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Original article

Ammonia agriculture emissions: From EMEP to a high resolution inventory

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ABSTRACT

Agriculture is the main source of atmospheric ammonia (NH_3). Methodologies are needed to quantify national NH_3 emissions. For European continental scale the EMEP emissions inventory with a 50×50 km^2 resolution is yearly available. However, current air quality models are often applied with higher spatial resolution, in order to obtain representative results, especially at urban and regional scales; therefore, a simple top-down approach based in the spatial interpolation of EMEP emissions is not sufficient.

The aim of this work is the development and application of a mixed top-down and bottom-up methodology for high resolution emissions inventory for the agriculture sector, based on EMEP and other public data sources (E-PRTR inventory, statistical data, etc.) for Western Spain and Portugal.

This new emission inventory was compared with EMEP and assessed using the WRF-CAMx air quality modelling system. Results highlighted the influence of the meteorology (high temperatures) and the magnitude of emissions on NH_3 air quality concentrations. The higher resolution emissions lead to the highest maximum NH_3 ground level concentrations, in specific locations.

1. Introduction

The agriculture activity emits species such as ammonia (NH_3), hydrogen sulfide (H_2S), methane (CH_4), nitrous oxide (N_2O), and volatile organic compounds (VOCs) which have particular important impacts on air quality, on the eutrophication of the ecosystems, as well as on global and regional warming (Zhang et al., 2013). Among these species, NH_3 is an important and singular pollutant, because of its large emissions and local effects. Moreover, it is the most abundant alkaline gas in the atmosphere, playing an important role in the nitrogen cycle (by neutralizing of acid gases in the air). Ammonia is also highly reactive either in forming aerosols (Erisman and Schaap, 2003), or by depositing rapidly to most surfaces including sensitive ecosystems (Sutton et al., 2007).

Emissions of ammonia cause considerable atmospheric concentrations near strong agriculture sources (Fowler et al., 1998; Geels et al., 2012; Hallsworth et al., 2010; Kryza et al., 2011), however the overall ammonia concentrations are quickly reduced to a low background level as ammonia is dispersed and incorporated into aerosols. These aerosols typically contribute with 30% of

Abbreviations: AA, Agriculture Areas in Corine Land Cover database; APA, Portuguese Environmental Agency; CAMx, Comprehensive Air Quality Model with Extensions; CB05, Carbon Bound V chemical mechanism; CEIP, Centre on Emission Inventories and Projections; CLRTAP, Convention on Long-Range Transboundary Air Pollution; CMR, Galician Regional Ministry of Rural; CORINAIR, Core Inventory Air Emissions; CTM, Chemical Transport Model; EEA, European Environment Agency; ECMWF, European Centre for Medium Range Weather Forecast; EF, emission factor; EMEP, European Monitoring and Evaluation Programme; E-PRTR, European Pollutant Release and Transfer Register; EMEPI, EMEP inventory air quality simulation; ERA Interim, ECMWF global atmospheric reanalysis; FAO, Food and Agriculture Organization of the United Nations; GIS, Geographic Information System; hd, Annual cattle head number; ha, hectare; INES, Spanish National Emission Inventory; MAGRAMA, Ministry of Agriculture and Environment (Spain); MARM, Ministry of the Environment and Rural and Marine Affairs (Spain); MOZART, Model for Ozone and related Chemical Tracers; NEMA, National Emission Model for Ammonia; NMI, new mixed inventory air quality simulation; NUTS, Nomenclature of Territorial Units for Statistics; PBL, Planetary Boundary Layer; PINE, Portuguese National Statistical Institute; PXRAG, Galician Regional Agriculture Waste Management Programme; SIA, Secondary Inorganic Aerosol; SINE, Spanish National Statistical Institute; SNAP, Standardized Nomenclature for Air Pollutants; VOCs, volatile organic compounds; WRF, Weather Research & Forecast model.

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$PM_{2.5}$ and 50% PM_{10} in total mass aerosol (Anderson et al., 2003), which may have adverse effects on human health (Moldanová et al., 2011).

Agriculture is the main source of ammonia emissions in Europe, contributing in average between 80% and 99% (EEA, 2009a). The main NH_3 sources from agriculture are related to the excretion of urine by livestock, i.e. referred to total urine excretion: livestock housing (33–43%) (Groenestein, 2006), manure storage and grazing (22–26%) (Bussink, 1992), and manure application (as mineral fertiliser, 17–26%) (Skjøth and Geels, 2013). Moreover, the application of fertilizers containing urea and of ammonia based mineral Nitrogen fertilizers on calcareous soils also constitutes a source of NH_3 (Bouwman et al., 2002).

Some studies on emission inventories of the agriculture sector in European countries have been performed. The last UK National Atmospheric Emissions Inventory Report (Misra et al., 2015) includes NH_3 agriculture emissions from 2010 to 2013 period, with 227 kt NH_3 in 2012; and 112 kt NH_3 came from dairy and non-dairy cattle. This is primarily due to the large losses measured from the land spreading of slurry and farmyard manure (59 kt NH_3 per year), housing of cattle (33 kt NH_3 per year) and storage of "wastes" (20 kt NH_3 per year). Also, Geels et al. (2012) apply an updated Danish NH_3 emissions inventory.

In Velthof et al. (2012) the NEMA (National Emission Model for Ammonia) results show that the total NH_3 emission from agriculture in the Netherlands in 2009 was 88.8 Gg NH_3–N, of which 50% from housing, 37% from manure application, 9% from mineral N fertilizer, 3% from outside manure storage, and 1% from grazing.

Guevara et al. (2013) introduced the data, methods and procedures to estimate the emissions for each SNAP sector using bottom-up approaches. However, due to the lack of specific information on agriculture activity data and *EF*s, emissions from this sector were estimated by performing a downscaling methodology of the original Spanish National Emission Inventory version 2009 (INESP09), which represents the official Spanish contribution to the EMEP emission inventory. It reports total annual emissions of primary pollutants by NUTS 2 level and SNAP elemental activity. In this case, agriculture land uses (EEA, 2011) are used as proxy data. In the referred work, NH_3 emissions were not included in the spatial distribution of the HERMESv2.0 annual emissions in the Iberian Peninsula domain (4×4 km^2) because most (90%) come from SNAP10.

Several attempts have been made to characterize and homogenize the emission inventories and their compilation and calculation procedures. The Convention on Long-Range Transboundary Air Pollution, CLRTAP, in 1979 laid the foundation for the 1984 Cooperative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe, EMEP (CEIP, 2007). Among the major objectives of current EMEP programme are the compilation and analysis of emission data and the regular supply of truthful and verified information about emissions to the scientific and politic communities. Usually following a bottom-up approach, these emissions are aggregated and reported for main pollutants, aerosols, heavy metals and persistent organic pollutants, by sector and geographically referenced over a grid with a spatial resolution of 50×50 km^2.

As EMEP emissions inventory is an aggregated inventory with a low spatial resolution, for CTMs applications in tropospheric studies it is usual to apply a top-down approach to achieve an appropriate higher resolution: the emissions are calculated for a total area and then distributed according to different downscaling or allocation patterns related to the emission source. This approach has an acceptable accuracy for global purposes, but not for regional purposes for which it is not sufficiently accurate. The characterization of the emissions for a specific country or country region requires the compilation of specific data about the region. The resolution of the EMEP inventory is not able to represent the internal variability of each cell of 50×50 km^2, especially when trying to incorporate industrial plants, urban areas, etc (Butler et al., 2008) and when using it for higher resolution air quality modelling applications. More recently, other inventories with higher spatial resolutions (Pouliot et al., 2012) are used in CTMs applications; however, none of those approaches allow control specific emissions sources processes, in order to consider the influence of those processes in air quality.

A bottom-up strategy would improve the emissions accuracy as it is based in the detailed calculation of each one of the emission sources, including specific information of the considered area or facility. The characterisation of every single emission source and activity is unachievable and would imply the compilation and handling of large amounts of information which is not always available, besides a great calculation effort. Since the bottom-up strategy is a complex procedure and the accuracy and distribution of the top-down resulting emissions may not be adequate, a joint methodology is often proposed, combining both approaches from public information sources (Maes et al., 2008). At the same time, Saarinen (2003) highlighted that every emissions inventory over the same region must be comparable, i.e., top-down and bottom-up inventories should achieved the same total emissions results.

In addition, for long term CTMs applications temporal variation throughout the seasons at shorter/longer time scales is a recent and interesting topic to be considered (Skjøth et al., 2011; Sutton et al., 2013; Skjøth and Geels, 2013). In that case, emissions dynamic modelling is highly recommend.

The aim of this study was therefore to develop and to apply a new high resolution emissions inventory from agriculture for Portugal and Western Spain, based on a mixed methodology, including detailed information regarding animal populations, manure management practices, farms location, and specific emission factors. Emission factors appropriate to the national context were selected from a literature review considering source characteristics and climate conditions (mainly, rainfall) in this region (Morán et al., 2014). The developed emission inventory was evaluated and compared to the EMEP inventory using an air quality modelling application in episodic basis.

2. Description of mixed methodology for emission estimation

A new high spatial resolution NH_3 emission inventory for agriculture has been developed for Portugal and the West of Spain (with a special focus in Galicia region). In order to characterize the agriculture NH_3 emissions (SNAP10), two main activity groups (farms and crops related) have been identified and different types of calculation strategies were adopted, as follows.

- Bottom-up strategy: farms with pig, poultry, dairy and beef cattle, including emissions from enteric fermentation and manure management regarding organic compounds for these different types of livestock.
- Top-down strategy: crops-related emissions, that is, emissions coming from crops with fertilizer (fertilized agricultural land), crops without fertilizers, burning of stubble, straw, the use of pesticides and limestone and fugitive sources of PM distributed.

It is important to notice that, although new emission estimations were done for animal farms emissions, in order to keep the same total SNAP10 EMEP emissions in the study region crop-related emissions were distributed by land use in the new high resolution grid, and added as residual emissions, cell by cell.

Strategies selection was driven by the availability of the information required, including both EMEP and E-PRTR emissions. In this work, year 2009 inventory was applied, as it was the last one with validated E-PRTR data (Dios et al., 2014), and metadata, also required in bottom-up strategy.

The resulting joint mixed approach combines.

a) Using a bottom-up strategy, emissions directly obtained from measurements (when available) and/or specific factors applied in E-PRTR database for pig and poultry farms, according to the current legislation (European Commission, 2006),
b) Also using a bottom-up strategy, estimated cattle emissions from the use of standard emission factors (and their corresponding activity factors), and,
c) Using a top-down strategy, residual emissions from EMEP inventory, spatially distributed by land use (Dios et al., 2012).

For the rest of the pollutants, namely CO, NMVOC, NO_x, PM and SO_x, a distribution by land use has been made, as these one are not the main goal of the present study, but higher emissions spatial resolution than EMEP inventory grid is required for the air quality simulations. In this work, this new SNAP10 inventory was set to a 9×9 km^2 horizontal resolution grid.

In the following sections, the two different methodologies applied (bottom-up and top-down) are described.

2.1. Bottom-up strategy

The new cattle emissions inventory was obtained from a bottom-up strategy, considering either each animal farm (in Galicia) or each municipality (in Portugal and the rest of Spanish regions) as a point source. However, because of this large number of point sources (usually, with relatively small emissions), their emissions were set to a 9×9 km^2 resolution grid over the inventory domain. In this new grid, a cell (i,j) was considered as an area source, and its emissions were obtained by adding all the emissions from farms/municipalities located in the cell (i,j).

For the animal farms emissions estimation, the different categories of cattle, the number of animals registered at municipal level, and the specific emission factors for each manure management systems were considered. NH_3 emissions were calculated by multiplying the number of animals (N) in each category (i) by an appropriate emission factor (EF) provided by the EMEP/CORINAIR Atmospheric Emission Inventory Guidebook (EEA, 2009a). Then, the total emission is obtained by adding the emissions of all animal categories,

$$Emission(t/year) = \sum EF_i \cdot \frac{N_i}{1000} \quad (1)$$

Table 1 shows the emission factors applied to calculate NH_3, emissions according to different livestock categories and manure management systems (EEA, 2009a).

According to the most usual manure management system applied (FAO, 2009; PXRAG, 2001), the study region was divided in two sections. In Galicia, Asturias and the North of Portugal (with 1093 mm annual rainfall in the year 2009; PINE, 2009a), the most usual management system is the liquid storage, due to their high rainfall and, also, the animal housing system, producing a fluid-pasty consistency excrement, namely suspension, which requires storage structures capable of containing run-offs (tanks and ponds). These leachates are liquid and semi-liquid effluent from the stables, consisting of a mixture of faeces, urine and cleaning water. Therefore, the dilution of these leachates is variable. When manure is either stored or processed as a liquid (eg., in tanks or wells) it produces large amounts of NH_3 (Webb et al., 2005).

Table 1
NH_3, *EF*s for each livestock category and manure management system (EEA, 2009a).

Livestock category	EF (liquid) (kg hd^{-1} yr^{-1}) for NH_3	EF (solid) (kg hd^{-1} yr^{-1}) for NH_3
Dairy cattle	39.3	28.7
Non-dairy cattle	13.4	9.2

In the rest of the study region (Southern parts of Spain and Portugal) the solid storage system is the most common, as this storage is carried out in unconfined piles, usually along several months. This is possible because of the large amount of bedding material and its high loss of humidity by evaporation. As a result, this solid manure is composed by solid animal excrements (faeces) with either solid or pasty form (due to its urine part), usually mixed to vegetable waste (straw or others) that serves as beds, absorbing the faeces and urine.

Fig. 1 shows the distribution of dairy and beef farms and different manure management systems in Spain (CMR, 2005; SINE, 2009) and Portugal (PINE, 2009b).

As it is shown, the Northern of Galicia and Asturias has more cattle farms, and most of them are dairy farms (which represent 60% of the total). Beef farms are mainly located in the South part, with small-sized farms (20.68 hd/farm). On the other hand, the rest of the region shows a well-balanced number of dairy and beef farms. This irregular distribution of farms is expected to be reflected in the pollutants emissions distribution.

According to the Portuguese National Statistics Institute, in 2009 the production of beef (which represents 79% of the total) in Portugal had its highest percentage in the Alentejo region representing 39% of the cattle population. Dairy cattle are concentrated in the Northern region of Portugal, where 78% of farms are focused on milk production, and also 78% of the total number of dairy cows are located (PINE, 2009b) (see Fig. 2).

Among the Spanish regions, Galicia (NW of Spain) is the region with more potential problems in terms of cattle emissions and their environmental impact: the number of cattle heads only represents 16% of the total in Spain; however, Galician farms are quite small so this region is leader in the number of livestock farms (CMR, 2005) and, also, in the number of animals per area (Fig. 2). In fact, between the Spanish regions, Galicia has the highest farms and animals densities. Regarding cattle farms production and feeding, Galicia is one of the most of important milk production regions in Spain, and its cows feeding is mainly based on wet forage (grass and maize silos), resulting in a moderate milk production per cow (6000–7000 kg yr^{-1}) (Blas et al., 2008).

Referred to cattle, Fig. 2 shows the evolution of the number of animals, and number of animals per farm in Galicia (1999–2012) and Portugal (1989–2013).

In Portugal, the average size of the cattle population has changed significantly in the last ten years. Over the time period 1999–2009, the number of animals per farm doubled, while in Galicia it increased 30% in the same period (Fig. 2). This is because of the trend in Galicia and Portugal to increase its productivity in dairy farms, associated to its reduction in the number of farms and total number of heads, and a higher yield per dairy cow ratio. These changes increase load livestock around the farms and their pollution risk, due to the decrease of the available area for the distribution of the manure; which is also increased as a result of the higher productive capacity per cow (PXRAG, 2001).

Other farms, not only cattle but also pig, poultry, were considered; in 2009 over the study region (Fig. 3): 152 farms of pig and poultry were registered in Portugal (E-PRTR, 2010) and 204 in

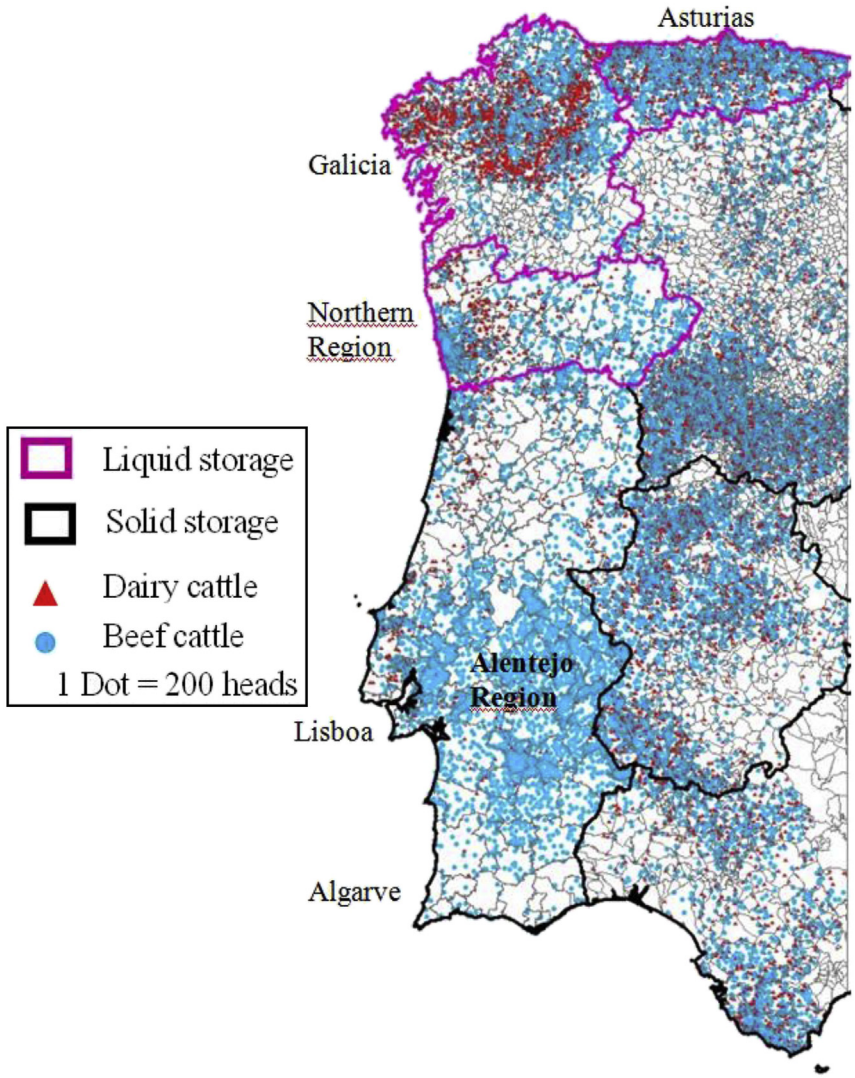

Fig. 1. Geographical distribution of dairy (red points) and beef farms (blue point) in West Spain and Portugal and different manure management systems in Portugal and Spain, for the year 2009.

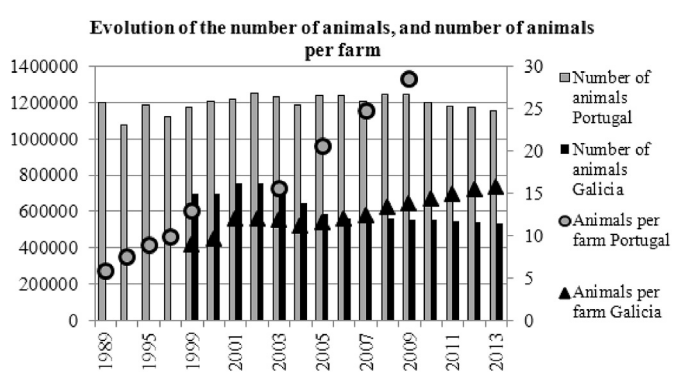

Fig. 2. Evolution of the number of animals, and number of animals per farm in Galicia (1999–2012) and Portugal (1989–2013).

Spanish regions (E-PRTR, 2012). Their emissions have also been estimated as point sources using the bottom-up strategy, using emission sources metadata collected in E-PRTR and emissions factors provided by EMEP/CORINAIR (EEA, 2009a).

2.2. Top-down strategy

As reference emission inventory for this air quality modelling experiment, the EMEP inventory is applied. To assess the effect of the new livestock activities emissions distribution in this air quality modelling results, the whole SNAP10 emissions must be substituted. However, livestock industry is only about 40–50% of SNAP10 total emissions (EEA, 1999), as emissions generated during the application of fertilizers over fields and agriculture wastes burning are also included. Therefore, these residual emissions (none livestock emissions) were estimated cell by cell as the difference between the EMEP SNAP10 emissions and the new calculated emission for livestock activities.

As agriculture emissions, EMEP SNAP10 residual emissions were spatially segregated to the 9 × 9 km^2 resolution grid, over those areas where agriculture activities take place (Dennis et al., 2009). EEA Corine Land Cover database (250 × 250 m^2 resolution; EEA, 2009b) was applied (Fig. 3). From the 6 main land uses classified in this database, agriculture emissions were distributed over the agriculture areas (AA) shown in Fig. 3. In Galicia, its agriculture area (37% of total land use, with forests and semi-natural areas covering 61% of the AA) is standing for complex cultivation patterns (64% of

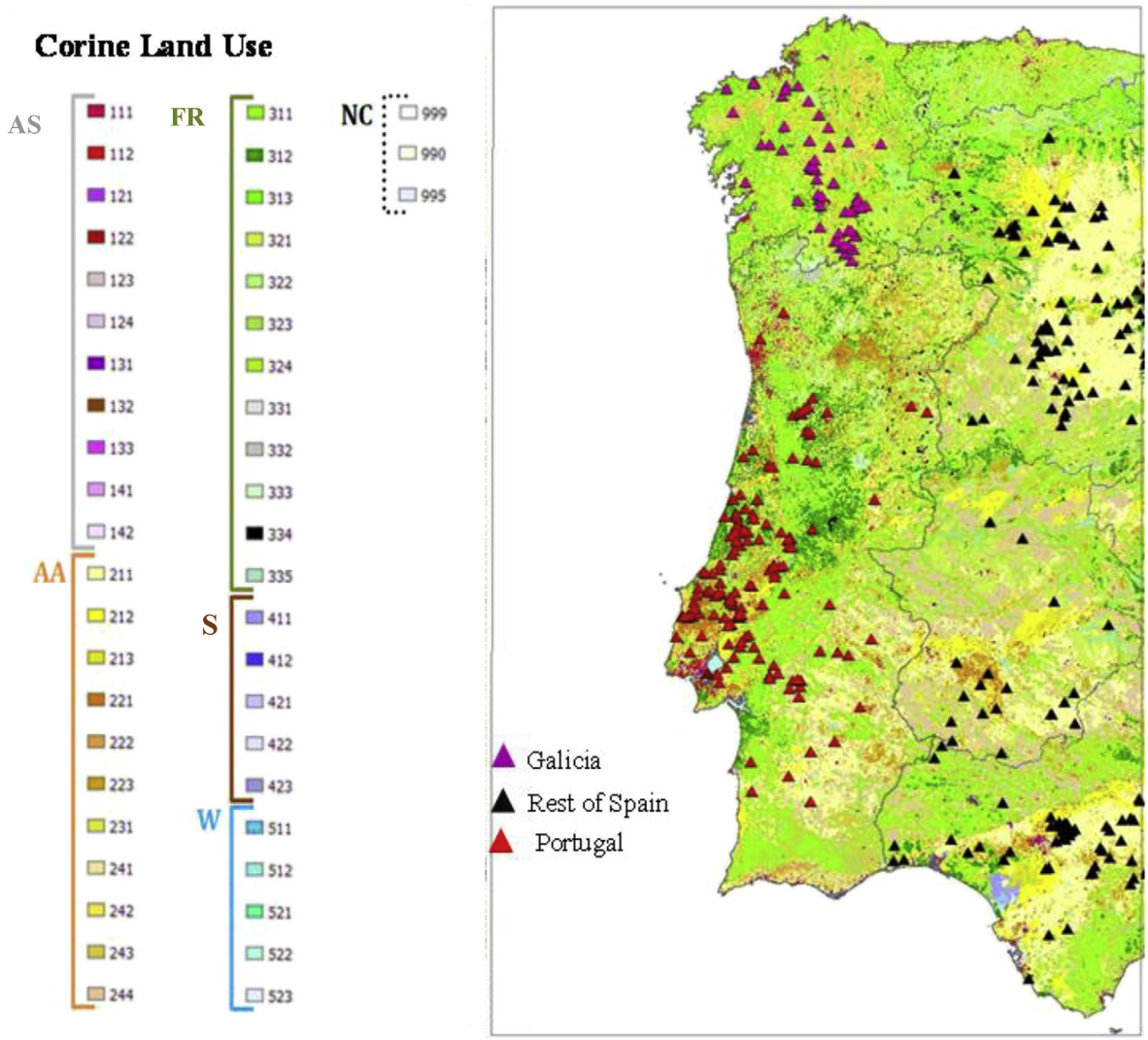

Fig. 3. Colored map of "Corine Land Cover" land use (EEA, 2009b) used for the segregation of the SNAP10 EMEP emissions. Also, poultry and pig farms locations (triangles) included in the emissions inventory are shown.

AA), mixed to forest and semi-natural areas, in many cases as small single-family properties or smallholdings with a lot of parcels directly managed by their owners. Therefore, a bottom-up strategy seems to be very complex, also because of the lack of specific activity factors per each parcel. In Portugal, the agriculture area accounts for 48% of its territory, with non-irrigated arable land covering to 26% of agriculture area. In the rest of Western Spain, where the agriculture area represents 53% of the total land use, heterogeneous agriculture and agro-forestry areas are also dominant (41% of AA), followed by the non-irrigated arable land (25% of AA).

3. The air quality modelling application

In order to apply this new emissions inventory to air quality modelling (Karvosenoja, 2008), the spatial distribution of the emission sources in a regular grid (9×9 km^2 horizontal resolution) was implemented by using a Geographic Information System (GIS) (Esri, 2011), which allows optimal emissions processing and graphical representation.

The air quality modelling application is focused on the impact assessment of two different SNAP10 inventories on air quality over Portugal and West of Spain: the new SNAP10 emissions inventory vs. the original EMEP SNAP10 inventory. Although both SNAP10 total emissions over the study region are equal, this assessment is driven by the impact of their NH_3 emissions spatial segregation (including bottom-up estimations) on the air quality levels. Therefore, two different simulations were performed by changing NH_3 agriculture emissions, but using the same modelling framework and the same emissions for the remaining atmospheric pollutants and activity sectors.

The WRF-CAMx air quality modelling system was applied in this study, which comprises the Weather Research & Forecast meteorological model (WRF) (Skamarock et al., 2008) and the Comprehensive Air quality Model with eXtensions (CAMx) chemical transport model (Morris et al., 2004). WRF is a well-known mesoscale numerical weather prediction system designed to serve both operational forecasting and atmospheric research needs that was previously tested over the study region. CAMx is a 3D chemistry-transport Eulerian photochemical model that allows for an integrated assessment of gaseous and particulate air pollution over many scales, ranging from sub-urban to continental; it was also applied over the study region in several air quality studies.

Two nested simulation domains were applied, covering Europe (D0) and the Western Iberian Peninsula (D1), with 27 × 27 and 9 × 9 km^2 horizontal resolutions, respectively. Fig. 4 compares the D1 domain, where new agriculture emissions were calculated cell by cell, and EMEP grid with 50 × 50 km^2 resolution over the same domain.

The WRF-CAMx modelling system was run along a period from June, 24th to July, 2nd 2011. The episode was selected based on both meteorological and air quality conditions (IPMA, 2015; APA, 2015). During these days, the Azores anticyclone was located northeast of the Iberian Peninsula and the study region was under the influence of continental warm and dry air masses. Consequently, this period was characterized by clear skies, very high solar radiation and temperature (maxima up to 40 °C on the 25th and 26th), dry conditions (no precipitation occurrences), which lead to high ozone concentration in almost all rural background air quality stations in the domain, especially on the 25th, 26th and 27th of June and on 1st and 2nd of July reaching hourly maximum concentrations above 200 μg m^{-3}. PM_{10} and $PM_{2.5}$ daily average concentrations were higher than 60 μg m^{-3} and 25 μg m^{-3} respectively, in almost all air quality stations on June 26th and 27th.

WRF model was initialized with ERA Interim global atmospheric reanalysis from the ECMWF (URL1), and its setup was defined according to previous studies conducted for Portuguese urban areas (Sá et al., 2012). Then, its resulting output fields were used as meteorological input to the CTM. CAMx, initial and boundary conditions for Europe were taken from the Model for OZone and Related chemical Tracers (MOZART), an offline global chemical transport model (Emmons et al., 2010). MOZART outputs were downloaded for June 2011 (http://www.acd.ucar.edu/wrf-chem/mozart.shtml), for every 6 h at 1.9° × 2.5° horizontal resolution and with 56 vertical levels. A pre-processing tool allowed for the conversion of MOZART gaseous and aerosol species into CAMx species according to the chemical mechanism in use – CB05.

Apart from NH_3 agriculture emissions (new inventory vs. EMEP inventory), other pollutants and SNAP sectors emissions were the same in both simulations, and they were based on the Portuguese (APA, 2014) and Spanish (MAGRAMA, 2015) national emission inventories, which are included in EMEP inventory. The total annual emissions of CO, NO_x, NH_3, NMVOC, SO_2, PM_{10} and $PM_{2.5}$ available at municipality level for each activity sector (SNAPs 2 to 10) were spatially disaggregated to the gridded simulation domain of 9 × 9 km^2 resolution. Emissions from energy production (SNAP1) were considered as point sources. Temporal profiles (month, week, day) were applied to the total emissions by SNAP activity sector. This preprocessing was performed for the emissions of both simulation domains.

4. Results

In this section, first, the new mixed agriculture SNAP10 inventory is presented and compared to EMEP inventory over the D2 simulation domain, focusing on NH_3; secondly, NH_3 ground level concentrations obtained by the WRF-CAMx simulation for the selected period, by using the new agriculture inventory and the EMEP inventory (CEIP, 2012) are compared in order to assess the main differences between them.

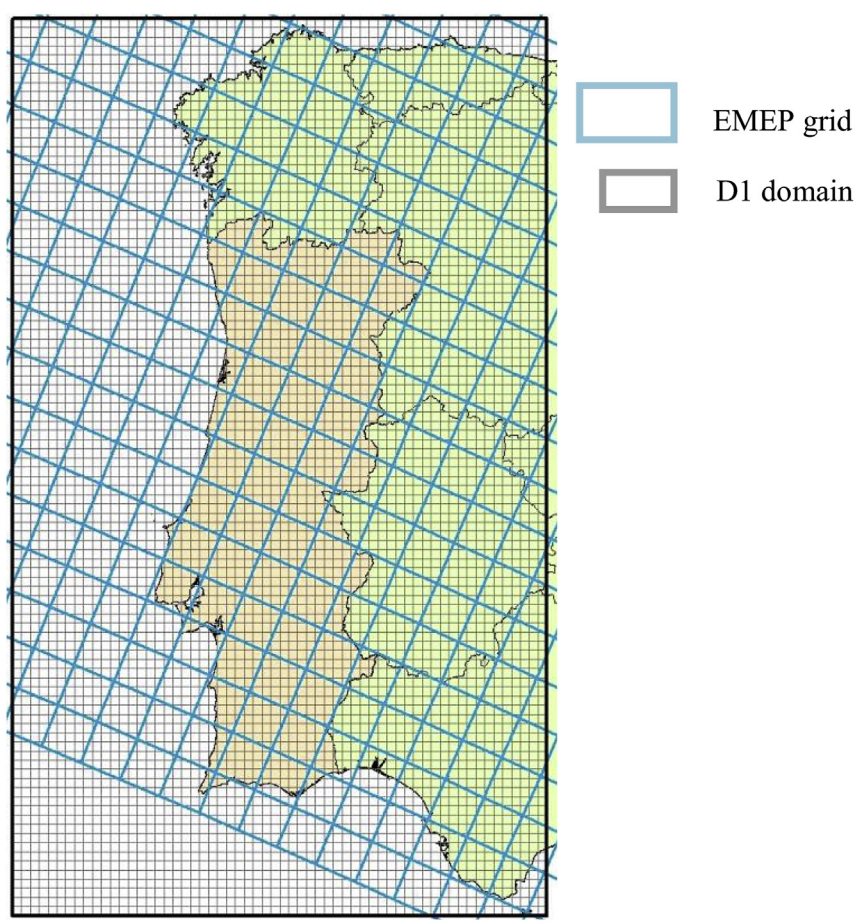

Fig. 4. Simulation domain D1 (9 × 9 km^2 resolution) considered for new agriculture emissions calculation and air quality simulation compared to EMEP grid over the same domain.

4.1. Agriculture mixed vs. EMEP inventories

Following the methodologies previously described, both SNAP10 inventories, new mixed inventory and EMEP inventory, were segregated over the same the 9 × 9 km^2 resolution grid covering a domain of Portugal and West of Spain, corresponding to the same regular D1 grid used in this air quality modelling application.

Fig. 5 shows NH_3 emissions in 2009 from the original EMEP inventory (50 × 50 km^2 resolution grid) for the agriculture sector segregated by area in the higher resolution D1 simulation grid (Fig. 5a) and the new mixed emissions inventory resulting from the new mixed methodology (Fig. 5b). First, significant differences in the spatial distribution are observed, namely the new mixed inventory shows more concentrated emissions in specific areas, accordingly to the actual farms geographical distribution in the study region; that is, the highest NH_3 emission values correspond to grid cells where more farms and cattle are located (see Figs. 1 and 3). Particularly, the highest emissions values are located in the Northern half of the Spanish territory, due to its higher density of farms and cattle; and in the West of Portugal, mainly due to its high concentration of poultry and pig farms. However, in the EMEP segregated inventory no significant spatial differences are observed in its emissions pattern over the study region.

Also, it is clear that cattle emissions have a strong contribution to SNAP10 agriculture sector emissions, as changing cattle emissions distribution between both inventories produces significant differences in their spatial distribution. Considering the new mixed inventory, the total NH_3 emissions from the agriculture sector are around 27 Mt/yr for Galicia and 42.5 Mt/yr for Portugal. Cattle farming, both dairy and beef, is the dominant source of NH_3 emission in Galicia (60%) and Portugal (48%) followed by the residual emissions (Galicia, 33%; Portugal, 39%) and pig and poultry farms (Galicia, 8%; Portugal, 13%).

However, it is not so clear whether these significant differences between both inventories may produce significant effects in air quality levels; particularly, in NH_3 gaseous concentrations. Therefore, air quality modelling results using both different emissions inventories were compared, as follows.

4.2. Air quality modelling

In order to consider possible relationships between emissions spatial segregation and air quality patterns, daily average simulated NH_3 ground level concentrations (glc), as well as PNH_4 (ammonium aerosol species considered in CAMx), were analysed in terms of spatial differences between new mixed inventory simulation (NMI) and EMEP inventory simulation (EMEPI). Fig. 6 shows the spatial distribution of those differences (NMI–EMEPI) for NH_3 daily average concentrations obtained for a group of representative simulated days. Positive values indicate that the new mixed inventory leads to higher NH_3 glc compared to the EMEP inventory.

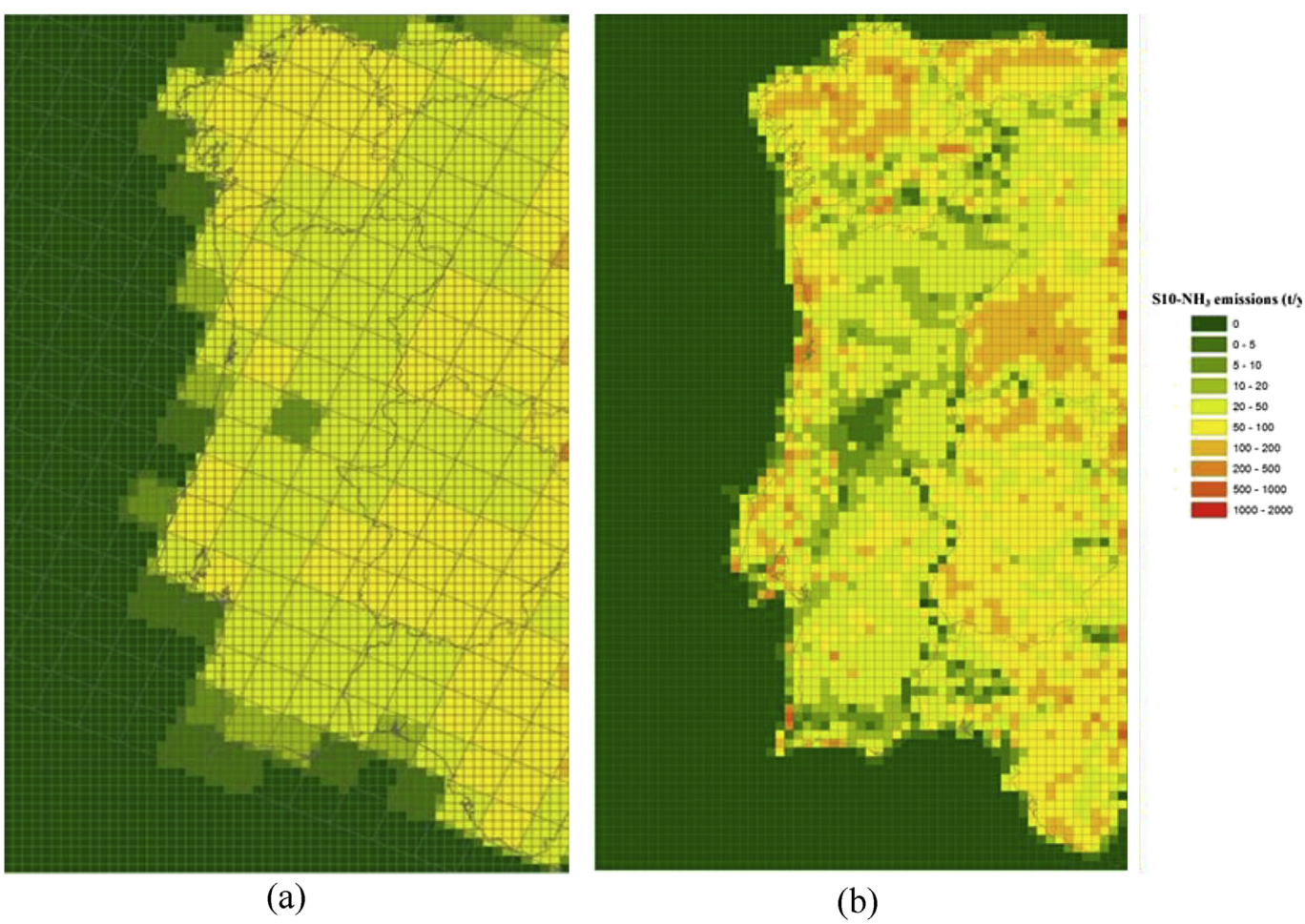

Fig. 5. EMEP (a) and mixed inventory (b) emissions of NH_3 in 2009 (in tons, t) segregated in 9 × 9 km^2 cells for SNAP10 – Agriculture (CEIP, 2012).

Most of the differences in glc between the use of both inventories are in the range of −1 to +1 μg m^{-3}. However maximum differences are also observed in specific dates and locations: on June, 25th and July, 1st (ranging from −3 to +12 μg m^{-3}, and from −3 to +24 μg m^{-3}, respectively, for NH_3). On June, 25th the maximum daily average concentrations simulated were 8.7 μg m^{-3} and 12 μg m^{-3} using the EMEP inventory and the new mixed inventory, respectively. On the July, 1st daily average concentrations were 10.8 and 23.8 μg m^{-3} using the EMEP inventory and the new mixed inventory, respectively.

As regards the maximum concentrations geographical distribution, the largest differences between both simulation results are positive (NMI−EMEPI), meaning that the new mixed inventory leads to higher maximum NH_3 concentrations in specific locations. These maximum differences are especially observed along the coastline, and also in the centre east of the domain, over the Spanish territory, not necessarily corresponding to the highest emission areas. On the other hand, negative differences also appear in specific areas over the coast, especially noticeable in June, 28th and July, 1st maps (see Fig. 6).

About the effect of this NH_3 emissions redistribution in secondary inorganic aerosol (SIA), Fig. 7 shows the spatial distribution of PNH_4 daily average concentration differences. Although the magnitude of the differences between the two simulations is lower than the obtained for NH_3, the spatial pattern is very similar, with higher positive and negative differences coinciding with the NH_3 pattern. However, both positive and negative differences along the coastline seem to be a consequence of the poor definition of the coastline in EMEP inventory due to its original coarse resolution, setting higher emissions than the new high resolution mixed inventory over some cells along the coastline.

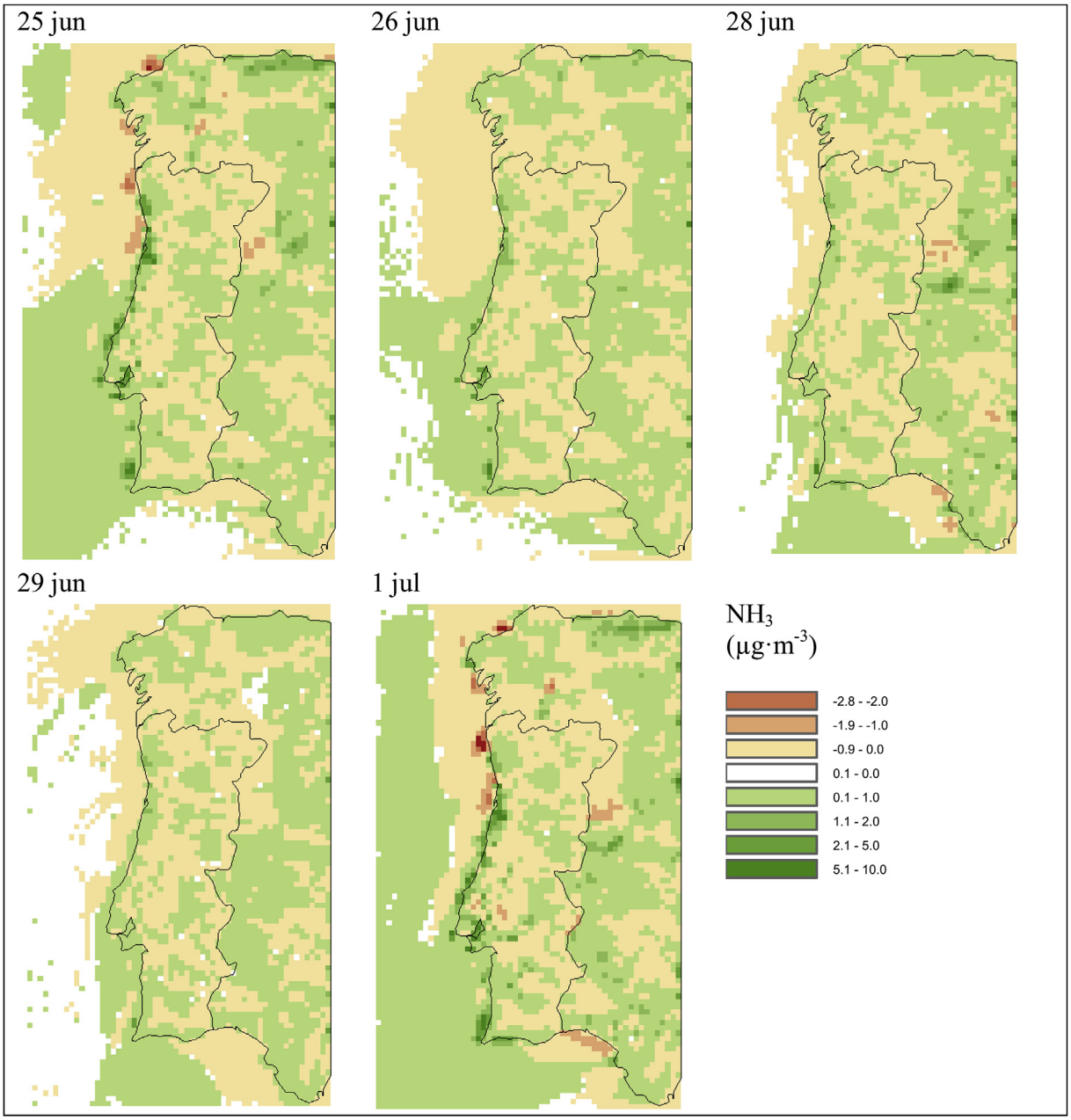

Fig. 6. Spatial differences (NMI − EMEPI) of NH_3 daily average concentrations (μg m^{-3}) using SNAP10 new mixed inventory vs. EMEP inventory, obtained in several days along the simulation period.

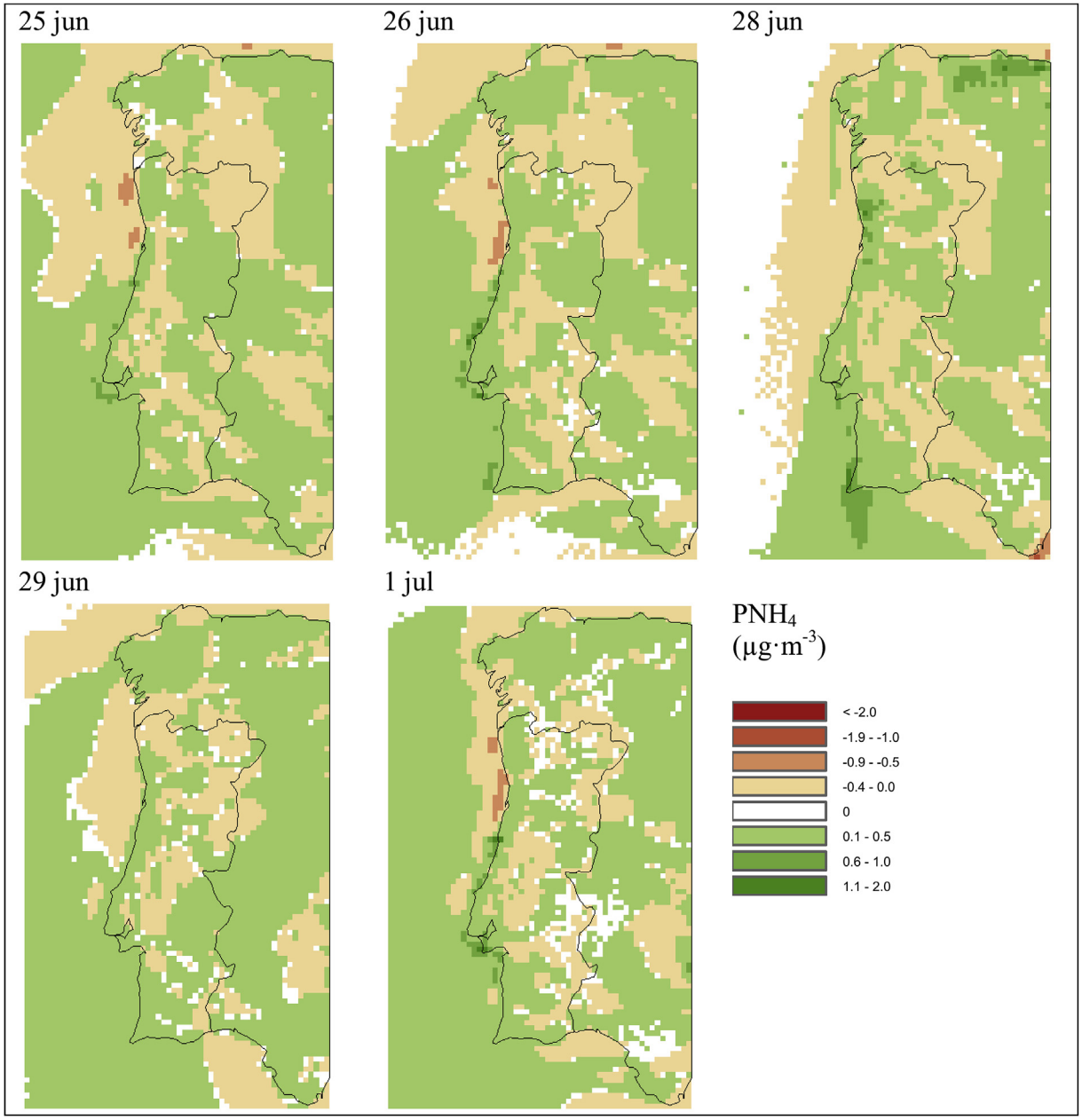

Fig. 7. Spatial differences (NMI − EMEPI) of PNH_4 daily average concentrations (μg m^{-3}) using SNAP10 new mixed inventory vs. EMEP inventory, obtained in several days along the simulation period.

In addition, photochemical conditions can also affect to the relationship between emissions and NH_3 glc. Therefore, an analysis of the hourly spatial differences patterns (NMI−EMEPI) for each simulated day was also performed. Differences between the two simulations are negligible from June, 26th till 29th; on the other hand, differences are very expressive along the other simulation days, highlighting the influence of the meteorological dynamic (more specifically, high temperatures), on NH_3 glc; even though NH_3 emissions are constant. Also, observing the differences between some hourly concentration fields on June, 25th and July, 1st (Figs. 8 and 9), it is clear that the spatial distribution of NH_3 glc differences significantly vary along the day: the highest concentrations were simulated at 6:00 UTC on both days, achieving an absolute glc of 63.5 μg m^{-3} with the mixed inventory on the July 1st. This result justifies the positive difference, above 20 μg m^{-3}, at that time of the day. Moreover, the highest positive differences are obtained on June, 25th at 9:00 UTC, reaching 27.6 μg m^{-3}. At midday almost only negative differences are observed, and mainly off the coast. This confirms that not only the emissions distribution is important in the NH_3 glc, but also they are driven by meteorological dynamic. For example, a well-mixed PBL can soft the differences in NH_3 emissions as this primary pollutant is quickly diluted, so the dependence of glc from the source location is lower; on the other hand, some days with stable conditions keep NH_3 close to its sources, so the emissions geographical distribution is more relevant. Extending possible effects of agriculture emissions distribution over the air quality, also chemical activity of other pollutants (as VOCs) can be affected in different way by its chemical activity.

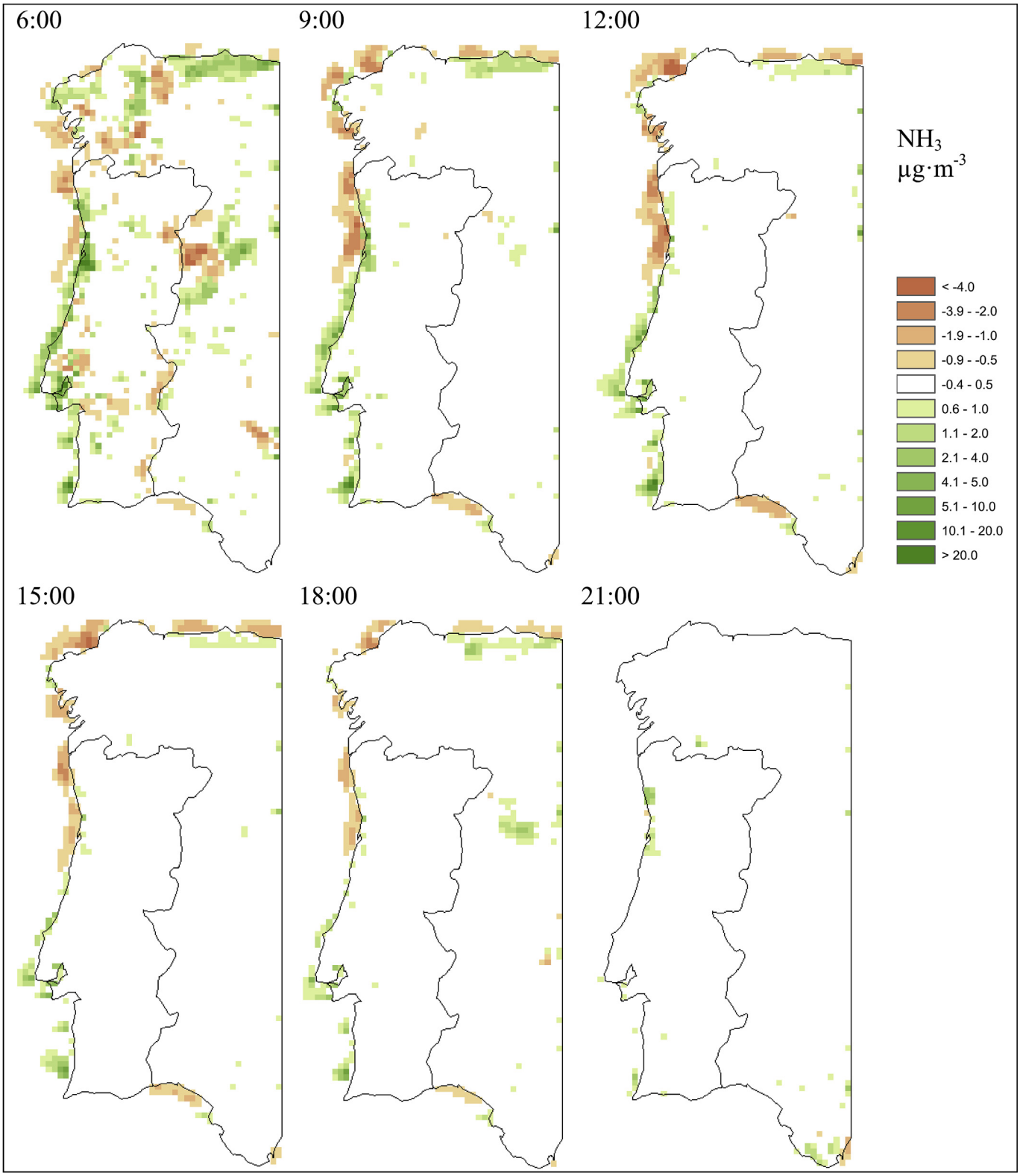

Fig. 8. Spatial differences (NMI – EMEPI) of NH_3 hourly ground level concentrations (µg m^{-3}) obtained by using the SNAP10 new mixed inventory and EMEP inventory on June, 25th at 6:00, 9:00, 12:00, 15:00, 18:00, and 21:00 UTC.

5. Conclusions

A new mixed methodology (bottom-up and top-down strategies) for estimating agriculture SNAP10 emissions inventory was developed for the Western of Iberian Peninsula, including Portugal and Spanish Western regions. The comparison of this new mixed inventory vs. EMEP inventory shows that the combination of the top-down and bottom-up strategies implies significant differences in emissions patterns; the new mixed inventory provides highly segregated spatial patterns, with specific high emission values

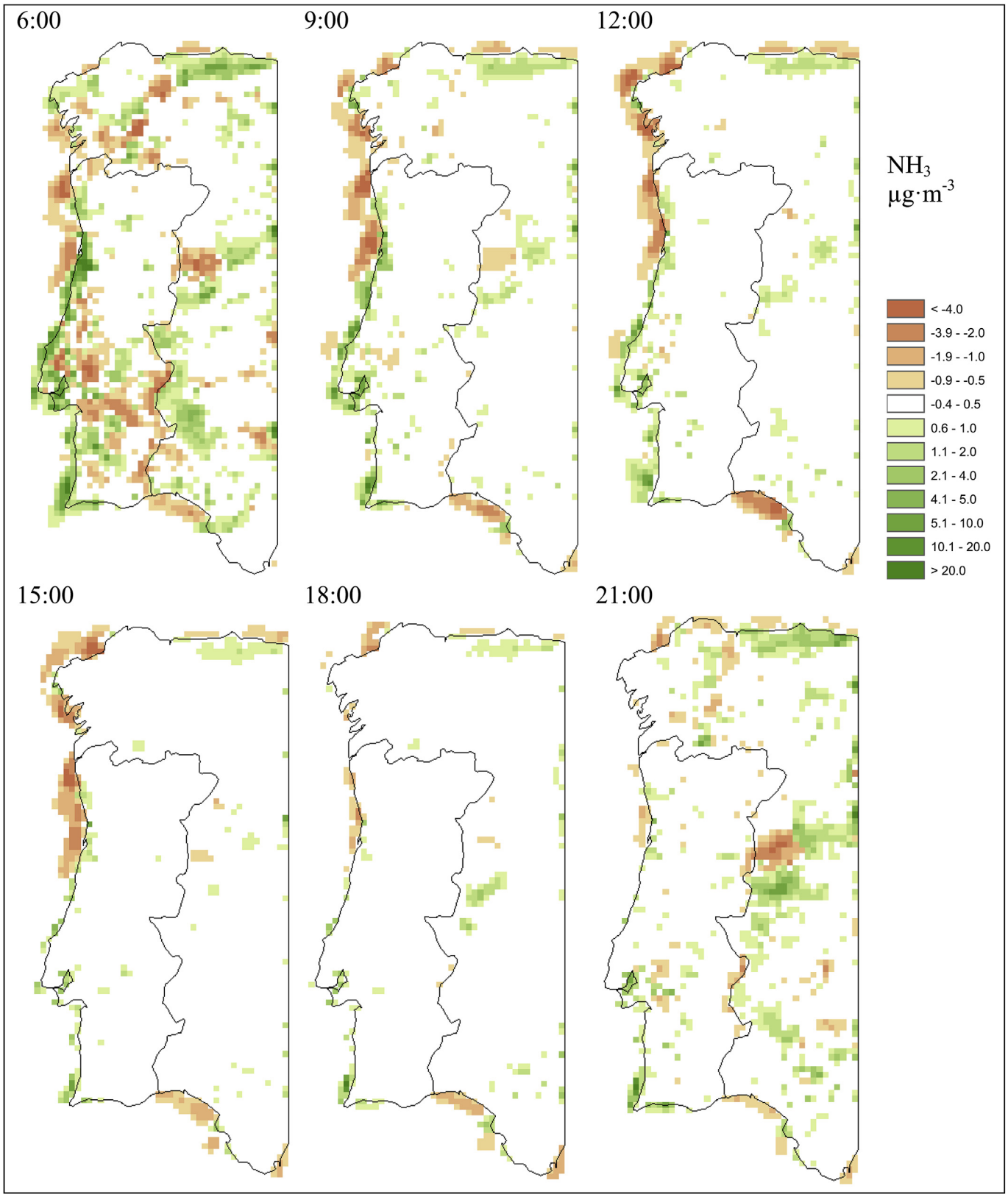

Fig. 9. Spatial differences (NMI − EMEPI) of NH_3 hourly ground level concentrations (µg m^{-3}) obtained by using the SNAP10 new mixed inventory and EMEP inventory for July 1st at 6:00, 9:00, 12:00, 15:00, 18:00, and 21:00 UTC.

locations; which are in agreement to the point (cattle farms) and area (landfill) agriculture sources locations. On the contrary, EMEP inventory shows very uniform spatial patterns.

As this new mixed inventory requires a large metadata input to perform bottom-up strategy calculations, its updating can be difficult. However, every applied input was based in EMEP, E-PRTR,

and other public environmental sources. Particularly, E-PRTR is one of the European emissions databases yearly updated and applied in this new mixed inventory. Unfortunately, cattle farms are not included in E-PRTR (EC, 2006), so their metadata must be obtained from other sources, not always available. Because of its significant contribution to agriculture emissions, cattle farms must be included in E-PRTR (Morán et al., 2014). In addition, the use of GIS tools allows the systematic application of this new mixed inventory, also including land use information and processing its emissions to provide as input to air quality modelling applications.

The use of this new mixed agriculture emission inventory, instead of the EMEP inventory, in air quality simulations over the study region shows that significant different NH_3 ground level concentrations (both daily and hourly averages) are achieved with this new inventory over specific locations. Particularly, along the coastline both positive and negative differences are observed, which are probably related to the farms locations respect to the grid cells; however, over central East zones of the domain the new inventory produces higher NH_3 levels.

Also, considering both NH_3 hourly glc and their differences between both simulations along some days with higher photochemical conditions, the influence of meteorological conditions is highlighted. The highest differences between both simulations are observed in the early morning, when photochemistry is not still under progress; and, simulated NH_3 glc are lower during midday, as higher temperature, solar radiation and, also, other pollutants concentrations are higher, causing faster NH_3 chemical transformation.

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