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Nitrogen deposition in Spain: Modeled patterns and threatened habitats within the Natura 2000 network

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HIGHLIGHTS

- CHIMERE and EMEP models acceptably estimate atmospheric N wet deposition in Spain.
- Total (wet + dry) atmospheric N deposition in Spain in 2008 was up to 19–23 kg N ha^{-1}.
- Natural grasslands are the habitats most threatened by N deposition.
- Biodiversity conservation in 3–7% of the assessed area could be threatened by N deposition.
- Habitats in mountain areas are particularly threatened by N deposition.

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ABSTRACT

The Mediterranean Basin presents an extraordinary biological richness but very little information is available on the threat that air pollution, and in particular reactive nitrogen (N), can pose to biodiversity and ecosystem functioning. This study represents the first approach to assess the risk of N enrichment effects on Spanish ecosystems. The suitability of EMEP and CHIMERE air quality model systems as tools to identify those areas where effects of atmospheric N deposition could be occurring was tested. For this analysis, wet deposition of NO_3^- and NH_4^+ estimated with EMEP and CHIMERE model systems were compared with measured data for the period 2005–2008 obtained from different monitoring networks in Spain. Wet N deposition was acceptably predicted by both models, showing better results for oxidized than for reduced nitrogen, particularly when using CHIMERE. Both models estimated higher wet deposition values in northern and northeastern Spain, and decreasing along a NE–SW axis. Total (wet + dry) nitrogen deposition in 2008 reached maxima values of 19.4 and 23.0 kg N ha^{-1} year^{-1} using EMEP and CHIMERE models respectively. Total N deposition was used to estimate the exceedance of N empirical critical loads in the Natura 2000 network. Grassland habitats proved to be the most threatened group, particularly in the northern alpine area, pointing out that biodiversity conservation in these protected areas could be endangered by N deposition. Other valuable mountain ecosystems can be also threatened, indicating the need to extend atmospheric deposition monitoring networks to higher altitudes in Spain.

1. Introduction

The global biogeochemical cycle of nitrogen (N) has been deeply altered by human activities to the extent that the planetary boundary for human safe operating 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

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formation, ecosystem acidification and eutrophication (Bobbink et al., 2010; Galloway et al., 2008; Sutton et al., 2011). Eutrophication is 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).

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

The 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 atmospheric emissions of N compounds in the period 1990–2009 in Europe (EEA, 2011). During the same period, Spanish emission of NH_3 increased 12.8% and NO_x emissions eventually decreased 17%, after a continuous increase until 2007 (MAGRAMA, 2013). In this sense, increases in NO_3^- deposition have been detected in the last decades in Catalonia (NE of Spain), while no significant changes were detected in NH_4^+ deposition (Àvila et al., 2010; Àvila and Rodà, 2012; Camarero and Catalan, 2012). The increase in NO_3^- deposition has been related with the increases in NO_x emissions (Àvila et al., 2010). Total annual atmospheric N deposition loads in eastern Spain have been estimated in 15–30 kg N ha^{-1} $year^{-1}$, with dry deposition representing about 40–70% of total N deposition (Rodà et al., 2002; Sanz et al., 2002; Àvila and Rodà, 2012). Atmospheric N deposition in Spain is lower than values recorded in central Europe, both measured (Lorenz and Becher, 2012) and modeled data (Nyíri and Gauss, 2010). However, since changes in species composition occur early in the sequence of N saturation (Emmett, 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 plant species 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). The reported rises of NO_3^- concentration in headwater streams detected in areas of NE Spain have been considered a sign of the onset of eutrophication (Àvila and Rodà, 2012; Camarero and Aniz, 2010).

Critical loads (CLs) are thresholds for N deposition, defined under the CLRTAP for the protection of the ecosystems. CLs 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 (CLRTAP, 2004). Different approaches have been adopted in the Convention to define N critical loads involving either modeling or field evidences. Empirical critical loads of N have been defined for specific ecosystems (Bobbink et al., 2010; Bobbink and Hettelingh, 2011) based on observed changes in the structure and function of the ecosystem, primarily in species abundance, composition and/or diversity (structure), or N leaching, decomposition or mineralization rate (functioning). Exceedances of critical loads are being used in Europe since 1990s to assess impacts on biodiversity in natural ecosystems. In this sense, the use of empirical CLs for nutrient N is recommended to inform whether N deposition should be recorded as a “threat to future prospects” in the framework of the Habitats Directive 92/43/EEC (Henry and Aherne, 2014; Whitfield et al., 2011). The Habitats Directive includes an Annex I with a list of habitat types of community interest requiring specific conservation measures. Unfortunately, the definition and application of N empirical critical loads in Mediterranean habitats is still limited and further research is urgently required (Bobbink et al., 2010; Ochoa-Hueso et al., 2011; Pinho et al., 2012).

Suitable N deposition data are needed to identify those areas where effects of N deposition could be occurring in natural ecosystems. Since the availability of air pollutant concentration and deposition data is 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 (Simpson et al., 2012), 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, in particular over Europe domain (Bessagnet et al., 2004; Vivanco et al., 2008, 2009).

The objectives of this work were 1) to document the performance of the EMEP and CHIMERE model-systems for estimating atmospheric N wet deposition under Mediterranean environmental conditions; 2) to analyze the distribution of atmospheric N deposition in Spain; and 3) to assess the risk of effects of atmospheric N deposition for biodiversity preservation in the Spanish Natura 2000 network. For this analysis, wet deposition of NO_3^- and NH_4^+ modeled by EMEP and CHIMERE 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. The aim was to evaluate two available and widely used “model-systems”, with their different input data, model setup and the model itself, as tools for ecosystem threat assessment. Modeled N deposition values, including wet and dry deposition, were used to detect those areas with high atmospheric N deposition and to calculate exceedances of empirical critical loads in the Natura 2000 network.

2. Material and methods

2.1. Measurements

2.1.1. ICP Forests Level II network

The ICP Forests 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 neighborhood 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 the 13 ICP Forests Level II plots located in Spain (Fig. 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 of the other years. Annual deposition was calculated adding

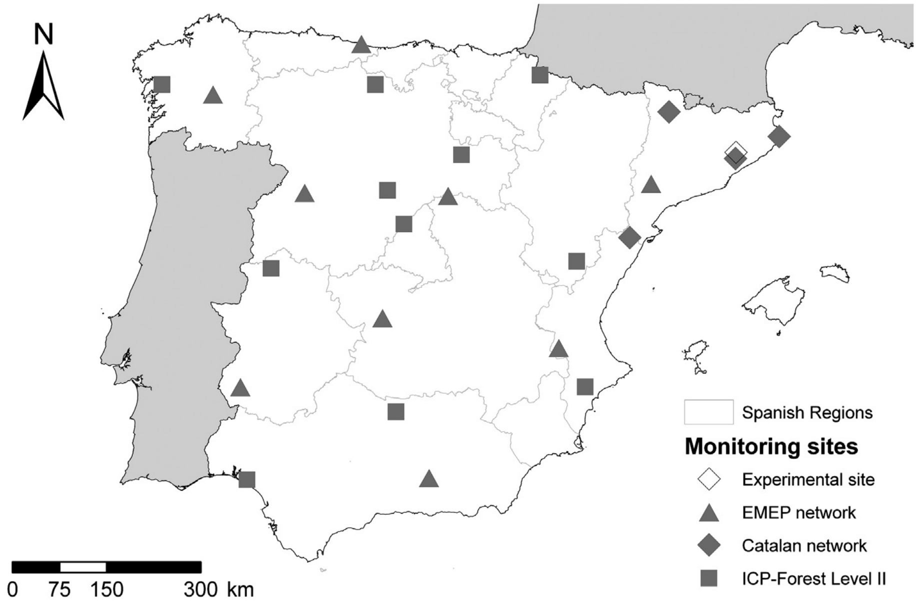


Fig. 1. Monitoring sites with observed wet deposition of nitrogen included in this study.

the product of concentration by 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 °C 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 measuring air pollutants in rural and background areas. These measurements, in combination with emission inventories and modeled deposition data, allow the assessment of concentration and deposition of air pollutants, the significance of transboundary fluxes and the related exceedances of 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, this network consists of 10 monitoring stations located from sea level to 1360 m.a.s.l. (http://www.aemet.es/es/idi/medio_ambiente/vigilancia). Daily samples of precipitation were collected with wet-only samplers in 9 of the monitoring stations for the period 2005–2008 (Fig. 1). Measured deposition data accumulated throughout the year were estimated following the EMEP protocols (www.emep.int).

2.1.3. Catalan Air Quality Network

Precipitation samples were obtained from four stations of the Catalan Air Quality Network (*Xarxa de Vigilància y Prevenció de la Contaminació Atmosfèrica* of the Gereralitat de Catalunya) in NE Spain (Fig. 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 than 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. (Fig. 1), making a total of 5 sites in the Catalan Region. All samples were analyzed by the CREAF laboratory following protocols published elsewhere (Àvila and Rodà, 2002). Concentrations were weighted by volume to give the annual volume weighted mean (VWM) concentration, 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 MSC-W model is used within CLRTAP for modeling regional atmospheric dispersion and deposition of air pollutants all over Europe. For standard EMEP calculations, the model employs emission data from the European countries. The performance of the model is regularly evaluated with the measurements of air quality and precipitation data from the EMEP stations. The EMEP rv3.8.1 uses 20 vertical layers and considers about 140 reactions among 70 chemical species. A detailed description of the model is provided in Simpson et al. (2012). For this study, annual 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 the EEA and CEIP Inventory Review of 2011 (Mareckova et al., 2011).

2.2.2. CHIMERE regional air quality model

CHIMERE model applications were performed using the regional V200603par-rc1 version for the 2005–2007 simulations and the V2008b version for 2008 simulations. In both cases, 8 vertical levels were used. More information and detailed description of the model can be found in http://www.lmd.polytechnique.fr/chimere/ and Menut et al. (2013). The simulations were performed at a 0.2°-horizontal resolution (approx. 20 km) for the period 2005–2007 (nested to a 0.5°-resolution European-scale simulation) and at a 0.1°-horizontal resolution (approx. 10 km) for 2008 (nested to a 0.2°-resolution European-scale simulation), 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). MM5 and WRF models were used to obtain 2005–2007 period and 2008 meteorological fields, respectively. Emissions were derived from the annual totals of the EMEP database on a 50 km grid basis (http://www.ceip.at/webdab-emission-database/emissions-as-used-in-emep-models/). Spatial emission distribution and NMVOC speciation were performed as indicated in Vivanco et al. (2009).

2.3. Comparison of measured and modeled 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). 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. Annual bulk deposition of NO_3^- and NH_4^+ measured in the ICP Forests plots and annual wet-only deposition measured in the EMEP and Catalan networks were compared with modeled wet deposition data obtained with EMEP and CHIMERE models. A set of 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, not normalized) 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 coefficient (r) and linear regression were used to study the relationships between modeled and measured values. All the analysis were performed using Statistica version 11 (StatSoft, Inc. Tule, OK, USA). Significance probability level 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 for 2008 with EMEP and CHIMERE models was used to evaluate the risk of N effects in the Spanish Natura 2000 designated areas. Only the habitat types of Community interest described in the Annex I of the Habitats Directive located within the Natura 2000 network were considered. Natural habitats of Community interest are those habitats which are in danger of disappearance in their natural range; or have a small natural range following their regression or by reason of their intrinsically restricted area; or present outstanding examples of typical characteristics of their biogeographical regions. These habitats covered 37% of the 188,856.9 km^2 included in the Spanish Natura 2000 network (about 30% of the Spanish territory). The spatial distribution of the habitat types of Community interest within the Natura 2000 network was obtained from the Spanish National Biodiversity Assessment (http://www.magrama.gob.es/es/biodiversidad/servicios/banco-datos-naturaleza/).

The habitat types were matched with the corresponding EUNIS habitat classification used for defining empirical CLs (http://eunis.eea.europa.eu/related-reports.jsp). Empirical critical loads (CLs) of N deposition recently revised in Bobbink and Hettelingh (2011) were used for estimating N exceedances, calculated as deposition minus CL (positive exceedance is taken to be undesirable). In order to focus on main terrestrial ecosystems, some habitats were excluded of the analysis:

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

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

coastal and halophytic habitats, freshwater habitats, rocky habitats and caves, and wetlands. Consequently, the area considered for estimating N exceedances occupied an extension of 52,182.9 km^2. The CL assigned to each habitat type was the average of the range of empirical CLs reported by Bobbink and Hettelingh (2011) for each habitat type. When an N empirical CL was not defined for a habitat, the CLs of similar or equivalent habitats were used (these cases represented about 30% of the total surface assessed). Annex 1 of the present work describes the details of the N empirical CLs applied to each habitat type included in the analysis. Habitat types of Annex I of the Habitats Directive have been gathered in habitats sub-groups in Table 2, showing the minimum and maximum CL used within the sub-group, given that different habitat types are included. The scientific background supporting the empirical CL of N 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. Additionally, for each habitat sub-group, CL exceedances were estimated weighting exceedances by the corresponding areas. All the analysis were performed using ARCGIS version 9.3 (ESRI, Redlands CA, USA) and MS Access 2010 (Microsoft, Seattle WA, USA).

3. Results and discussion

3.1. Comparison of measured and modeled data

Measured values of annual precipitation and N wet deposition were compared with values estimated with the EMEP and CHIMERE air quality models (Table 3, Fig. 2). In general, the CHIMERE model performed better for estimating WDON than EMEP, since better correlation and IOA and a lower error metrics (RMSE, MNB and MNAE) were obtained (Table 3). The scatterplots of model results vs. observations showed, in general, similar regression functions for both models. The slope and interception values indicate an underestimation of the high and overestimation the low N deposition values. In the case of WDRN, the CHIMERE model provided less correct estimates than EMEP as deduced from the lower correlation and IOA, higher MNB and MNAE (Table 3), and regression functions and scatterplots (Fig. 2). CHIMERE clearly underestimated WDRN (with a MNB of −46%). For total wet deposition (WDTN), the correlation coefficients for the CHIMERE results were better, while the EMEP model provided higher IOA. However, CHIMERE clearly underestimated WDTN (with a MNB of −26%), mostly due to the strong underprediction of WDRN. The values of RMSE and MNAE were very similar for both models. The RMSE metrics indicated that the average difference between both model estimations of WDTN was about 0.2 kg N ha^{-1} year^{-1}.

Interestingly, annual precipitation estimates used by both models correlated better with measured values than wet deposition. Some underestimation of high precipitation was shown by both models, but all the evaluation metrics indicated an adequate model performance (high IOA values and relatively low values of MNB and MNAE). The estimates of precipitation for the Spanish ICP Forest plots showed that both EMEP and CHIMERE performed better than values reported when comparing EMEP model with ICP-Forest data across Europe (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 in previous comparisons (Erisman et al., 2003).

Nitrogen wet deposition estimations were also compared with observed values for each measurement network independently. Modeling 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). In fact, a recent review reported that EMEP model performance for estimating N compounds concentration in precipitation in the Mediterranean area was comparable to the one found in other parts of Europe (Aas et al., 2010).

Model estimates of N wet deposition for the ICP Forests sites were similar or slightly more incorrect than for EMEP sites. In this case, both EMEP and CHIMERE models underestimated wet N deposition

Table 2
Surface area assessed of habitat sub-groups from Annex I of Habitats Directive, nitrogen empirical critical loads (CLs) and exceedance of empirical critical loads (CL_{exc}) according to EMEP and CHIMERE estimations of nitrogen deposition.

Sub-groups from Annex I of Habitats Directive	Area assessed (km^2)	CL ($kgN\ ha^{-1}\ year^{-1}$)[a]	EMEP CL_{exc} area (km^2 (%))[b]	CHIMERE CL_{exc} area (km^2 (%))	EMEP CL_{exc} avg. (kgN/ha)[c]	CHIMERE CL_{exc} avg. (kgN/ha)
21. Sea dunes of the Atlantic coast	30.3	11.5–15.0	n.e.	1.0 (3.4)	n.e.	1.55
22. Sea dunes of the Mediterranean coast	241.6	9.0–11.5	2.4 (8.1)	25.0 (10.3)	1.75	1.53
40. Temperate heath and scrub	13,576.4	10.0–15.0	102.9 (0.8)	1262.5 (9.3)	2.42	2.19
51. Sub-Med. and temperate sclerophyllous scrub	1661.1	10.0–25.0	2.1 (0.1)	176.7 (10.6)	3.24	1.85
52. Mediterranean arborescent matorral	2303.6	25.0	n.e.	n.e.	n.e.	n.e.
53. Thermo-Mediterranean and pre-steppe brush	4077.1	25.0	n.e.	n.e.	n.e.	n.e.
54. Phrygana scrub	2.2	15.0	n.e.	n.e.	n.e.	n.e.
61. Natural grasslands	2054.4	7.5–20.0	613.5 (29.9)	1229.9 (59.9)	1.87	4.90
62. Semi-natural dry grasslands and scrubland facies	6250.2	12.5–20.0	n.e.	86.6 (1.4)	n.e.	1.77
63. Sclerophyllous grazed forests (dehesas)	5133.4	20.0	n.e.	n.e.	n.e.	n.e.
64. Semi-natural tall-herb humid meadows	337.4	7.5–20.0	34.5 (10.2)	67.6 (20.0)	1.50	3.44
65. Mesophile grasslands	234.9	25.0	n.e.	n.e.	n.e.	n.e.
71. Sphagnum acid bog	37.8	12.5	n.e.	14.2 (37.5)	n.e.	0.65
72. Calcareous fens	31.8	22.5	n.e.	n.e.	n.e.	n.e.
91. Forest of temperate Europe	1931.1	15.0–17.5	68.3 (3.5)	129.4 (6.7)	3.79	0.77
92. Med. deciduous forests	3900.5	15.0–25.0	23.6 (0.6)	34.0 (0.9)	4.21	2.56
93. Mediterranean sclerophyllous forests	7531.0	15.0–17.5	497.4 (6.6)	487.6 (6.5)	3.81	1.98
94. Temperate mountainous coniferous forests	141.2	10.0	54.6 (38.7)	121.9 (86.3)	3.36	3.34
95. Med. and Macaron. mountainous coniferous forests	2706.9	9.0–15.0	41.4 (1.5)	148.8 (5.5)	1.33	1.01
Total	52,182.9	7.5–25.0	1440.8 (2.8)	3785.3 (7.3)	2.74	2.97

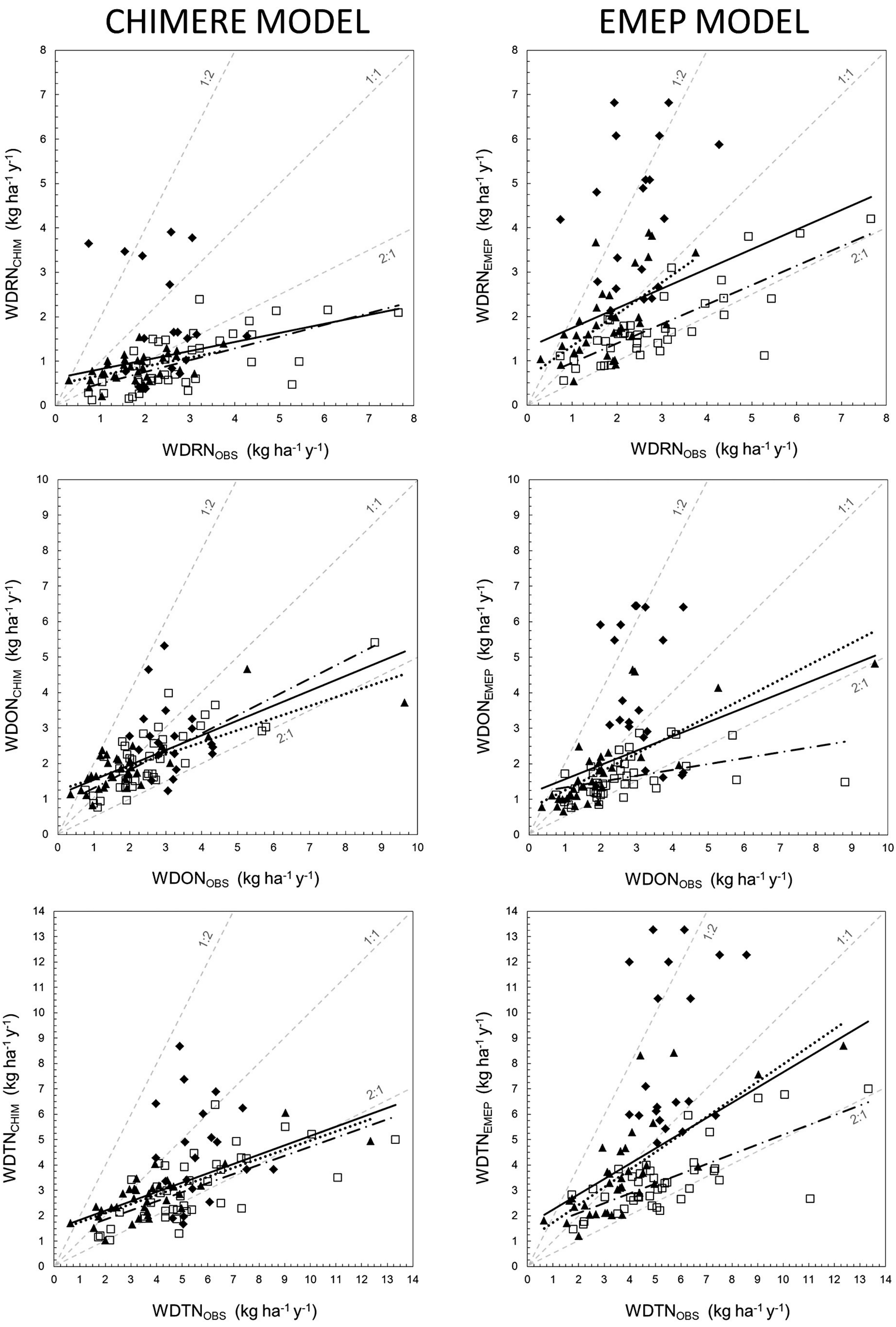
[a] Range of empirical critical loads, according to Bobbink et al. (2010), used within each habitat sub-group given that different vegetation types are included.
[b] Sum of areas with CL_{exc}, expressed in total area (km^2) and in percentage (%) of the area assessed for each sub-group.
[c] CL_{exc} averaged and weighted for each subgroup; n.e.: no exceedance was found within this sub-group.

values of reduced and oxidized N forms (Table 3). These underestimations can be partially explained by the bulk samplers used by the ICP Forests network to collect wet deposition, since some influence of dry deposition onto the funnels cannot be disregarded. The proportion of

Table 3
Correlation results and comparison metrics of measured and modeled N deposition and precipitation. Values are given for the entire dataset (All) and, by network subset.

Metric	Network	CHIMERE model				EMEP model			
		WDON	WDRN	WDTN	PRECIP[a]	WDON	WDRN	WDTN	PRECIP
n[b]	All	97	95	95	97	97	95	95	97
	Catalan	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[c]	All	0.67	0.32	0.55	0.63	0.40	0.37	0.47	0.73
	Catalan	−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[d]	All	1.13	0.62	1.47	355.7	1.17	1.30	1.64	343.6
	Catalan	n.s.	n.s.	n.s.	229.6	n.s.	n.s.	n.s.	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[e]	All	0.42	0.20	0.37	0.38	0.40	0.44	0.60	0.50
	Catalan	n.s.	n.s.	n.s.	0.71	n.s.	n.s.	n.s.	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
	Catalan	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
	Catalan	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%
	Catalan	−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%
	Catalan	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.s.: no significant correlation/regression was found.
[a] Annual precipitation.
[b] Number of pairs of data compared.
[c] Correlation coefficient.
[d] y-Axis intercept of the regression equation.
[e] Slope of the regression equation.


CHIMERE MODEL
EMEP MODEL
1:2
1:1
2:1
$WDRN_{CHIM}$ (kg ha^{-1} y^{-1})
$WDRN_{OBS}$ (kg ha^{-1} y^{-1})
$WDRN_{EMEP}$ (kg ha^{-1} y^{-1})
$WDON_{CHIM}$ (kg ha^{-1} y^{-1})
$WDON_{OBS}$ (kg ha^{-1} y^{-1})
$WDON_{EMEP}$ (kg ha^{-1} y^{-1})
$WDTN_{CHIM}$ (kg ha^{-1} y^{-1})
$WDTN_{OBS}$ (kg ha^{-1} y^{-1})
$WDTN_{EMEP}$ (kg ha^{-1} y^{-1})

dry deposition collected in the funnels depends on location, climate, sampler aerodynamic characteristics and chemical component (Erisman et al., 2003). Results from bulk vs. wet-only comparison in the experimental Catalan site (La Castanya) indicated an overestimation of about 10% of nitrate concentration in bulk collectors, although ammonium was underestimated by 25% (Izquierdo and Àvila, 2012).

Surprisingly, model predictions of N wet deposition were fairly poor when comparing with measurements obtained in the five Catalan monitoring sites. Correlations between modeled and measured deposition were not significant and the IOA metrics were always below 0.5 for both model approaches (Table 3). The lack of correlation in the Catalan region was not directly explained by poor predictions of precipitation, which were acceptable with both model systems. The small range of deposition values collected in the area could hinder statistic correlation. Also the complex topography of this region and the influence of local emissions might explain the poor model performance at small regional scale. In these conditions, the EMEP model with a 50 × 50 km resolution cannot be expected to reproduce small-scale variations in deposition regimes as it is argued in previous studies (e.g. Simpson et al., 2006a). However, CHIMERE model, despite its finer resolution, obtained only slightly better error metrics for the Catalan sites.

The higher resolution used with CHIMERE for 2008 estimations (10 × 10 km compared to 20 × 20 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). Similarly, increasing EMEP model resolution and a finer placement of emission sources are expected to have significant improvements in polluted areas but a similar performance has been described for wet deposition and concentration in precipitation estimations in rural areas (Cuvelier et al., 2013; Hirst and Storvik, 2003; Nyíri and Gauss, 2010).

In summary, evaluation metrics and scatterplots of modeled vs. measured values indicate that both CHIMERE and EMEP models generally underestimate the high and overestimate the low measured atmospheric N deposition values. Nevertheless, estimations of total N wet deposition performance in Spain provided by both models are in general within acceptable ranges (Table 3, Fig. 2), although results should be applied with caution, especially at small regional scale. Differences on the results obtained with both model systems can be explained by the different input data, setup and model estimations. The models' setup was not harmonized because the analysis performed did not intend to compare both models. A more detailed comparison of both models is currently being developed considering monthly values.

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 kg N ha^{-1} year^{-1} of WDRN, 0.4–9.6 kg N ha^{-1} year^{-1} of WDON, and 0.7–13.3 kg N ha^{-1} year^{-1} of WDTN. For each monitoring station, interannual variability of measured wet deposition represented about 25–30% of the average value. Similar variability was observed in wet deposition values estimated with CHIMERE in the cells corresponding to those sites, while EMEP model presented lower interannual variability (13–14%). The difference in scale between EMEP and CHIMERE could be the reason for this disparity. 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 14% reduction of oxidized N emissions reported in 2008 with respect to the previous year (MAGRAMA, 2013) was not reflected in measured nor in modeled WDON (Fig. 3). This result is probably related to the

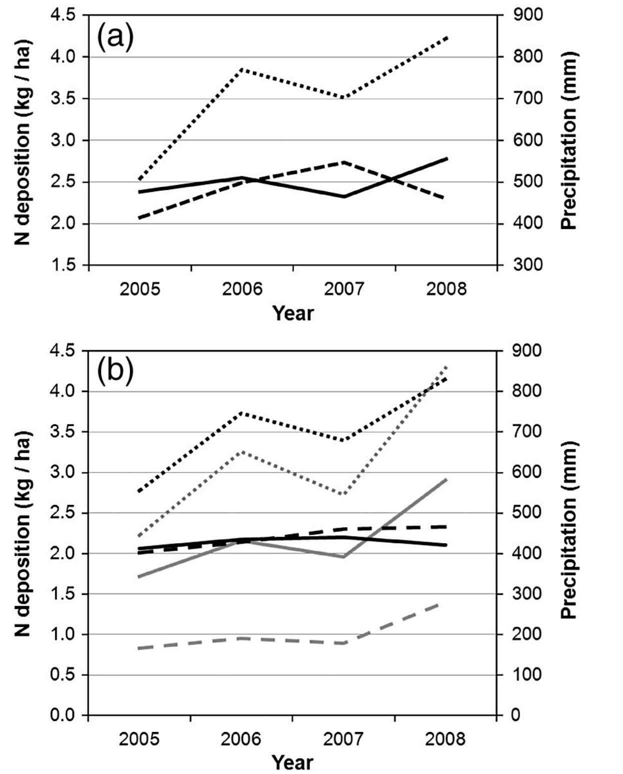


Fig. 3. (a) Annual averages of wet deposition of N-nitrate (WDON), N-ammonium (WDRN) and precipitation observed at monitoring sites. (b) Annual averages of wet deposition of WDON and WDRN and precipitation at monitoring sites, predicted by EMEP (black lines) and CHIMERE (gray lines) models. Solid lines: WDON; dashed lines: WDRN; dotted lines: precipitation rate.

higher precipitation rate registered in 2008 compared to 2007, and highlights the importance of considering precipitation variability when evaluating the effectiveness of control emission strategies on deposition trends. In fact, measured total N wet deposition (WDTN) was significantly correlated with precipitation ($r = 0.61$; $p < 0.05$) for the period considered. Accordingly, maximum wet deposition was mainly located in the Northern area of Spain where the highest precipitation occurs.

Average measured wet deposition of oxidized N (WDON) for the period 2005–2008 was 2.33 kg N ha^{-1} year^{-1}, a 12% higher than the 2.08 kg N ha^{-1} year^{-1} of reduced N (WDRN). However, 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 total national emissions of reduced and oxidized N, since average values for the period 2005–2008 of oxidized N were 26% higher than emissions of reduced N (400.3 kTon of N-NO_x vs 318.3 kTon of N-NH_3 respectively; MAGRAMA, 2013). On the other hand, 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).

Modeled N wet deposition in Spain showed a decreasing distribution along a NE–SW axis, with higher deposition in the northern and eastern coastal regions than inland and southern areas (Fig. 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 kg N ha^{-1} year^{-1}, respectively). CHIMERE showed higher deposition

Fig. 2. Scatterplots and regression lines for modeled vs. observed annual values of oxidized (WDON), reduced (WDRN) and total N wet deposition (WDTN) at monitoring sites. ▲·······▲ EMEP monitoring sites; □ —•—•□ ICP-forests level II monitoring sites; ◆ Catalan monitoring sites. Solid line shows the regression line for all data together.

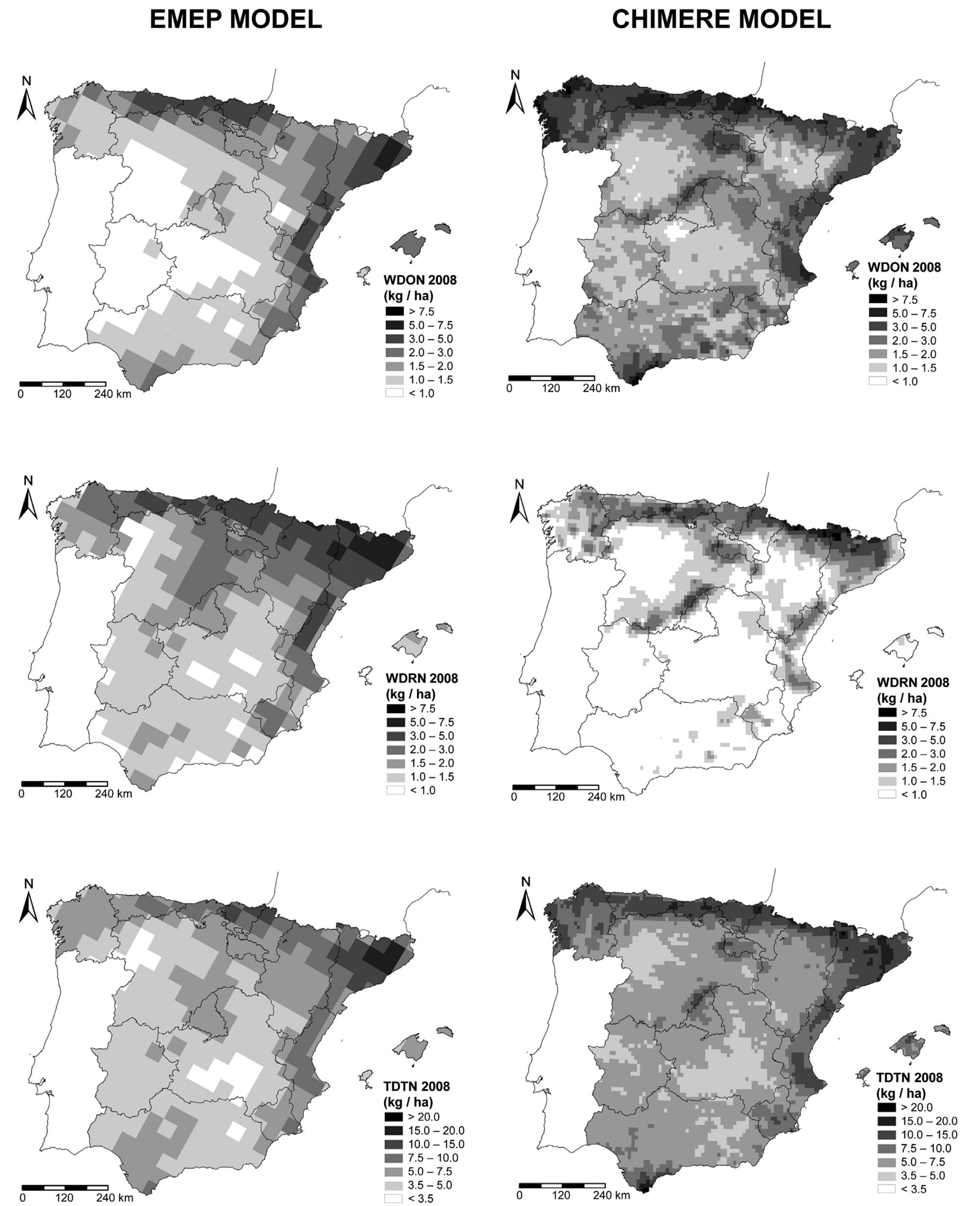


Fig. 4. Wet deposition of oxidized and reduced nitrogen (WDON and WDRN), and total deposition of nitrogen (TDTN) in 2008, according both EMEP and CHIMERE models.

of reduced N in the Pyrenees along the border with France, with values up to 12.1 kg N ha^{-1} $year^{-1}$. On the other hand, oxidized N estimated with CHIMERE showed maxima values throughout the northern coast (including the Cantabrian Range) 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) (Fig. 4).

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 receiving the highest loads of N wet deposition, mainly located in the north and NE regions, enclose some highly populated and industrialized areas and present high precipitation rates (AEMET, 2011). Transboundary pollution can also represent an important contribution (up to 60–70%) in some of the areas that show high N deposition such as Northern Spain or the vicinity of the Strait of Gibraltar (Nyíri et al., 2010).

Air quality models also provide estimations of N dry deposition. Spanish WDTN estimated for 2008 was within the range 1.5–13.4 kg N ha^{-1} $year^{-1}$ when using EMEP and 0.9–16.1 kg N ha^{-1} $year^{-1}$ when using CHIMERE. 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, dry deposition represented 11–83% of total N deposition with an average value of 54%. Previous studies performed in Spain calculated that dry deposition represented 62–67% of total N deposition in *Quercus ilex* forests (Rodà 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 grid cells 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 this Mediterranean area. More detailed studies are needed to characterize dry deposition in ecosystems under typically Mediterranean climate conditions. When considering both dry and wet N deposition, total N deposition in 2008 in Spain reached maxima values of 19.45 kg N ha^{-1} $year^{-1}$ and 22.98 kg N ha^{-1} $year^{-1}$ for EMEP and CHIMERE, respectively. Distribution of total N deposition followed similar patterns 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 (Fig. 4).

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 habitats of Community interest included in the Natura 2000 network. Exceedances of empirical N critical load and the area affected were calculated for the different habitat types (Annex 1) and subgroups (Table 2). The CHIMERE model predicts an area at risk more than twice as large as the one foreseen with EMEP model (3785.3 and 1440.8 km^2 respectively, Table 2). The threatened areas are mainly located in high N deposition regions (Figs. 4 and 5) and mostly involve habitats with high sensitivity to N deposition, based on their low empirical CLs. Sensitive habitats with N empirical CLs of 10 kg N ha^{-1} $year^{-1}$ or lower include natural grasslands and humid meadows, mountain forests, and typically Mediterranean heaths (Table 2, Annex 1).

The most sensitive habitat to atmospheric N deposition based on the low empirical CLs and the percentage of area affected is the 'natural grasslands' (subgroup 61). This category presents 30–60% of its area at risk of N enrichment due to atmospheric N deposition (Table 2). This sub-group includes the habitat at highest risk within the Spanish Natura 2000 network, the 'siliceous Pyrenean *Festuca eskia* grasslands' (habitat type 6140), with a threatened surface from 79 to 100% of the assessed area depending on the model considered (Annex 1). In fact, this habitat type is located in the Pyrenees, where both models predict the highest exceedance occurrence. Most of the empirical CLs used for natural grasslands were ascribed to their specific habitat type, and had good reliability ('#' in Annex 1) according to Bobbink and Hettelingh (2011). For this reason, the major uncertainty of the potential threat of N deposition to Pyrenean grasslands, and to other grasslands located in alpine areas, is that no monitoring sites are available to test model performance for estimating N deposition in this alpine level. Moreover, other high-altitude vegetation types like *Pinus uncinata* or *Abies pinsapo* forests, oro-Mediterranean heathlands or *Cytisus purgans* formations seem to be highly threatened by N deposition according to the models (Annex 1). Therefore, further deployment of atmospheric deposition monitoring networks should be implemented in Spanish mountain areas for monitoring atmospheric pollution and assess the risk of effects on these particularly rich and valuable ecosystems.

Other habitat category which requires special attention is the 'Mediterranean sclerophyllous forests' (subgroup 93). These forests represent a distinctive ecosystem and landscape of the Mediterranean Basin, including forests of Holm oak (*Q. ilex* L.), the dominant tree species in the Iberian Peninsula. The surface of these forests potentially affected is only 6.5–6.6% (Table 2) of the total area assessed in Spain, according to EMEP and CHIMERE models respectively. However, most of the threatened area of this sub-group corresponds to Holm oak forests located in NE Spain, close to Barcelona city (Fig. 5), where average exceedances up to almost 4 kg N ha^{-1} have been predicted with EMEP. In this sense, high N atmospheric deposition of 15–30 kg N ha^{-1} $year^{-1}$ has been previously reported in this area, together with increases of NO_3^- concentration in streamwater (Rodà et al., 2002; Àvila and Rodà, 2012). The low N concentration found in streamwater suggests that these ecosystems are still far from N saturation since most of the deposited N is still retained within the ecosystem (Àvila and Rodà, 2012; Bernal et al., 2013). Estimated N amounts annually stored in Holm oak above ground biomass are in the range of the N wet deposition occurring in this area (Escarré et al., 1999). However, other effects of N deposition could be already occurring before N saturation (Emmett, 2007) and need further investigation. An empirical CL of 15 kg N ha^{-1} $year^{-1}$ was ascribed to these sclerophyllous forests for preventing nitrate leaching from the ecosystem following

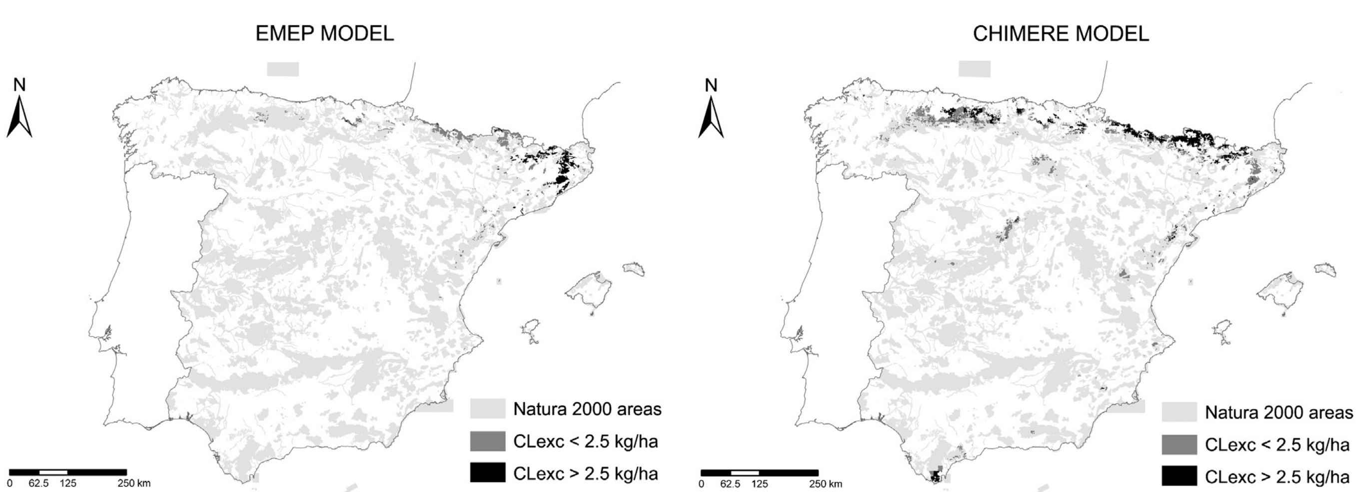


Fig. 5. Natura 2000 areas experiencing an exceedance of the assigned critical load (CL_{exc}) according to EMEP and CHIMERE models.

expert criteria (Bobbink and Hettelingh, 2011). However, critical loads from 5.5 kg N ha^{-1} $year^{-1}$ to 26 kg N ha^{-1} $year^{-1}$ have been proposed for the protection of epiphytic lichens in similar natural ecosystems (Fenn et al., 2010; Pinho et al., 2012).

Both models highlight that the highest occurrence of threatened areas happen in NE Spain, particularly in the Pyrenees mountain range, where 41% and 71% of the area assessed within the Spanish Alpine Bio-geographical Region could be experiencing CL exceedances, according to EMEP and CHIMERE models, respectively. This high risk is explained by the elevated N deposition and the presence of sensitive habitats such as mountain grasslands, heaths and some forest ecosystems. This result agrees with the effects of N deposition already reported in the area of Central Pyrenees (*Aigüestortes i Estany de Sant Maurici* National Park, 2236 m.a.s.l.), where increases of nitrate concentration in headwater streams of high altitude catchments have been associated with a N saturation process due to atmospheric N deposition (*Aigüestortes i Estany de Sant Maurici* National Park, 2236 m.a.s.l.; Camarero and Catalan, 2012; Camarero and Aniz, 2010). Other areas, detected with the CHIMERE model, where exceedances of N empirical CLs could be occurring are the mountainous regions located north of Madrid City (central Spain), in the Eastern Coast, on the Cantabrian Range (northern Spain) and near the Strait of Gibraltar (southern Spain).

The present analysis represents the first approach to assess the risk of effects of N enrichment for Spanish ecosystems within Natura 2000 network. Exceedances of N critical loads were related with high WDON more often than with high WDRN or dry deposition rates. Although further investigation is urgently needed to confirm the suitability of N empirical critical loads used, this study points out that some natural ecosystems could be receiving atmospheric N deposition above safety thresholds and, consequently, suffering harmful effects. The habitats most at risk are the Pyrenean grasslands, mountain forests of *P. uncinata* or *A. pinsapo*, Mediterranean sclerophyllous forests of Catalonia and the oro-Mediterranean heathlands of the Cantabrian Range. Interestingly, some evidences of N effects have been already reported in some of these areas (Àvila and Rodà, 2012; Blanes et al., 2013; Camarero and Catalan, 2012). These agreements suggest that the methodology applied in this analysis results suitable for risk assessment of N deposition effects in Spanish natural and semi-natural habitats.

4. Conclusions

EMEP and CHIMERE air quality models constitute suitable tools to provide acceptable estimates of N wet deposition, particularly for oxidized N in Spain. However, estimates should be applied with caution in studies at small regional scale and in regions with complex topography and the influence of local emissions. Measured wet deposition of nitrogen in Spain reached maxima values of WDTN up to 13.3 kg N ha^{-1} $year^{-1}$ in northern Spain for the period 2005–2008. Both models estimated higher wet deposition of N in the north and northeast Spain. Adding dry deposition, total N deposition in 2008 in Spain reached maxima values of 19.5 kg N ha^{-1} $year^{-1}$ and 22.9 kg N ha^{-1} $year^{-1}$ calculated with EMEP and CHIMERE, respectively. Distribution of total N deposition followed similar patterns observed for wet deposition.

Total atmospheric N deposition exceeded in many areas the empirical critical loads proposed for the protection of terrestrial habitat of Community interest included in the Spanish Natura 2000 network. The habitats presenting the highest risk of N effects are the natural grasslands of mountain areas located in the north (Pyrenees, Cantabrian Range), together with some forests and endemic heaths in the same areas. Biodiversity conservation in these protected areas could be endangered by N deposition. Other habitats showing significant exceedances of N empirical critical loads were located in mountain areas close to high emission sources, such as Mediterranean forests and mountain scrublands close to Barcelona and Madrid cities, in the Eastern Coast, and near the Strait of Gibraltar.

These results highlight that atmospheric N deposition should be considered as a factor that could be affecting the biodiversity and health of the protected natural ecosystems in Spain. Since most of the threatened habitats are located in mountain areas, atmospheric deposition networks should be extended and include some monitoring stations in mountain regions. More detailed investigations should be carried out to quantify current effects, to improve empirical critical loads definition for some Mediterranean ecosystems and to explore possible management practices that might ameliorate these effects.

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Conflict of interest

The authors declare that there are no conflicts of interest.

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References

Aas W, Solberg S, Gauss M, Simpson D. The Mediterranean Region. Transboundary acidification, eutrophication and ground level ozone in Europe in 2008. EMEP status report 1/2010Oslo, Norway: The Norwegian Meteorological Institute; 2010. p. 99–104.

AEMET. Iberian climate atlas. In: National Meteorological Agency and Ministry of Environment, Marine and Rural Affaris, editors. Air temperature and precipitation (1971–2000); 2011. [Available at http://www.aemet.es/documentos/es/conocermas/publicaciones/Atlas-climatologico/Atlas.pdf].

Ariño AH, Gimeno BS, Pérez de Zabalza A, Ibáñez R, Ederra A, Santamaría JM. Influence of nitrogen deposition on plant biodiversity at Natura 2000 sites in Spain. In: Hicks WK, et al, editors. Nitrogen deposition and Natura 2000. Science & practice in determining environmental impacts. COST729/Nine/ESF/CCW/JNCC/SEI Workshop ProceedingsCOST; 2011. p. 140–6. [http://cost729.ceh.ac.uk/n2kworkshop].

Àvila A, Rodà F. Assessing decadal changes in rainwater alkalinity at a rural Mediterranean site in the Montseny Mountains (NE Spain). Atmos Environ 2002;36:2881–90.

Àvila A, Rodà F. Changes in atmospheric deposition and streamwater chemistry over 25 years in undisturbed catchments in a Mediterranean mountain environment. Sci Total Environ 2012;434:18–27.

Àvila A, Molowny-Horas R, Gimeno BS, Peñuelas J. Analysis of decadal time series in wet N concentrations at five rural sites in NE Spain. Water Air Soil Pollut 2010;207(1–4):123–38.

Bernal S, Belillas C, Ibáñez JJ, Àvila A. Exploring the long-term response of undisturbed Mediterranean catchments to changes in atmospheric inputs through time series analysis. Sci Total Environ 2013;458–460:535–45.

Bessagnet B, Hodzic A, Vautard R, Beekmann M, Rouil L, Rosset R. Aerosol modelling with CHIMERE — first evaluation at continental scale. Atmos Environ 2004;38(18):2803–17.

Blanes MC, Viñegla B, Merino J, Carreira JA. Nutritional status of *Abies pinsapo* forests along a nitrogen deposition gradient: do C/N/P stoichiometric shifts modify photosynthetic nutrient use efficiency? Oecologia 2013;171:797–808.

Bleeker A, Hicks WK, Dentener E, Galloway J, Erisman JW. N deposition as a threat to the world's protected areas under the convention on biological diversity. Environ Pollut 2011;159(10):2280–8.

Review and revision of empirical critical loads and dose–response relationships. In: Bobbink R, Hettelingh JP, editors. Coordination centre for effectsNational Institute for Public Health and the Environment (RIVM); 2011. [www.rivm.nl/cce. 244 pp.].

Bobbink R, Hicks K, Galloway J, Spranger T, Alkemade R, Ashmore M, et al. Global assessment of nitrogen deposition effects on terrestrial plant diversity: a synthesis. Ecol Appl 2010;20(1):30–59.

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

Camarero L, Catalan J. Atmospheric phosphorus deposition may cause lakes to revert from phosphorus limitation back to nitrogen limitation. Nat Commun 2012;3:1118.

Chang JC, Hanna SR. Air quality model performance evaluation. Meteorol Atmos Phys 2004;87:167–96.

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

Cuvelier C, Thunis P, Karam D, Schaap M, Hendriks C, Kranenburg R, et al. ScaleDep: performance of European chemistry-transport models as function of horizontal special resolution. EMEP Technical report 1/2013; 2013. [63 pp.].

Dentener F, Drevet J, Lamarque JF, Bey I, Eickhout B, Fiore AM, et al. Nitrogen and sulfur deposition on regional and global scales: a multi-model evaluation. Global Biogeochem Cycles 2006;20(4):GB4003.

Dise NB, Ashmore M, Belyazid S, Bleeker A, Bobbink B, de Vries W, et al. Nitrogen as a threat to European terrestrial biodiversity. In: Sutton MA, et al, editors. The European nitrogen assessment. Sources, effects and policy perspectivesCambridge University Press; 2011. p. 463–94.

EEA. Air quality in Europe — 2011 report. European Environment Agency Technical Report 12/2011; 2011. [Available on-line at http://www.eea.europa.eu].

EEA. Air quality in Europe — 2013 report. European Environment Agency Technical Report No. 9/2013; 2013. [Available on-line at http://www.eea.europa.eu].

Emmett AB. Nitrogen saturation of terrestrial ecosystems: some recent findings and their implications for our conceptual framework. Water Air Soil Pollut Focus 2007;7: 99–109.

Erisman JW, Mols H, Fonteijn P, Geusebroek M, Draaijers G, Bleeker A, et al. Field intercomparison of precipitation measurements performed within the framework of the Pan European Intensive Monitoring Program of EU/ICP forest. Environ Pollut 2003; 125:139–55.

Escarré A, Rodà F, Terradas J, Mayor X. Nutrient distribution and cycling. In: Rodà F, Retana J, Gracia CA, Bellot J, editors. Ecology of Mediterranean evergreen oak forests. Ecological studiesBerlin: Springer; 1999. p. 253–69.

Fagerli H, Gauss M, Benedictow A, Griesfeller J, Jonson JE, Nyiri A, et al. Transboundary acidification, eutrophication and ground level ozone in Europe in 2009. EMEP Status Report 1/2011. Oslo: Norwegian Meteorological Institute; 2011. [127 pp.].

Fenn ME, Allen EB, Weiss SB, Jovan S, Geiser LH, Tonnesen GS, et al. Nitrogen critical loads and management alternatives for N-impacted ecosystems in California. J Environ Manage 2010;91:2404–23.

Galloway JN, Townsend AR, Erisman JW, Bekunda M, Cai ZC, Freney JR, et al. Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science 2008;320(5878):889–92.

Henry J, Aherne J. Nitrogen deposition and exceedance of critical loads for nutrient nitrogen in Irish grasslands. Sci Total Environ 2014;470–471:216–23.

Hirst D, Storvik G. Estimating critical load exceedance by combining the EMEP model with data from measurement stations. Sci Total Environ 2003;310:163–70.

Izquierdo R, Àvila A. Comparison of collection methods to determine atmospheric deposition in a rural Mediterranean site (NE Spain). J Atmos Chem 2012;69(4):351–68.

Lorenz M, Becher GForest condition in Europe, 2012. Technical report of ICP forests. Work report of the Thünen Institute for World Forestry 2012/1Hamburg: ICP Forests; 2012. [165 pp.].

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

Mareckova K, Wankmüller R, Tista M, Murrells T, Walker H. Inventory review 2011 (review of emission data reported under the LRTAP Convention and NEC Directive, stages 1 and 2 review, shipping emissions, status of gridded data and LPS data). EEA & CEIP technical report 2011; 2011. [70 pp.].

Menut L, Bessagnet B, Khvorostyanov D, Beekmann M, Blond N, Colette A, et al. CHIMERE 2013: a model for regional atmospheric composition modeling. Geosci Model Dev 2013;6(4):981–1028.

Myers N, Mittermeier RA, Mittermeier CG, da Fonseca GA, Kent J. Biodiversity hotspots for conservation priorities. Nature 2000;403(6772):853–8.

Nyíri Á, Gauss M. Improved resolution in the EMEP model. Transboundary acidification, eutrophication and ground level ozone in Europe in 2008. EMEP Status Report 2010Oslo, Norway: The Norwegian Meteorological Institute; 2010. p. 99–104.

Nyíri Á, Gauss M, Klein H. Transboundary air pollution by main pollutants (S, N, O_3) and PM in 2010. Spain. MSC-W Data Note 1/20101890-0003; 2010. [24 pp.].

Ochoa-Hueso R, Allen EB, Branquinho C, Cruz C, Dias T, Fenn ME, et al. Nitrogen deposition effects on Mediterranean-type ecosystems: an ecological assessment. Environ Pollut 2011;159(10):2265–79.

Peñuelas J, Filella I. Herbaria century record of increasing eutrophication in Spanish terrestrial ecosystems. Glob Chang Biol 2001;7:427–33.

Pinho P, Theobald MR, Dias T, Tang YS, Cruz C, Martins-Loução MA, et al. Critical loads of nitrogen deposition and critical levels of atmospheric ammonia for semi-natural Mediterranean evergreen woodlands. Biogeosciences 2012;9:1205–15.

Rockström J, Steffen W, Noone K, Persson Å, Chapin FS, Lambin EF, et al. A safe operating space for humanity. Nature 2009;461(7263):472–5.

Rodà F, Àvila A, Rodrigo A. Nitrogen deposition in Mediterranean forests. Environ Pollut 2002;118:205–13.

Sanz MJ, Carratalá A, Gimeno C, Millán MM. Atmospheric nitrogen deposition on the east coast of Spain: relevance of dry deposition in semi-arid Mediterranean regions. Environ Pollut 2002;118:259–72.

Simpson D, Fagerli H, Hellsten S, Knulst JC, Westling O. Comparison of modelled and monitored deposition fluxes of sulphur and nitrogen to ICP-forest sites in Europe. Biogeosciences 2006a;3:337–55.

Simpson D, Butterbach-Bahl K, Fagerl H, Kesik M, Skiba U, Tang S. Deposition and emissions of reactive nitrogen over European forests: a modelling study. Atmos Environ 2006b;40(29):5712–26.

Simpson D, Benedictow A, Berge H, Bergstrom R, Emberson LD, Fagerli H, et al. The EMEP MSC-W chemical transport model — technical description. Atmos Chem Phys 2012; 12(16):7825–65.

Sutton MA, Billen G, Bleeker A, Erisman JW, Grennfelt P, van Grinsven H, et al. The European nitrogen assessment. Technical summary. In: Sutton MA, et al, editors. The European nitrogen assessment. Sources, effects and policy perspectivesCambridge University Press; 2011. [pp. xxxv-li].

Vivanco MG, Correa M, Azula O, Palomino I, Martín F. 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 5072Germany: Editorial: Springer; 2008. p. 165–78. [ISBN-10: 3-540-69838-8].

Vivanco MG, Palomino I, Vautard R, Bessagnet B, Martín F, Menut L, et al. Multi-year assessment of photochemical air quality simulation over Spain. Environ Model Software 2009;24:63–73.

Whitfield C, Strachan I, Aherne J, Dirnböck T, Dise N, Franzaring J, et al. Assessing nitrogen deposition impacts on conservation status. Working group report. In: Hicks WK, et al, editors. Nitrogen deposition and Natura 2000: science and practice in determining environmental impacts. COST729/Nine/ESF/CCW/JNCC/SEI workshop proceedingsCOST; 2011. p. 88–100.

Yu S, Eder B, Dennis R, Schwartz SH. New unbiased symmetric metrics for evaluation of air quality models. Atmos Sci Lett 2006;7:26–34.