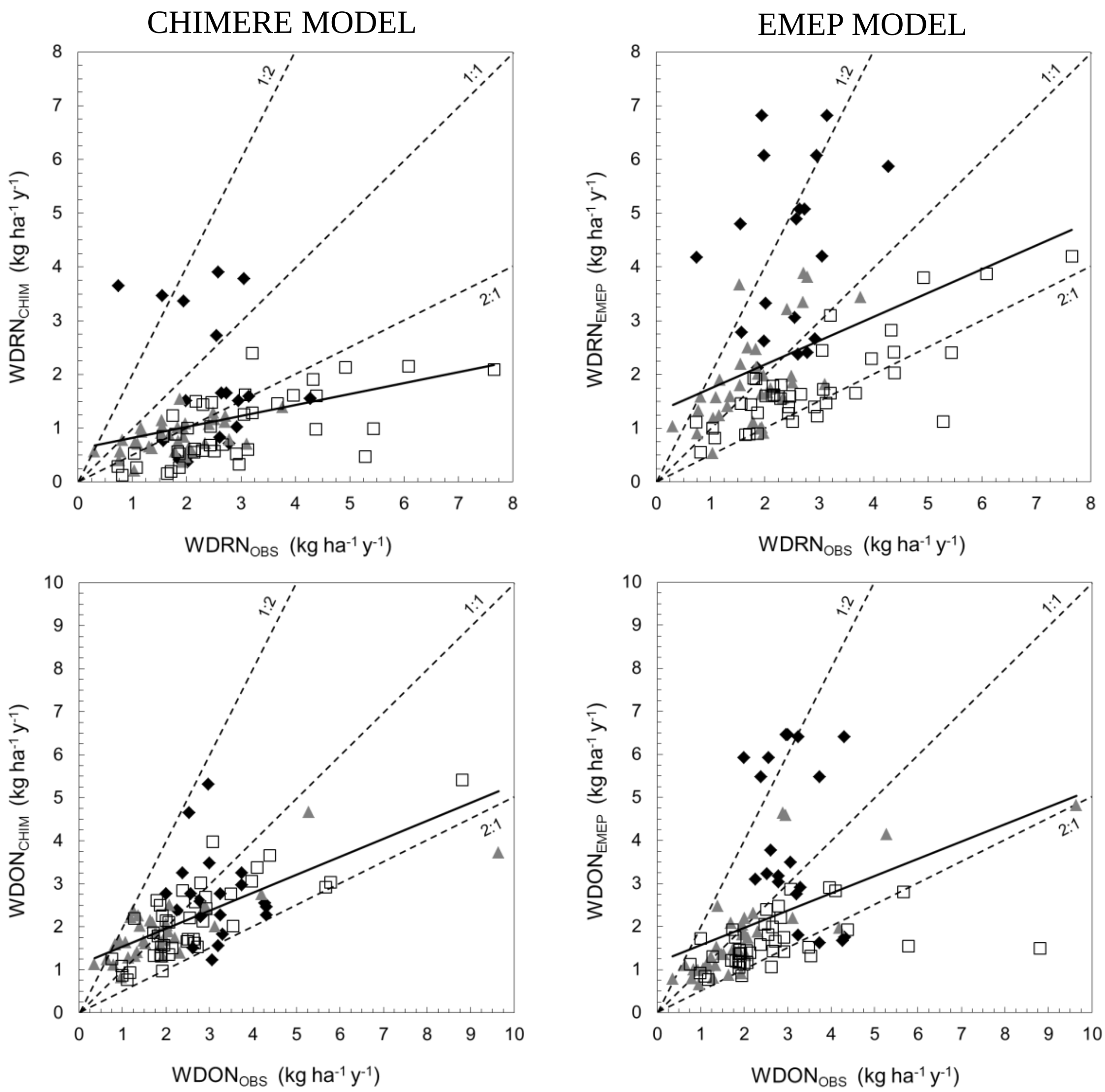


Figure 2. Scatterplots and regression line for observed-modelled deposition values at monitoring sites.

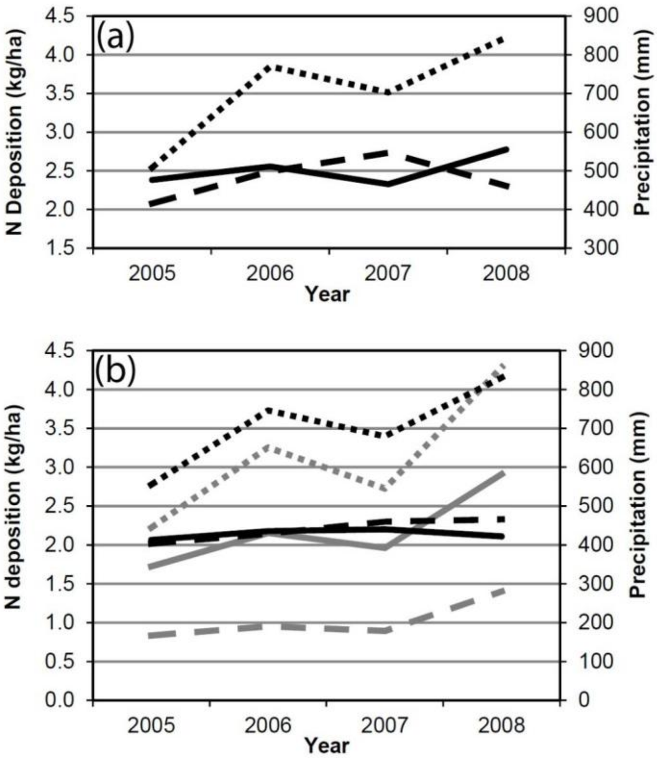


▲EMEP monitoring sites

□ICP-Forests Level II monitoring sites

♦ Catalan monitoring sites

Figure 3. a) Annual averages of wet deposition of nitrogen and precipitation rate observed at monitoring sites. (b) Annual averages of wet deposition of nitrogen and precipitation rate at monitoring sites, predicted by EMEP and CHIMERE model.



(a) Solid line: wet deposition of N-Nitrate; dashed line: wet deposition of N-Ammonium; pointed line: annual precipitation rate.

(b) Solid line: wet deposition of N-Nitrate; dashed line: wet deposition of N-Ammonium; pointed line: annual precipitation rate. Black lines correspond to EMEP model estimations, grey lines correspond to CHIMERE model estimations

Figure 4. Wet deposition of oxidized and reduced nitrogen (WDON and WDRN), and total deposition of nitrogen (TDTN) in 2008, according both EMEP and CHIMERE models.

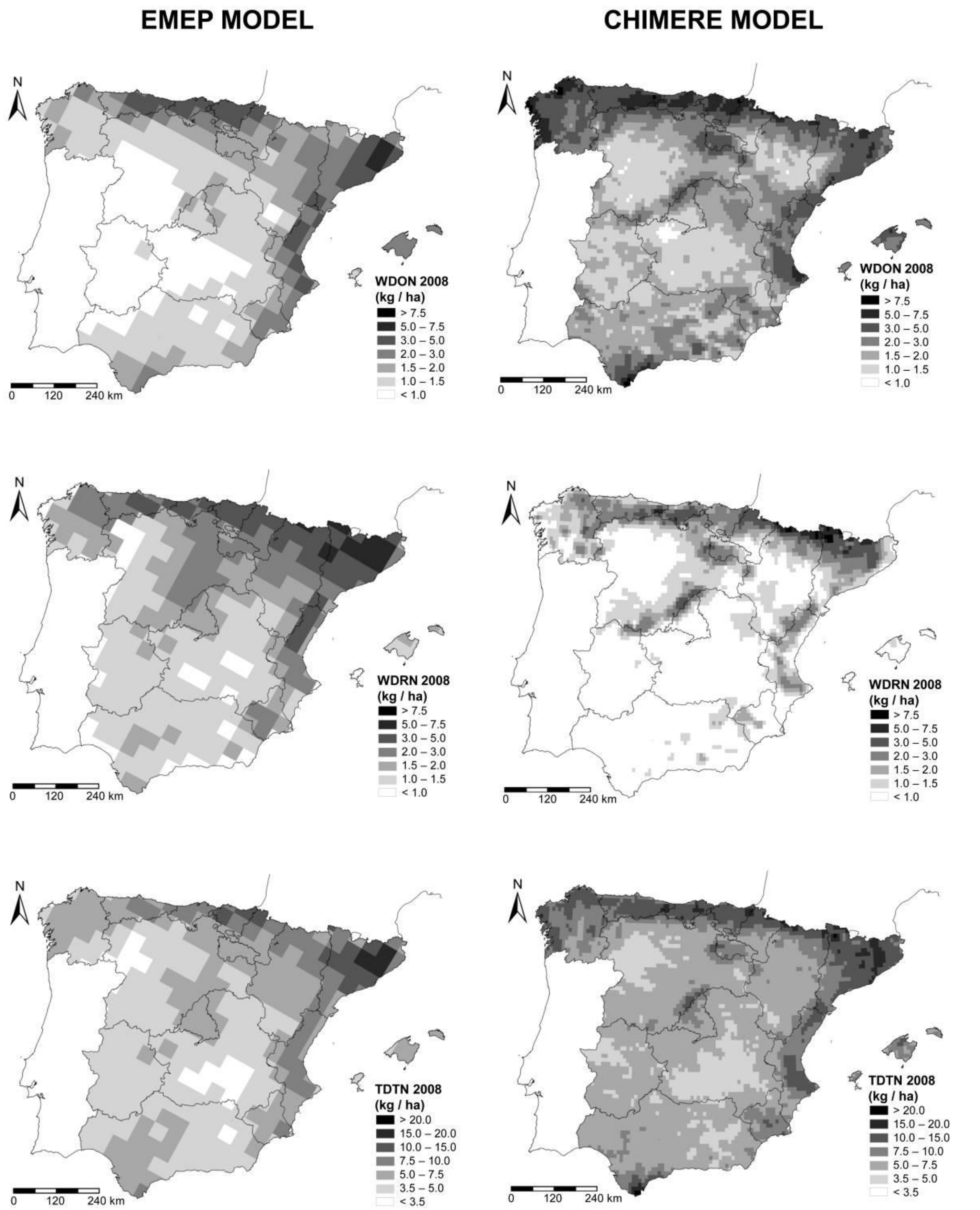


Figure 5.Natura 2000 areas withstanding an exceedance of the assignated critical load (CL_{exc}) according EMEP and CHIMERE models.