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Gas emissions on rice culture and its importance on air quality

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Resumo

No sentido de avaliar o impacte das emissões gasosas provenientes do sector agrícola na qualidade do ar foi utilizado o modelo de transporte químico CHIMERE. O modelo considera as emissões devidas aos vários sectores de actividade de origem antrópica e também as devidas à actividade biogénica e com origem natural.

O modelo foi sujeito a testes de sensibilidade fazendo variar apenas as emissões de NH_3 provenientes do sector agrícola, de origem antrópica, em regiões onde se identificou a cultura do arroz através das cartas do uso do solo do CORINE Land Cover (versão de 2006). A análise das séries temporais das concentrações de espécies químicas resultantes da aplicação do modelo foram avaliadas em duas regiões: sobre a área de cultura de arroz de Salvaterra de Magos, onde estão localizados os talhões experimentais que estão na base de toda a experimentação levada a cabo no projeto de investigação "Emissões gasosas medidas em campos regados de arroz produzido em dois solos diferentes, em Portugal, por efeito das práticas culturais, do clima e do aumento da concentração de CO_2 na atmosfera" (PTDC/AGR-AAM/102529/2008); e sobre a região de Lisboa, que se encontra a jusante. Foi feita, também, uma avaliação dos campos de concentrações médias obtidos sobre o domínio de aplicação do modelo CHIMERE durante o período de simulação.

A escolha dos compostos químicos incidiu sobre os compostos azotados nas três fases e em material particulado indiferenciado.

Palavras-chave: emissões gasosas; cultura do arroz.

Abstract

In order to assess the impact of emissions from the agricultural sector to the atmosphere on the air quality the chemical transport model CHIMERE was applied. The model considers emissions due to the various sectors of anthropogenic origin and also due to biogenic activity and natural origin.

Sensitivity tests to the model results concentrations were performed by varying the NH_3 emissions from the agricultural sector of anthropogenic origin, over rice culture regions identified through land use shapes of the CORINE Land Cover (2006 version). The analysis of time series concentrations of chemical species resulting from the application of the model were evaluated in two areas: on the rice cultivation area of Salvaterra de Magos, where the experimental plots of the research project *"Trace gas emissions from Portuguese irrigated rice fields in contrasting soils, by the influence of crop management, climate and increase concentration of CO_2 in the atmosphere"* (PTDC/AGR-AAM/102529/2008) are located; and on the Lisbon region, downwind of Salvaterra de Magos. An evaluation of the mean concentrations fields obtained over the CHIMERE model domain during the simulation period was also done.

The choice of chemical species was focused on the nitrogen compounds in the three phases and on undifferentiated particulate material.

Keywords: gas emissions; rice culture.

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Acronyms and abbreviations

ARBVS	*Associação de Regantes e Beneficiários do Vale da Sorraia*
CH_2O	Formaldehyde
CH_3CN	Acetonitrile
CH_3OH	Methanol
CH_4	Methane
C_2H_2	Acetylene
C_2H_6	Ethane
C_2H_6O	Ethanol
C_3H_6O	Acetone
C_3H_8	Propane
C_4H_{10}	Butane
C_5H_8	Isoprene
C_5H_{12}	Pentane
$C_6H_5CH_3$	Toluene
C_6H_6	Benzene
CHIMERE	Chemical Transport Model
CLC	Corine Land Cover
CO_2	Carbon dioxide
CTM	Chemical transport models
DMS	Dimethyl sulphate
EEA	European Environment Agency
EMEP	European Monitoring and Evaluation Programme
FAO	Food and Agriculture Organization of the United Nations
GHG	Greenhouse gases
INIAV	*Instituto Nacional de Investigação Agrária e Veterinária*
ISORROPIA	Thermodynamic equilibrium model
MEGAN	Model of Emissions of Gases and Aerosols from Nature
MODIS	Moderate Resolution Imaging Spectroradiometer
N_2O	Nitrous Oxide
NH_3	Ammonia
NH_4^+	Ammonium
O_3	Ozone
PM	Particulate matter
PM_{10}	Particulate matter with aerodynamic diameter smaller than 10 µm
$PM_{2.5}$	Particulate matter with aerodynamic diameter smaller than 2.5 µm
SNIRH	*Sistema Nacional de Informação de Recursos Hídricos*
SO_x	Sulfur Oxide
VOC	Volatile Organic Compounds

1. INTRODUCTION

The main objective of this work is to contribute to the understanding of regional air quality models responses of air pollutants concentrations to particulate and gaseous emissions to the atmosphere, resulting from human activities and natural sources, particularly focusing on agricultural activity and emissions from rice cultivation.

The motivation for the present work relies on data collected through the execution of the research project "*Trace gas emissions from Portuguese irrigated rice fields in contrasting soils, by the influence of crop management, climate and increase concentration of CO_2 in the atmosphere*", coordinated by Doutora Corina Carranca, researcher at Instituto Nacional de Investigação Agrária e Veterinária – INIAV, Portugal. As stated in the project purpose, flux measurements of nitrogen compounds to the atmosphere from rice cultures are rare in Southern Europe. However, the knowledge of these emissions fluxes is of paramount importance to air quality modeling, both on global and regional scales.

The emissions considered in models are one of the terms, and an important one, of the chemical mechanisms concentrations calculated through diferential equations in several chemical transport models (CTM). This is one of the reasons why the knowledge of emissions fluxes is very important. However, downstream implications may arise from it since these CTM were and are used to develop air quality policies in Europe. As it is the case of the European Monitoring and Evaluation Programme (EMEP) model which since the seventies of last century start to support the work under the "Convention of Long-Range Transboundary air Pollution". It has become the reference dispersion model in the frame of the Integrated Assessment Models supporting air quality policies under the EU Commission (EMEP, 2013). Examples are the impacts on air quality of the implementation of the National Emissions Ceilings Directive (NEC Directive), the impact assessment of the Thematic Strategy on Air Pollution, the Directive on Ambient Air Quality and Cleanear Air for Europe, the "Clean Air For Europe – CAFE" programme (EU, 2013).

Examples of European projects using CTM models for EU policy assessment and guidelines are: Air4EU (http://www.air4eu.nl/) and the more recent EC4MACS (http://www.ec4macs.eu/) that is an European Consortium for Modelling of Air Pollution and Climate Strategies. This project intends to give a contribute on the revision of the Thematic Strategy on Air Pollution in 2013 and the European Climate Change Programme on climate strategies beyond 2012. Within this project the health and ecosystem impacts of emission estimations is done through air pollutants concentrations calculated by the CHIMERE dispersion model.

In general, the main scope of this study is to assess the sensitivity of a CTM model concentrations results to the nitrogen compounds emissions, as NH_3, from the agricultural sector. Due to its wide use, the considered emissions are the ones available by EMEP. The chosen CTM was the CHIMERE model.

The sensitivity study was performed changing the value of the NH_3 emissions considered by the model over three main regions over Portugal, which are Mondego, Tejo and Sado Estuaries. Analysis of particulate matter and chemical compounds on gas phase resulting from the CHIMERE model applications were done over a period were rice paddies fertilization has occurred in Salvaterra de Magos, the experimental site of the Portuguese project "*Trace gas emissions from Portuguese irrigated rice fields in contrasting soils, by the influence of crop management, climate and increase concentration of CO_2 in the atmosphere*", above mentioned.

The emissions considered by the CHIMERE model during the period of simulation were compared to the ones measured in the site experiment and made available on the last report of the project, early March 2013.

1.1. RESEARCH SCOPE AND OBJECTIVES

- What is known about the natural and anthropogenic agents that contribute to air quality, and the underlying processes that are involved?
- Indentify importance and complementarily of global and regional projections;
- Understanding the processes involved in the exchange of trace gases between the earth´s surface and the atmosphere;
- Importance of the emissions of the agricultural sector used as inputs on air quality models;
- Analyze how different land cover representations potentially introduce systematic errors into the results of regional N emission inventories;
- Analyze NH_3 emissions from the agricultural sector;
- Estimate emission factors for the simulated years and compare with the emissions factors on rice field.

1.2. DISSERTATION STRUCTURE

The present dissertation is divided in the following chapters:

1. Introduction: details of research scope, main objectives and structure of the dissertation are revealed.

2. Literature Review: this chapter includes earlier work developed on the scope, main studies and relation between them.

3. Methods and Data: description of methods of analyses, details how the data will be treated.

4. Results and Discussion: all data obtained by methodology and formulation of hypotheses.

5. Conclusions: responses of the objectives and future investigations.

6. References

Annexes

2. LITERATURE REVIEW

Air pollutant emissions, either greenhouse gases (GHG), reactive gases or particulate matter, resulting from anthropogenic or natural sources are variable in space and time. However, their atmospheric lifetime[1] (or residence time) is highly dependent on the atmospheric chemical specie reactivity and the chemical mechanisms on which they are involved. Examples of few GHG and reactive gases are presented in Table 2.1.

The previously referred research project (Carranca *et al.*, 2013) that motivated the present work presented as principal objectives measuring N and C fluxes and microbial population in two soils cultivated with flooded rice *(Oryza sativa L. cv. Ariete)* in open field and open chambers, in three replicated plots, during two years (Carranca *et al.*, 2013; Carranca *et al.*, 2012; Carranca *et al.*, 2011; Figueiredo, 2011). Parallel results with interest for the present work are the ones concerning the emissions due to the fertilization process, since they are responsible for the NH_3 agricultural emissions with further impacts on aerosol particles formation in the atmosphere, as will be shown.

The importance on the knowledge of the emissions of the agricultural sector used as inputs on air quality models will also be acknowledged. Hence, the literature review will start with an overview of the exchanges between the atmosphere and surface activities (either anthropogenic or natural), focusing then on rice culture and on the compounds measurements, finally a short mention on air quality modelling systems, their needs as emission input data and uncertainties.

Table 2.1 - Atmospheric lifetime of GHG and reactive gases.

Greenhouse gas	Atmospheric lifetime
CO_2	~ 100 years
CH_4	~12 years
N_2O	~ 114 years
Reactive gases	
O_3 (in ppb)	hours - days
C_2H_6	2-4 months
C_3H_8	3 weeks
C_2H_2	3 weeks
C_5H_8	1-2 hours
Terpenes	1 hour
Dimethyl sulphate (DMS)	1 day
CH_2O	2 hours – 2 days

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[1]Atmospheric lifetime, " The atmospheric lifetime is used to characterize the decay of an instantaneous pulse input to the atmosphere, and can be likened to the time it takes that pulse input to decay to 0.368 (l/e) of its original value. The analogy would be strictly correct if every gas decayed according to a simple exponential curve, which is seldom the case". For a more complete definition please link to *http://cdiac.ornl.gov/pns/current_ghg.html.*

Reactive gases	Atmospheric lifetime
CH_3CN	0.4 – 1 year
CH_3OH	2 weeks
C_2H_6O	1 week
C_3H_6O	1 month
C_6H_6	1 week
$C_6H_5CH_3$	2 days
Iso-/n-C_4H_{10}	2-3 days
Iso-/n-C_5H_{12}	2-3 days

*Adapted from CDIAC 2013 and WMO 2013.

2.1. MASS EXCHANGES BETWEEN THE ATMOSPHERE AND SURFACE ACTIVITIES

Human activities contribute to climate change by causing changes in Earth's atmosphere in the amounts of greenhouse gases, aerosols (small particles), and cloudiness. The largest known contribution comes from the burning of fossil fuels, which releases carbon dioxide gas to the atmosphere. Greenhouse gases and aerosols affect climate by altering incoming solar radiation and outgoing infrared (thermal) radiation that are part of Earth's energy balance. Changing the atmospheric abundance or properties of these gases and particles can lead to a warming or cooling of the climate system. Since the start of the industrial era (about 1750), the overall effect of human activities on climate has been a warming influence. The human impact on climate during this era greatly exceeds that due to known changes in natural processes, such as solar changes and volcanic eruptions (Forster *et al.*, 2007).

For better understanding of the processes involved in the exchange of trace gases and aerosols between the earth's surface and the atmosphere it is necessary to consider the soil environment is a complex ecosystem with numerous interacting physical, chemical and biological processes. This complexity is exemplified by transitions between flooded and non-flooded conditions. Some system elements are complex to model and the relevant variables even more complex to measure, making it difficult to directly confirm correct simulation (Gaydon *et al.*, 2012).

2.1.1. AIR POLLUTION EMISSIONS

Air pollution emissions is the term used to describe any gases, liquid droplets and solid particulates which are emitted or discharged into the atmospheric air and adversely affect the health of humans, animals, ecosystems or the usefulness of a natural resource. They can be distinguished as anthropogenic and natural or biogenic emissions. The first one is the result from human activities, the second one consider events that are not the result of any human

activities (Beychok and Hogan, 2012). This study will take in to account emissions result from both types: anthropogenic and biogenic sources of air pollution emissions.

Sources of air pollution anthropogenic emissions enclose stationary point sources, which is a single, identifiable source of air pollutant emissions such as combustion furnace flue gas stack or diesel engine exhaust stack. Point sources are also characterized as being either elevated or at ground-level, a point source has no geometric dimensions (Beychok and Hogan, 2012; MDAQMD, 2013).

Another is mobile sources from exhaust emission from vehicles driven by fuel burning engines. Area sources is an area that is a two-dimensional source of diffuse air pollutant emissions such as the emissions from a forest fire, a landfill or the evaporated vapors from a large spill of volatile liquid. Evaporative sources are volatile liquids that, when not completely enclosed in a tank or other container, evaporate and release vapors overtime; controlled burns which occurs in forestry management and in agriculture; waste disposal landfills.

Examples by source, of such anthropogenic emissions are following presented in Table 2.2.

Table 2.2 - Sources and examples of anthropogenic emissions (Beychok and Hogan, 2012).

	Source of air pollution	Example
Anthropogenic Emissions	Stationary point sources	Combustion furnace flue gas stack
	Mobile sources	Automobiles, trucks, trains, airplanes, marine vessels.
	Area sources	Methane emissions from livestock
	Evaporative sources	Solvents, pesticides, perfumes, aerosols sprays and gasoline
	Controlled burns	Release of smoke, ash, dust, CO_2, nitrogen oxides and other air pollutants
	Waste disposal landfills	Gas escaped from landfill (CH_4, CO_2 and others)

When we talk about biogenic emissions we consider emissions from sources like volcanic activity; geysers; digestive gases by digestion of food and emitted by animals; oceans, rivers and estuaries by digestive systems of marine life, methanogenesis in sediments and drainage areas along coastal regions and possibly seepage from methane hydrates on the ocean floors. Biogenic sources, a subset of natural sources, include only those sources that result from some sort of biological activity. Biogenic emissions represent a significant portion of the natural source emissions, and VOC, NO_x, and the greenhouse gases discussed above can all be emitted from biogenic sources (Beychok and Hogan, 2012; EPA, 1996).

Natural sources that are not biogenic sources include lightning, a source of nitric oxide (NO) and oil and gas seeps, which are sources of VOC, CH_4 and hazardous air pollutants (HAPs).

The estimated contributions of these sources may be significant when a modeling domain extends into areas that do not have a high anthropogenic contribution (EPA, 1996).

Other sources are dust from windblown from areas with little or no vegetation such as desert areas; sea salt from windblown sea water; radioactive decay occurring in the Earth´s crust; forest fires created by lightning, or other natural causes (Table 2.3).

It is important to distinguish primary air pollutants and secondary air pollutants. The first ones are those that are directly emitted from an emission source mentioned on Table 2.2 and Table 2.3. The second ones are those that are formed by reactions between the primary air pollutants and normal atmospheric constituents, using energy derived from sunlight. Examples of secondary air pollutants are: sulfuric acid, nitric acid, nitrogen dioxide, ozone, ammonium nitrate and ammonium sulfate.

Table 2.3 - Sources and examples of biogenic emissions (Beychok and Hogan, 2012).

	Source of air pollution	Example
	Volcanoes	Smoke, ash, CO_2, sulfur dioxide among others
	Geysers	Hydrogen sulfides, arsenic and other heavy metals
	Digestive gases	Methane
	Oceans, rivers and estuaries	Methane
Biogenic Emissions	Dust	Windblown dust
	Sea-salt	Windblown sea water that releases sodium chloride
	Radioactive decay	Radon gas
	Forest fires (natural causes)	Smoke, ash, dust, CO_2, nitrogen dioxides and others
	Plants and trees	Volatile Organic Compounds (VOC) emissions
	Wetlands	Methane
	Termites	Methane
	Lightning	Nitrogen oxides
	Soil outgassing	Nitrogen oxides

There is a compound present in the atmosphere – Particulate Matter (PM) both a primary and a secondary air pollutant. So-called primary PM is released into the atmosphere directly from a specific source, such as mentioned above. Secondary PM is produced in the atmosphere in the form of ammonium nitrate and ammonium sulfate. An example of secondary PM is the fraction known as $PM_{2.5}$, particulate matter with aerodynamic diameter smaller than 2.5 µm or less. They can be from fuel combustion, agricultural burning, woodstoves, etc. (Beychok and Hogan, 2012; EPA, 2001a).

The nitrogen compounds data set regarding the nitrogen cycle of the rice crop in Salvaterra de Magos have permitted the calculation of the NH_3 losses from the system soil/plant (Carranca *et al.*, 2013). In order to understand the factors that may have impact in this loss, a small review of the nitrogen cycle was carried out.

2.1.2. NITROGEN CYCLE

Human alteration of the nitrogen cycle represents a major driver of global environmental change (Sutton *et al.*, 2012). As nitrogen is a limiting nutrient in many ecosystems, these modifications of the natural cycling have profound effects on ecosystem function, biodiversity and atmospheric composition.

The highest nitrogen cycle mass flows are found in terrestrial ecosystems mostly because of biological nitrogen fixation from free living microorganisms or symbiotic nitrogen fixing plants, and also due to the decomposition of organic matter which may occur both as denitrification to nitrous oxide and volatilization of ammonia (Figure 2.1). Nitrogen is often most limiting in many ecosystems, as only few *bacteria* can fix nitrogen. Plants from the *legume* family (*Fabaceae or Leguminosae*) like clover, host N-fixing bacteria in their roots as suppliers of reactive forms of nitrogen - NO_3^- and NH_4^+ (Watanabe and Ortega, 2011; Nol, 2010).
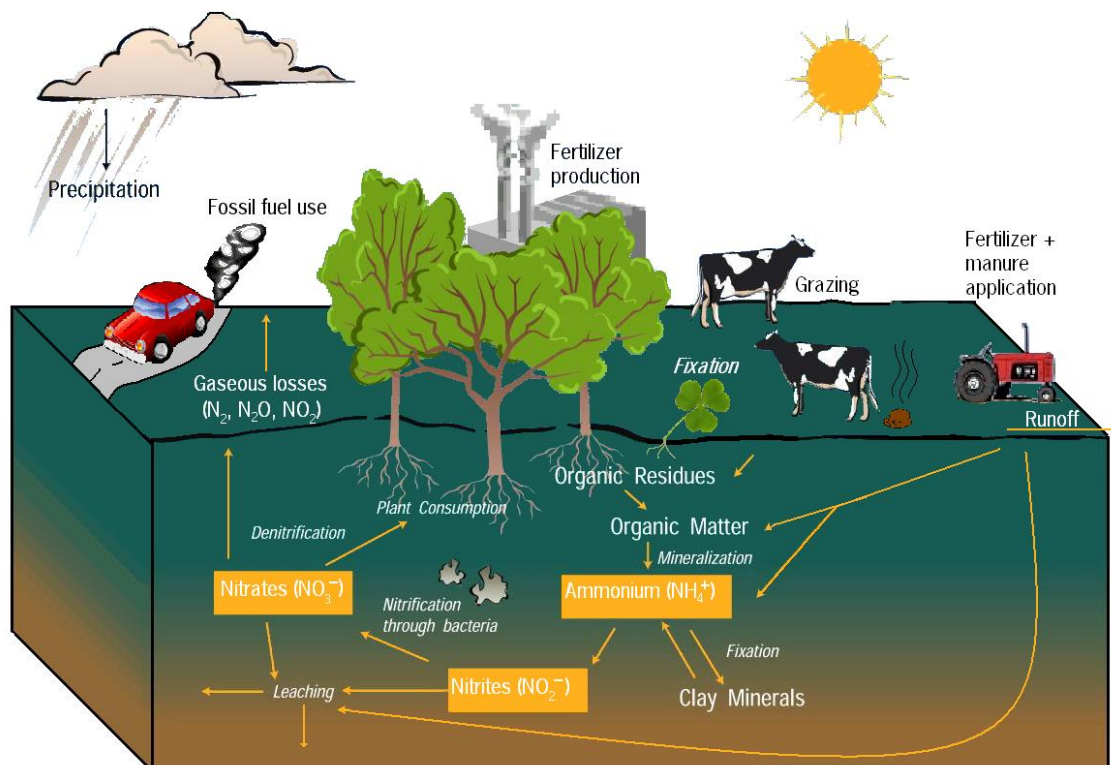
Figure 2.1 - Nitrogen cycle – sources and flows of N (Nol, 2010).

According to Nol, (2010), human activities are responsible for causing increased nitrogen deposition in a variety of ways, including burning of both fossil fuels and forests, which releases nitrogen into the atmosphere, fertilizing crops with nitrogen-based fertilizers, which then enter the soil and water, ranching, during which livestock waste releases ammonia into the soil and water, allowing sewage and septic tanks to leach into streams, rivers, and groundwater.

The consequences of human-caused nitrogen deposition are profound and influence many aspects of the Earth system, including ecosystems: nitrogen additions to the soil can lead to changes that favor weeds over native plants, which in turn reduce species diversity and changes ecosystems. Research shows that nitrogen levels are linked with changes in grassland species, from mosses and lichens to grasses and flowers; precipitation: nitrogen oxides react with water to form nitric acid, which along with sulfur dioxide is a major component of acid rain.

Acid rain can have broad impacts in several human made structures as well as on different reservoirs, it may damage and kill aquatic life and vegetation:

- on human building structures, it can corrode buildings, bridges, and other structures;

- on air quality: high concentrations of nitrogen oxides in the lower atmosphere are a precursor to tropospheric ozone which is known to damage living tissues, including human lungs, and decrease plant production;

- on water quality: adding large amounts of nitrogen to rivers, lakes, and coastal systems results in eutrophication, a condition that occurs in aquatic ecosystems when excessive nutrient concentrations stimulate blooms of algae that deplete oxygen, killing fish and other organisms and ruining water quality. Parts of the Gulf of Mexico, e.g., are so inundated with excess fertilizer that the water is clogged with algae, suffocating fish and other marine life;

- on the carbon cycle: the impacts of nitrogen deposition on the global carbon cycle are uncertain, but it is likely that some ecosystems have been fertilized by additional nitrogen, which may boost their capture and storage of carbon. Sustained carbon sinks are unlikely, however, because soil acidification, ozone pollution, and other negative effects eventually compromise nitrogen-enhanced carbon uptake.

Other environmental impacts are identified from such gases like nitrous oxide (N_2O) absorbs infrared radiation contributing to the greenhouse warming and the depletion of the stratospheric ozone layer and nitric oxide (NO) contributes to the formation of tropospheric ozone, a major atmospheric pollutant that affects human health, agricultural crops, and natural ecosystems; is

also a precursor to nitric acid, a principal component of acid deposition; (Nol, 2011; Choudhury and Kennedy, 2005).

Five gases, NH_3, N_2O, NO, NO_2 and N_2, dominate the movement of nitrogen between the earth's surface and the atmosphere (Jenkinson, 2001).

Nitrogen oxide (NOx)

Nitrogen oxides are emitted by soil microbes during nitrification and denitrification processes. Yienger and Levy (1995) compute NO emission fluxes as a function of vegetation type, temperature, precipitation history, fertilizer usage if any, and a canopy reduction factor, η. Parameter η is the fraction of soil emitted NO_x that is deposited within the canopy before it is exported to the atmosphere; it reflects the oxidation of NO to NO_2 in the canopy air followed by uptake of NO_2 by vegetation (Jacob and Bakwin, 1991). NO_y refers to all oxides of nitrogen, principally NO_2, NO, nitric acid, dinitrogen pentoxide, nitrate aerosol and peroxyacetylnitrate. Deposition fluxes of NO_2 are more commonly observed than emission fluxes (Skiba *et al.*, 1997).

NOx are a class of compounds that are respiratory irritants and that react with VOC to form ozone (O_3). The primary combustion product of nitrogen is nitrogen dioxide (NO_2). However, several other nitrogen compounds are usually emitted at the same time (nitric oxide [NO], nitrous oxide [N_2O], etc.), and these may or may not be distinguishable in available test data. The convention followed in emission factor documents is to report the distinctions wherever possible, but to report total NOx on the basis of the molecular weight of NO_2. NOx compounds are also precursors to acid rain. Motor vehicles, power plants, and other stationary combustion facilities emit large quantities of NOx (EPA, 2001).

For regional climate model applications, due to the chemical species involved which are also part of the chemical mechanisms of the majority of the CTM, the most interesting reactions are the nitrification, the nitrifier - denitrification and denitrification,

Nitrification

The oxidation of NH_4^+ (ammonium) to NO_2^- (nitrite) and to NO_3^- (nitrate),

Nitrifier Denitrification

NO_3^- and NO_2^- are transformed into N_2 and N_2O

Denitrification

The reduction of NO_3^- to N_2O (nitrous oxide) and N_2 (nitrogen gas)

Nitrous oxide is emitted by human activities such as fertilizer use and fossil fuel burning. Natural processes in soils and the oceans also release N_2O. Nitrous oxide and NO are products of the denitrification process in soil. The formation of N_2O is associated with high nitrate concentrations in soil, with environments which are not strongly reducing and with acid soils. The main concern about N_2O and NO has to do with their role in ozone destruction (Shaviv and Mikkelsen, 1993)

N_2O emissions affected by nitrogen fertilizers were measured in rice paddy fields under intermittent irrigation in 1994, by *Cai et al., (1997)*. Their results shows that N_2O emission increased significantly with the increase in the nitrogen application rate and the N_2O flux was very small when the rice paddy plots were flooded, but peaked at the beginning of the disappearance of floodwater.

Ammonia (NH_3)

Volatilization

NH_3 emissions are related to agricultural activities such as storage of manure, soil fertilizing, animal husbandry. Particularly conditions in lowland (wetlands) rice field are conducive to ammonia volatilization loss. During the volatilization process, gaseous ammonia is formed:

$$NH_4^+ \leftrightarrow NH_3 + H^+$$

(2.1)

That is, H^+ is released for each conversion of:

$$NH_4^+ \rightarrow NH_3 \text{ (g)}$$

(2.2)

The pH and buffering capacity of oxidized, as well as reduced, soil layers, thus influence the process. The overall inorganic ammonium nitrogen (equilibrium) system (Nt) in floodwater can be written as:

$$N_t = NH_3 \text{ (aq)} + NH_4^+$$

(2.3)

According to Batyee *et al.*, 1994 and FAO, 2004, influencing factors of NH_3 emissions include:

- Meteorological conditions such as temperature, air humidity, wind speed and precipitation. In generally, emissions increase with temperature, but decrease with air humidity and during and after precipitation periods. The temperature increase the relative proportion of NH_3 to NH_4^+, decreases the solubility of NH_3 in water, and

increases the diffusion of NH_3 away from the air-water or air-soil interface. Wind speed regulates the exchange between soil and air;

- Irrigation water as a regulating factor;
- Properties of soil (pH, calcium content, water content, buffer capacity and porosity. The emissions generally increase with pH, calcium content, and porosity, but decrease with increasing buffer capacity and water content;
- Properties of manures (pH, viscosity, content of dry matter). The emissions generally increase with increasing pH, viscosity and content of dry matter. A high viscosity prevents the manure or fertilizer form entering the soil;
- Fertilizer applied/area. The fraction of N in manure which evaporates increases with the amount applied;
- The way of applying the manure or fertilizer. If it is by injection, a much lower emission results (Batyee *et al.*, 1994; FAO, 2001).

Atmospheric methane (CH_4) is mainly originated from biogenic sources, such as rice paddies and natural wetlands; the former account for at least 30 % of the global annual emission of methane to the atmosphere. Approximately 10-30 % of the methane produced by methanogenesis in rice paddies is consumed by methane-oxidizing bacteria associated with the roots of rice. Methane has increased as a result of human activities related to agriculture, natural gas distribution and landfills. Methane is also released from natural processes that occur, for example, in wetlands. Methane concentrations are not currently increasing in the atmosphere because growth rates decreased over the last two decades (Forster *et al.*, 2007).

The reasons for the decrease in the atmospheric CH_4 growth rate and the implications for future changes in its atmospheric burden are not understood (Prather *et al.*, 2001) but are clearly related to changes in the imbalance between CH_4 sources and sinks. Most CH_4 is removed from the atmosphere by reaction with the hydroxyl free radical (OH), which is produced photochemically in the atmosphere (Prather *et al.*, 2001).

Methane will introduce long-term climate forcings. However, in the short term the environmental problems involved on these processes are eutrophication and acidification of natural ecosystems. In the denitrification process it is expected the formation of tropospheric ozone, a major atmospheric pollutant that affects human health, agricultural crops, and natural ecosystems.

A FAO report from 2001 indicates that global estimates of global NH_3 loss from mineral N fertilizers is about 9 million tons of NH_3-N, constituting more than 10 % of global N fertilizer use. But there are several ways to reduce ammonia volatilization in the soil-water system which include application of soluble salts of calcium, potassium and magnesium; use of urease and

algal inhibitors; deep placement of nitrogen fertilizers; and use of modified forms of urease and a slow-release fertilizers (Choudhury and Kennedy, 2005).

As pointed out in the introductory part and is further developed under the section 2.4 (Air quality modelling systems), measurements of nitrogen compounds emissions to the atmosphere are crucial to further development on emissions estimates to be included in emission inventories and subsequent use atmospheric composition assessment and studies. Due to the implications of several aspects above described, on the emissions from the ecosystems (natural or from agriculture), the knowledge on fluxes compounds is limited.

2.2. NITROGEN COMPOUNDS MEASUREMENTS

Regarding the nitrogen cycle and its influence on the GHG balance, several partners from all over the world joined together in the NitroEurope project (NEU, 2013a). Within this project, nitrogen and GHG were measured, and budgets were calculated for 56 sites across Europe. The sites cover the main European climate zones and key ecosystems types: 30 forests, 8 wetlands/shrublands, 9 grasslands and 9 arable. Given the infeasibility of deploying a large network for all reactive nitrogen (N_r) measurements, a measurement strategy was developed that matches different data objectives to three levels of measurements. This tiered strategy included 3 different levels (NEU, 2013a):

- Level 1: 56 'Inferential Sites', combining basic reactive nitrogen concentration monitoring and indicators with micrometeorological data-sets to infer nitrogen fluxes;
- Level 2: 9 'Regional Sites', focusing on long-term time integrated flux measurements, increasing regional coverage;
- Level 3: 13 'Super Sites' with intensive measurements quantifying nitrogen budgets and advancing process understanding.

Portugal was also a partner in this project, where two sites were located. These sites are classified as Level 1 and represents two types of ecosystems grassland (Mitra) and forest (Espirra) (NEU 2013b).

The obtained results under the frame of the project "*Trace gas emissions from Portuguese irrigated rice fields in contrasting soils, by the influence of crop management, climate and increase concentration of CO_2 in the atmosphere*" may help to complement the database created in the aim of the NitroEurope over agricultural fields, namely on flooded rice crops.

2.3. RICE CULTURE

Rice paddy ecosystems are complex, with crop growth, soil thermo–hydro conditions, and microbial activities interacting through a number of processes. For example, any change in irrigation will simultaneously affect the temperature, moisture, pH, Eh, and substrate concentration in the soil. The altered soil environmental factors will simultaneously and collectively affect a series of biochemical or geochemical reactions that finally determine transport and transformation of the chemical elements, including C sequestration and trace gas emissions. There is usually not a linear or monotonic correlation between the cause and the result. Only models containing the fundamental processes can be capable of predicting the behaviors of the complex systems (Li *et al.*, 2006).

Figure 2.2 presents the mechanism involved in a flooded rice environment, according to Gaydon *et al.* (2012).
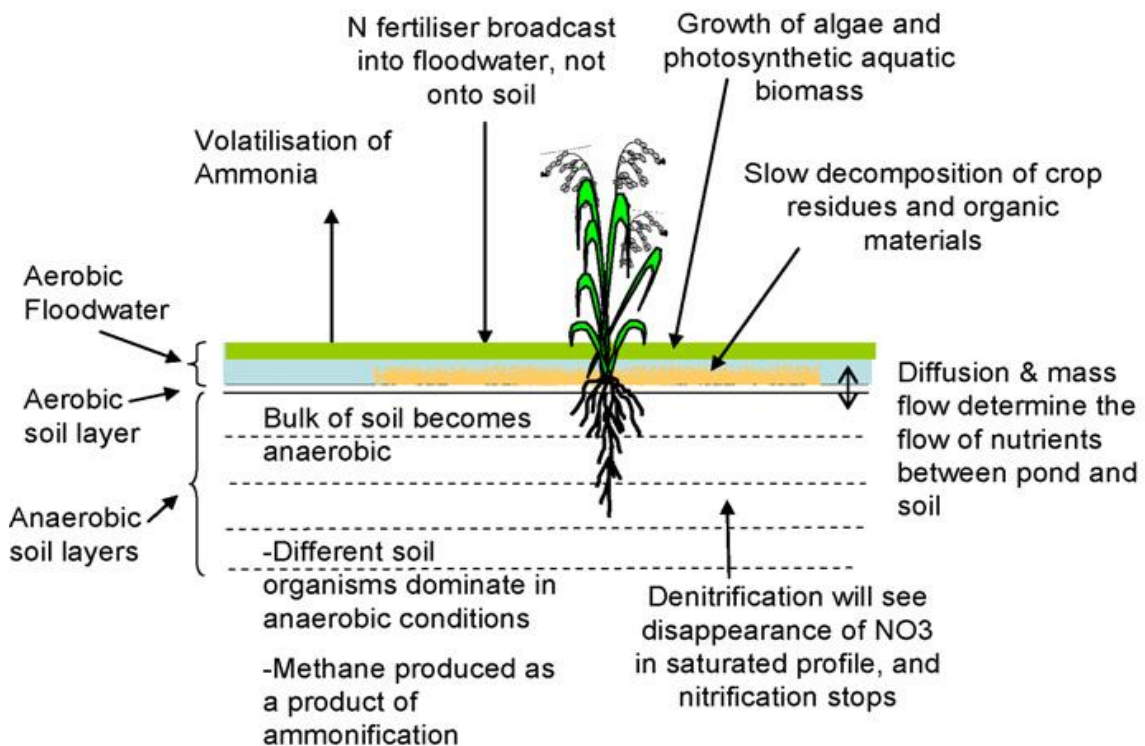
Figure 2.2 - Mechanisms involved in a flooded rice environment (Gaydon *et al.*, 2012).

Ammonium (NH_4), the major source of mineral N for rice crops, is rapidly nitrified to nitrate (NO_3) when the soil is drained. Nitrate is the major form in which mineral N exists in aerobic soil environments and is used by non-flooded crops such as wheat. When aerobic soil is re-flooded, nitrate present in the system is promptly lost by denitrification to the atmosphere (Gaydon *et al.*, 2012).

2.3.1. IMPORTANCE OF RICE CULTURE

According to FAOSTAT (2010), rice paddies from 1992 to 2010 present China as the major rice producer of the world with 1.875×10^8 tonnes, representing 31 % of world production (Figure 2.3). India follows the tendency with a close percentage of 21 %, becoming second world producer. Asia, by cultural alimentary reasons, climate conditions, soil properties among others allows and represents the highest producers and consumers of this cereal.
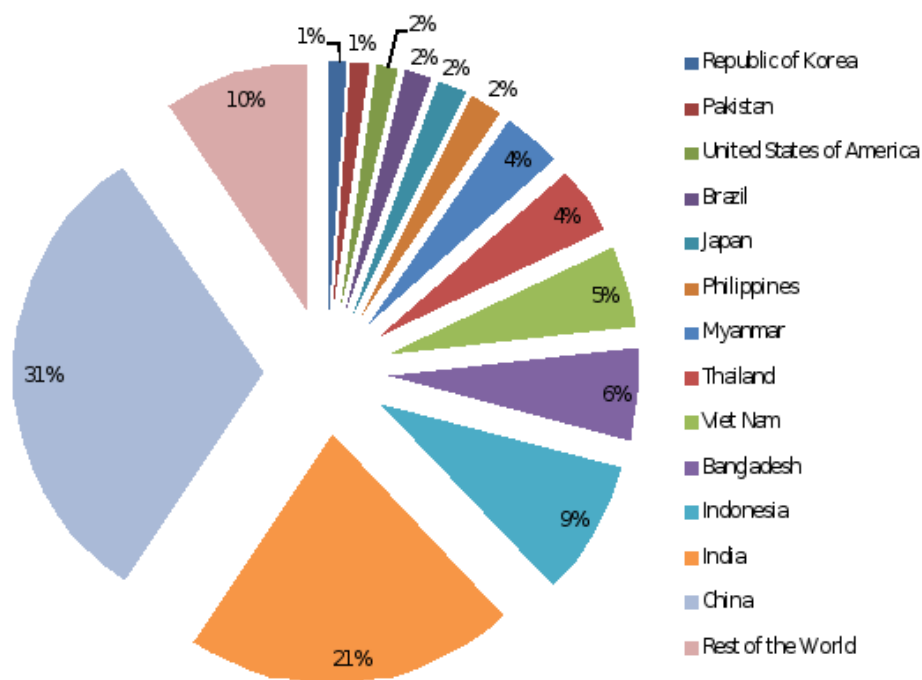
Figure 2.3 - Rice production (%) worldwide from 1992 to 2010 (adapted from FAOSTAT, 2010).

Rice culture will be productive under certain condition and environment including soil, water and nutrients. Some researchers have shown that traditional method with continues flooding need tremendous amount of water for rice cultivation and gives low water productivity. To increase the water productivity, a number of water saving irrigation techniques have been studied and applied. Sujono *et al.*, (2011) studied the effect of number of a water irrigation treatments on water productivity of rice.

To improve water use efficiency is necessary in every aspect of life, including irrigation to support agriculture, especially for paddy cultivation. This is a major challenge for paddy rice cultivators, to increase the water productivity (Hidayah *et al.*, 2009; Sujono *et al.*, 2011).

Rice cultivation is both an important sequester of carbon dioxide from atmosphere and an important source of GHG emission (methane and nitrite oxide). According to FAO (2004), rice

sequestered about 1.74 billion tones of CO_2 from the atmosphere to produce about 1.16 billion tonnes of biomass at 0% moisture content (FAO, 2004).

2.3.2.   WETLANDS

The Intergovernmental Panel on Climate Change (IPPC) considers wetlands (peat lands, marshes, bogs and mangroves) a globally major carbon store and that understanding is increasing, so in 2011 they decided to extend their methods to cover wetlands. More available information is expected to be published in the next year (Krug and Hiraishi, 2012).

A range of solutions has been proposed to meet the challenges of providing food security while adapting to climate change and reducing the environmental footprint of agriculture. The global bodies such as the United Nations Framework Convention on Climate Change (UNFCC), the Group of 20 nations (G20) and the United Nations Convention on Sustainable Development (Rio+20) have a fundamental role in the adoption of appropriate policy and financial actions to support implementation of these solutions on a global level.

Food insecurity and climate change are already inhibiting human well-being and economic growth throughout the world and these problems are poised to accelerate. Countries vary in their vulnerability to climate change, the amount and type of GHG they emit and their opportunities to reduce GHG emissions and improve agricultural productivity (Beddington *et al.*, 2012).

Recommendations from the Commission on Sustainable Agriculture and Climate Change include (Beddington *et al.*, 2012):

1. Integrate food security and sustainable agriculture into global and national policies;
2. Significantly raise the level of global investment in sustainable agriculture and food systems in the next decade;
3. Sustainably intensify agricultural production while reducing GHG emissions and other negative environmental impacts of agriculture;
4. Develop specific programmes and policies to assist populations and sectors that are most vulnerable to climate change and food security;
5. Reshape food access and consumption patterns too ensure basic nutritional needs are met to foster healthy and sustainable eating patterns worldwide;
6. Reduce loss and waste in food systems, targeting infrastructure, farming practices, processing, distribution and household habits;
7. Create comprehensive, shared, integrated information systems that encompass human and ecological dimensions.

2.3.3. NITROGEN COMPOUNDS GAS EMISSIONS FROM RICE AGRICULTURE FIELDS

The five nitrogen compounds gases above identified as dominating the movement between earth's surface and the atmosphere were NH_3, N_2O, NO, NO_2 and N_2 (Jenkinson, 2001). Since N_2O is a GHG not considered into the chemical mechanism of regional CTM, N_2 is the major gas present in the atmosphere (~ 78 % by volume), major interest arise on the emissions of NO, NO_2 and NH_3, namely derived by the fertilizer application.

Yan *et al.*, (2003) refer that the percentage of NO emitted due to fertilization over rice crop fields over Southern East, East and Southern Asia is around 0,48 %.

According to authors cited by Figueiredo (2011), volatilization of NH_3 may be 50 % of the N in fertilizer applied application. These discrepancies justified the values encountered by EMEP estimations in the agricultural sector in Portugal.

Previous work carried out by Mathews (1994) has identified that the most widely used fertilizers are urea and NH_4NO_3. The estimate as their annual consumption rates are of 28 Tg N and 17 Tg N, respectively, which together account for 64 % of the total global N use. In terms of cost, urea is much cheaper than NH_4NO_3 and is predominantly applied in Asia and South America. NH_4NO_3 is most commonly used in Europe and North America (Skiba, 2007).

Bouwman *et al.*, (2002) have compiled a set of 1667 NH_3 volatilizations measurements. In their work the authors have assessed several factors influencing the NH_3 volatilization due to fertilization on several crop types, namely crop type, fertilizer type, and rate and mode of application and temperature, as well as soil organic carbon, texture, pH, CEC, measurement technique, and measurement location. Based on their work, Table 2.4 summarizes what they have found only for wetland rice crops in several regions of the world.

They came to the conclusions that in developing countries the NH_3 volatilization losses are greater than in industrialized countries, either for synthetic (18 % vs 7 %) or animal manure applications (21 % vs 26 %). This is mainly due to the type of synthetic fertilizer used by the farmers (urea, ammonium sulfate, and ammonium bicarbonate) and the temperature.

Table 2.4 - Area, use of animal manure N, use of synthetic N fertilizers, and NH_3 volatilization for wetland rice for different regions of the World for 1995 (based on Bouwman *et al.*, 2002).

Region	Fertilized			Animal manure N	
	Area, Mha	N use kt	NH_3-N loss kt	N use kt	NH_3-N loss kt
U.S.A	1	168	15	10	2
Central America	0	32	5	3	0
South America	3	234	43	32	5
North Africa	1	78	16	3	1
Western Africa	1	26	4	3	1
Eastern Africa	1	1	0	6	1
Southern Africa	0	3	0	2	0
OCDE Europe	0	32	3	7	1
Eastern Europe	0	1	0	0	0
Former USSSR	1	14	1	15	2
Middle East	1	71	18	2	1
South Asia	44	4646	1031	965	175
East Asia	26	4490	829	1650	276
Southeast Asia	35	1811	335	396	62
Oceania	0	12	2	0	0
Japan	2	171	24	175	28
Total	117	11788	2328	3270	555

Based on the presented studies, Bouwman *et al.*, (2002) have developed a model to estimate the global NH_3 losses to the atmosphere from agriculture on a grid of 0.5° resolution data on land use and soils.

Sommer *et al.*, (2004) have also organized in a review paper filed and laboratory experimental data regarding NH_3 volatilization from fertilizers and fertilized crops. They concluded this loss ranges between 0 and 50 % of the nitrogen applied as fertilizers. This interval is dependent on the fertilizer type, soil parameters as calcium content, cation exchange capacity, acidity and meteorological conditions, namely temperature, wind speed and rain.

Global estimations of NH_3 losses by volatilization were made by Bouwman *et al*, (2002) tend to give lower values as presented in Figure 2.4. Lower Bounder (LB) and Upper Bounder (UB) are represented in percentage.
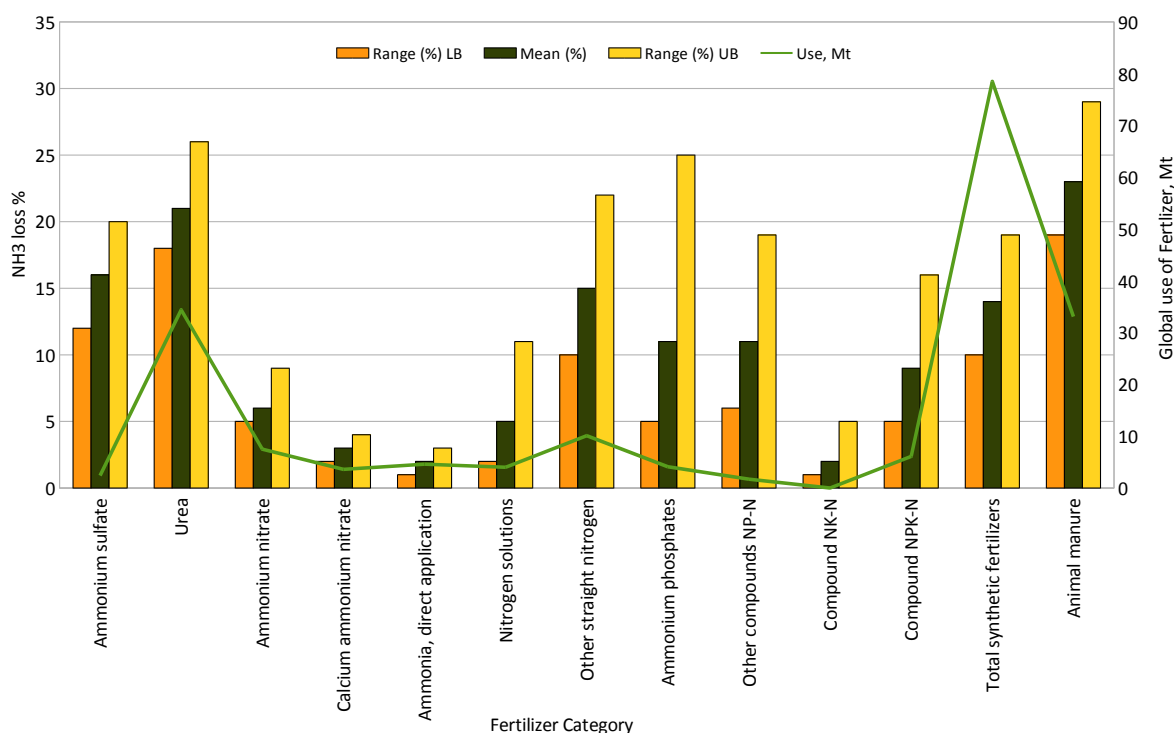
Figure 2.4 - Global consumption and estimated mean and range of NH_3 volatilization loss rates for synthetic fertilizer categories (adapted from Bouwman *et al.*, 2002).

Studies cited by the European Environmental Agency on the emission inventory guidebook (EEA, 2012), focused on flooded rice soils pointed that NH_3 losses due to fertilization is greater than from other cropping systems (work performed by Fenn and Hossner 1985). Older work carried out by Vlek and Crasswell (1979) have shown that NH_3 losses depend on the fertilizer type ranging from 50 % tp 60 %, if urea or ammonium sulfate was applied respectively. Also over flooded soils, the EMEP, 2009 show ammonia losses median values of 30 %, framed in a range between 8-56 %.

The above mentioned studies give an insight of the uncertainties expected for NH_3 loss estimation, mainly for rice croplands.

2.3.4.   EFFECT OF INCREASED TEMPERATURE AND CO_2 ON GROWTH, YIELD AND QUALITY OF CROPS

Rise in atmospheric temperature (+1 to +3 ºC) caused substantial reduction in yield of rice, groundnut and wheat at varying N levels.

The crops showed greater thermal sensitivity for reproductive shoot growth than for vegetative growth. On the other hand elevated CO_2 (560 ppm) in the air enhanced the biomass and

economic yield of rice, groundnut and wheat substantially at low, medium and high N levels owing to increase in leaf area, photosynthetic rate, spikes and grains/spike. Elevated CO_2 caused a reduction of grain protein content in rice and wheat, while it increased under high temperature (IARI, 2011).

Flooded rice culture studies carried out by Allen *et al.,* (2003) evidence that both elevated CO_2 and higher temperatures cause increased CH_4 emissions in flooded rice culture they also showed that the effect of the combination of CO_2 enrichment and elevated temperature on increasing photosynthetic CO_2 uptake, and subsequent impact of increasing photosynthesis on increasing CH_4 emissions.

2.4. AIR QUALITY MODELLING SYSTEMS

The use and interpretation of complex models through models that are either conceptually simpler, or limited to a number of processes or to a specific region, have been investigated, therefore enabling a deeper understanding of the processes at work or a more relevant comparison with observations. With the development of computer capacities, simpler models have not disappeared; on the contrary, a stronger emphasis has been given to the concept of a 'hierarchy of models' as the only way to provide a linkage between theoretical understanding and the complexity of realistic models (Held, 2005). The notion of model hierarchy is linked to the idea of scale: global circulation models are complemented by regional models that exhibit a higher resolution over a given area, or process oriented models, such as cloud resolving models or large eddy simulations (Solomon, 2007).

Atmospheric composition studies on the physical and chemical processes associated to it are mainly done on global and regional scales. Recently, due to the increase on power computional efforts, they are also made with models at local scale. These studies comprehend past (e.g. PMIIP, 2009), actual and future (IPPC, 2007a).

For example, in the 2007 IPCC report on The Physical Science Basis, the so call AR4 reports, global ozone budget estimates are driven by 13 global chemical transport models (IPPC, 2007b), developed mainly by European and North American Research Institutions. The results obtained by these models are subject of analysis but may also be used as inputs in a hierarchy of models from global to local scale, passing through the regional scale.

Regarding air quality issues, climate change scenarios impacts (IPCC 2007a, AR4), compliance policies (e.g, *http://www.ec4macs.eu/*) and air quality forecast (*http://www.gmes-atmosphere.eu/services/aqac/*) are three main fields of these model cascate applications. For that both GHG and reactive gases and particulate matter emissions are needed for global

chemical transport models. However, due to its atmospheric lifetime, on regional applications GHG are considered well mixed in the atmosphere since their reactions are slow when compared to the time step of the model run calculations. In this case, emissions of reactive gases and particulate matter are of great concern.

In the present study regional Eulerian chemical transport models was used. These models are forced by global concentrations at their lateral and top boundaries, meteorological fields (including information on temperature, wind, cloudiness, radiation, relative humidity, among others), air pollutants emissions, orography, land use, with the objective to produce atmospheric concentration species (Figure 2.5). These concentrations are calculated in time updating all the variations in the above mentioned factors.
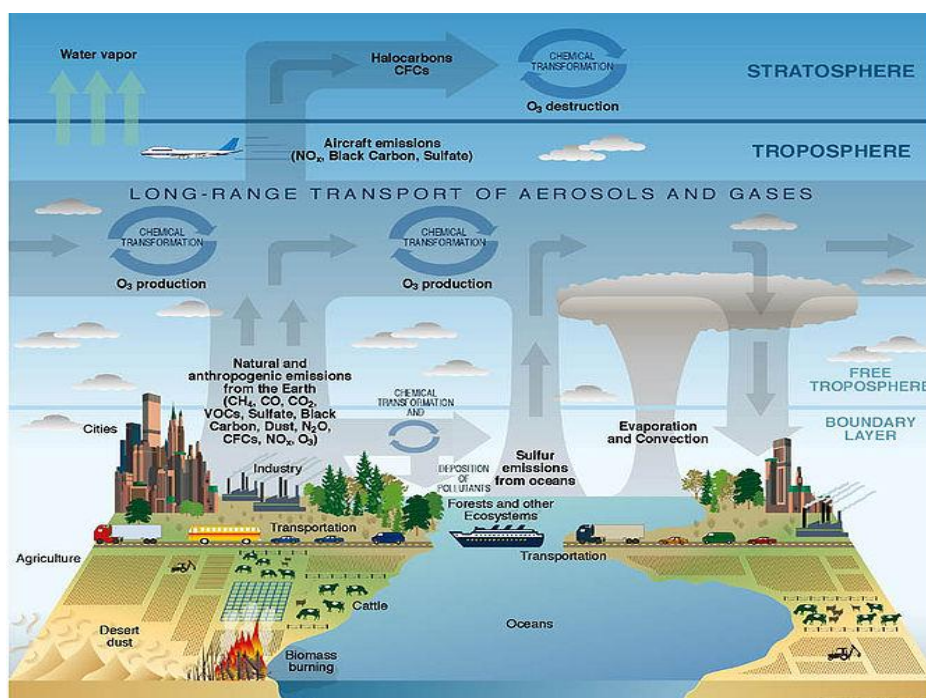
Figure 2.5 - Schematic of chemical and transport processes related to atmospheric composition (Rozaini, 2012).

2.4.1.   EUROPEAN MONITORING AND EVALUATING PROGRAMME (EMEP) EMISSIONS

"The European Monitoring and Evaluation Programme (EMEP) is a scientifically based and policy driven programme under the Convention on Long-range Transboundary Air Pollution (CLRTAP) for international co-operation to solve transboundary air pollution problems." (http://www.emep.int/).

In order to achieve its goals, the EMEP programme has four main task forces were assigned and work is performed in five centers, which relies on three main activities: collection of emission data, measurements of air quality as well as precipitation quality and modelling of atmospheric transport and deposition of air pollutions. As already previously pointed out the EMEP model is one of the reference models regarding policy compliance and European legislation concerning the air pollutants concentrations and depositions obtained by it.

Hence, and up to recent times, due to the amount of data and coordination among the reporting countries, the emissions collected by the EMEP programme were the only ones available for regional chemical transport models applications. These emissions are available as officially reported by the Parties to the Convention on Long Range Transboundary Air Pollution to the EMEP programme and as grid emissions to be used, primarily by the EMEP dispersion model, but also by other models, namely by the CHIMERE model and the EURAD model (Colette *et al.*, 2011). Other studies, comparing chemical transport model results over Europe considering the EMEP emissions, may be found in Vautard *et al.*, (2009).

Figure 2.6 presents the portuguese trends of pollutants from 2010 for all sectors of activity (adapted from EMEP database in: http://www.ceip.at/webdab-emission-database).

The grid EMEP emissions considered by the air quality models includes several reactive pollutants emitted by eleven sectors. The pollutants are: CO (carbon monoxide), NH_3 (ammonia), NMVOC (non methane volatile organic compounds), NO_x (nitrogen oxides as NO_2), SO_X (sulphur oxides as SO_2), PM_{coarse} and $PM_{2.5}$. These pollutants are then considered to be emitted by Sector 1 (S1) - Combustion in energy and transformation industries; S2 - Non-industrial combustion plants; S3 - Combustion in manufacturing industry; S4 - Production processes; S5 - Extraction and distribution of fossil fuels and geothermal energy; S6 - Solvents and other product use; S7 - Road transport; S8 - Other mobile sources and machinery; S9 - Waste treatment and disposal; S10 - Agriculture and S11 – Other sources (*http://webdab1.umweltbundesamt.at/scaled_country_year.html?cgiproxy_skip=1*).

The EMEP emissions are available since 1980, but last inventory is from 2010, updated in 2012, in a grid of 50 x 50 km^2.
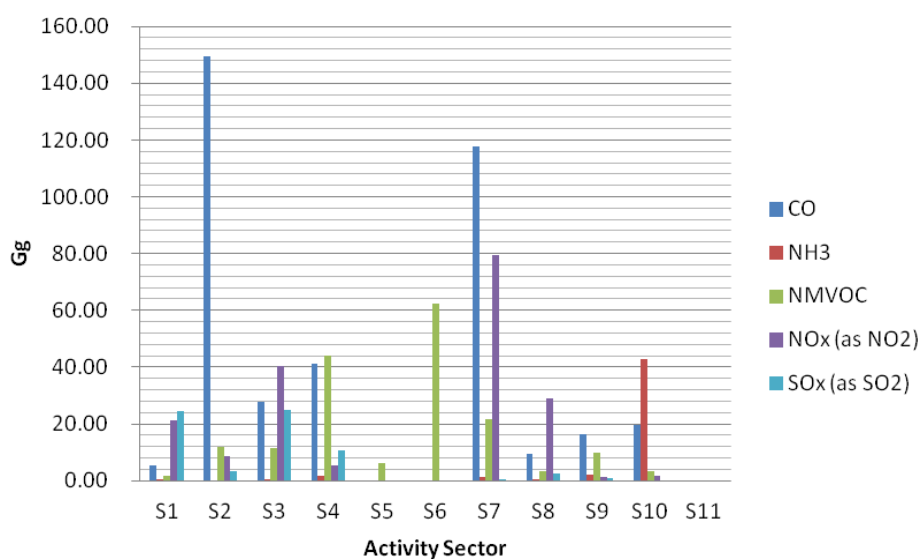
Figure 2.6 - National trends of pollutants from 2010 for all sectors of activity (adapted from EMEP database in: http://www.ceip.at/webdab-emission-database).

From the EMEP official data used in the models (*http://www.ceip.at/webdab-emission-database/emissions-as-used-in-emep-models/*), as the CHIMERE model, the emissions reported regarding the year 2010 (updated in 2012) in Figure 2.6, it is possible to identify S2 and S7, respectively, non-industrial combustion plants (stationary sources) and road transport, as major activities of CO emissions. NH_3 emissions are clearly emitted by S10 – Agriculture as long as S9 – waste treatment and disposal but in a smaller quantity. Solvent use and other product use (S6), production processes (stationary sources) (S4) and S7 present the highest values of NMVOC emissions, followed by S2, S9 and S3 – combustion in manufacturing industry (stationary sources). NO_x (as NO_2) are emitted by road transport in a very high scale and followed by S3 and S8 -other mobile sources and machinery, as long as S1 – combustion in energy and transformation industries (stationary sources). S1 and S3 present a similar emission in what concerns SO_x (as SO_2).

Low temperature combustion processes, from domestic burning of coal, wood, dung and burning of forests and other land, have led to an increase in both NO_x and ammonia (NH_3) emissions. Together with the emissions of N_r from agricultural systems in the form of NH_3, NO_x, nitrous oxide (N_2O), nitrates (NO_3) and many organic nitrogen forms, this human alteration of the nitrogen cycle is causing multiple effects on global change (Sutton *et al.*, 2012).

Analyzing S10 sector, agriculture practices, by the same source, in 2010 the tendencies are presented in Figure 2.7. The highest emission by agriculture is from NH_3 compounds, followed by CO, NMVOC in a very lower scale and NO_X (as NO_2). Emissions of NH_3 decrease from 2002

to 2007, from that year on the emission of the last 3 years (2008, 2009 and 2010) seem to increase in a smaller scale.
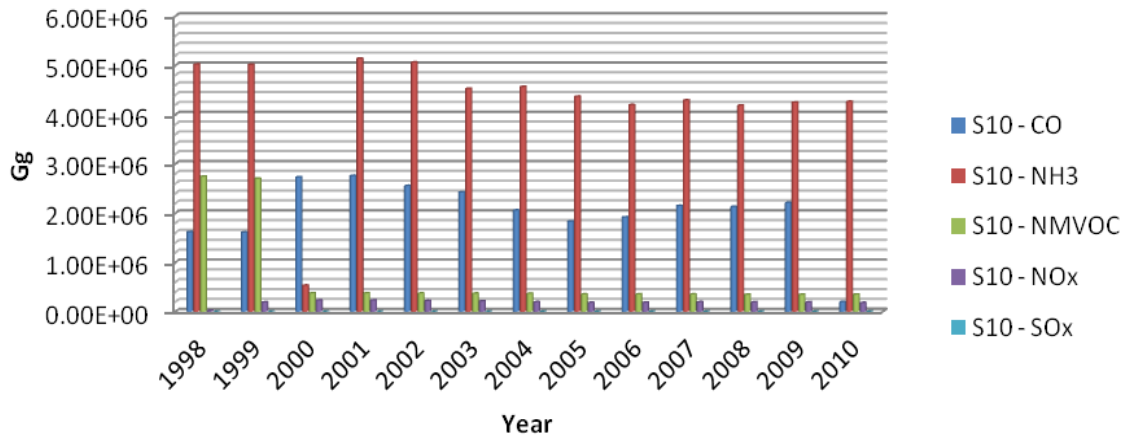
Figure 2.7 - National trends of pollutants from 1998-2010 in agriculture sector -S10 (Gg) (adapted from EMEP database in: http://www.ceip.at/webdab-emission-database).

Longe-range transport of aerosol particles was specifically added to the work programme in 1999. Some of the major challenges were to evaluate formation of secondary and organic particulate matter and particle dynamics among others (NILU, 2012).

EMEP emissions for the agriculture sector accounts for animal husbandry and manure management, agricultural soils, field burning and other sources (EMEP, 2009). The methodology followed by the Portuguese Environmental Agency on the estimation for the reporting emissions of NH_3 and the GHG under IPCC and the EMEP programme is sketched in Figure 2.8.
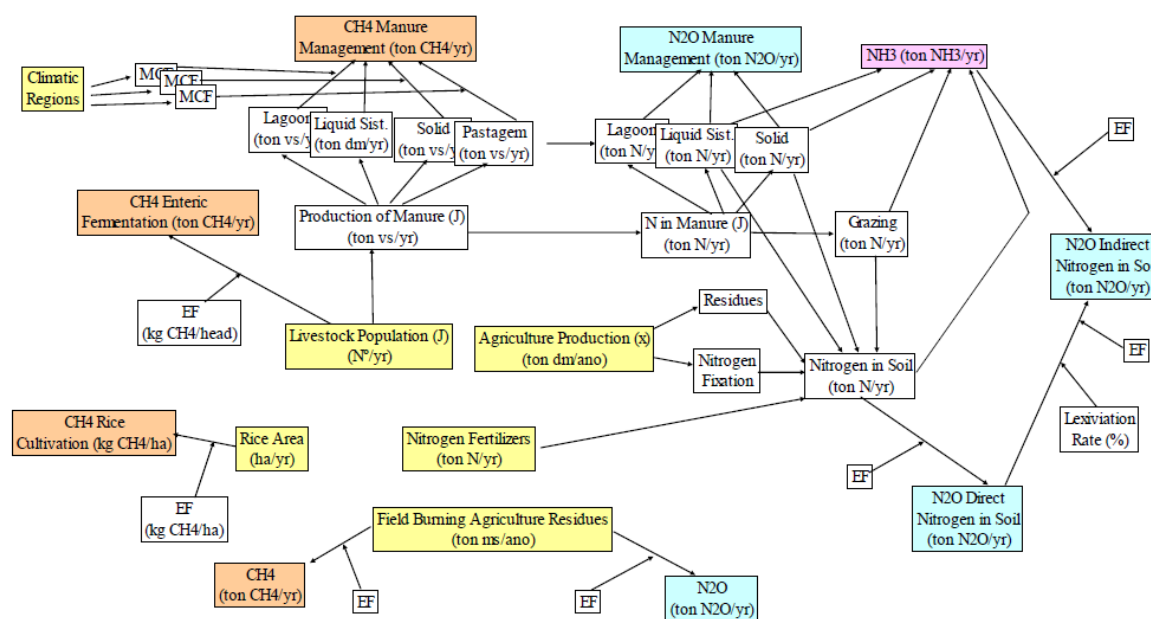
Figure 2.8 - Methodology for emissions estimations for report to the EMEP programme and the IPCC (APA, 2012).

Ammonia volatilization due to mineral fertilizers (SN_NH$_3$) is estimated based on:

$$SN\_NH_3 = N_{Fert} * Frac_{GASF}$$

(2.4)

where,

N_{fert} is the total amount of nitrogen in synthetic fertilizers consumed (annual);

$Frac_{GASF}$ is the fraction of nitrogen in fertilizers that volatilizes as NH$_3$ or NO$_x$.

The NH$_3$ volatilization emission factors considered by EMEP varies according to the fertilizer category (Table 2.5).

Table 2.5 - NH$_3$ volatilizations emissions factors used by the Portuguese Environmental Agency (APA, 2012) according to fertilizer category.

Fertilizer	EF (kg NH$_3$/kg N)
Nitrogen solution	0.08
Urea	0.15
Ammonium sulfate	0.08
Sulpho-ammonium nitrate	0.05

Fertilizer	EF (kg NH3/kg N)
Ammonium nitrate	0.02
Calcium ammonium nitrate	0.02
Other nitr. fertilizers	0.053
Di-ammonium phosphate	0.05
NPK fertilizers	0.02
NP fertilizers	0.02

Regarding ammonia emissions from manure, EMEP considers four stops in the life cycle of manure, which implies different emissions factors (APA, 2012):

- (i) housing;
- (ii) outside storage;
- (iii) land spreading of manure collected in each manure management system;
- (iv) ammonia volatilized from direct soil deposition of droppings during grazing.

Table 2.6 - NH_3 volatilizations emissions on the main phases of manure of life cycle (APA, 2012).

Manure life cycle phase	Emissions estimations
Housing Outside storage	$MMS_{NH3} = \sum_i [N_{(i)} \times Nex_{(t)} \times (1 - MS_{GRAZ_{(i)}}) \times EF_{NH3_{(i)}}]$
Manure management system	$AM_{NH3} = \sum_t \{N_{(i)} Nex_{(t)} \times \sum_s [MS_{(i,s)} \times MSSD_{(i,s)} \times (1 - EF_{NH3_{(i,s)}})] \times EF_{NH3SD_{(i)}}\}$
Grazing	$GZ_{NH3} = \sum_t [N_{(i)} \times Nex_{(t)} \times (1 - MS_{GRAZ_{(i)}}) \times EF_{NH3_{(i)}}]$

The factors included into the expressions shown in Table 2.6, are subsequently defined, according to APA (2012).

Emissions from nature during housing and storage are estimated together, hence factors in the expression for MMS_{NH3} estimation are:

- $N_{(i)}$: number of individuals from livestock category I in the country;
- $Nex_{(t)}$: annual country average N excretion per head of animal specie/categorie I;
- $EF_{NH3_{(i)}}$: fraction of nitrogen from livestock category I that is lost to the atmosphere as ammonia during housing and manure storage;
- $MS_{GRAZ_{(i)}}$: fraction of Manure/Nitrogen from livestock category I that is managed in Pasture Range and Paddock;

Regarding Manure management systems, their ammonia emissions include:

- $N_{(i)}$: Number of individuals from livestock category I in the country;

- $Nex_{(t)}$: annual country average N excretion per head of animal specie/category i;

- $MS_{(i,s)}$: fraction of manure/nitrogen from livestock category that is managed in Manure Management systems s, except grazing;

- $MSSD_{(i,s)}$: fraction of manure/nitrogen from livestock category I treated in Manure Management system s that is used as fertilizer in agriculture soils;

- $EF_{NH3_{(i,s)}}$: fraction of nitrogen in manure management systems S from livestock category I that is lots to atmosphere as ammonia during housing and manure storage;

- $EF_{NH3SD_{(i)}}$: fraction of nitrogen in mature that is lost to the atmosphere as ammonia after application to soil fertilizer.

Finally, ammonia emission from grazing includes the knowledge of data on;

- i : animal/species category of livestock;

- $N_{(i)}$: number of individuals from livestock category I in the country;

- $Nex_{(t)}$: annual country average N excretion per head of animal specie/category i;

- $MS_{GRAZ_{(i)}}$: fraction of manure/nitrogen from livestock category I that is managed in pasture Range and Paddock;

- $EF_{NH3_{(i)}}$: fraction of nitrogen excreted from livestock category i during grazing that is lost to the atmosphere as ammonia.

Table 2.7 summarizes the emissions factors used for NH_3 emissions estimations during whole manure life cycle.

The values of emission factors illustrate the amount of information needed regarding NH_3 volatilizations in the agricultural sector. An uncertainty value for the overall estimation will depend of each individual value uncertainty, which the will be higher when national total emissions are considered.

Table 2.7 - Emission factors used in the NH_3 volatilizations from animal housing, land spreading and grazing in pasture (kg $N-NH_3$/kg N excreted).

Classe	Housing & Outside Storage	Land spreading of Manure	Grazing in Pasture
Dairy cows	0.17	0.17	0.08
Other cattle	0.17	0.17	0.08
Sheep	0.10	0.07	0.04
Goats	0.10	0.07	0.04
Swine	0.22	0.16	0.08
Equines	0.12	0.07	0.08
Poutry	0.22	0.16	
Hens	0.23	0.15	
Rabbits	0.22	0.16	

According to APA (2011), the total amount of NH_3 emitted in 2009 was of 52 kt. At the national level, the higher contributors to this value are livestock and agriculture, 47.6 % and 37.2 %, respectively.

The relevance of the total treated above relies on the fact that emissions are considered into the chemistry transport models as input values, that need further treatment, in order to be used in any CTM calculation.

2.4.2. THE CHEMICAL TRANSPORT MODEL CHIMERE

The purpose of this multi-scale chemistry-transport model, developed by *Institut Pierre-Simon Laplace,* is to produce daily forecasts of ozone, aerosols and other pollutants and make long-term simulations for emission control scenarios. In what concerns spatial scale, it runs over a range of spatial scales from the regional scale (several thousand kilometers) to the urban scale (100-20 km), with resolutions from 1-2 km to 100 km. Most data are valid only for Europe and should be revisited for applications on other continents. This model proposes many different options for simulations which make it a powerful research tool for testing parameterizations and hypotheses (CHIMERE, 2012). Among others the input data required by CHIMERE can be divided in meteorology, boundary conditions, land-use and emissions.

Emissions are usually coming from local, nonpublic databases. In this case, emissions are proposed for Western Europe and for the region around Paris. Due to the integration of the MEGAN model biogenic emission potentials and emission rate parameterizations, the biogenic emissions can now be calculated outside Europe.

Input data required

As a portable model it can run with different types of initial input data, among them the model consider meteorological data, boundary conditions, land-use information and emissions. The user of the model is responsible by the refinements of the input data in what concerns the following conditions:

- Meteorology: Meteorological data is not provided on the server, but CHIMERE interfaces for the WRF and MM5 mesoscale models are proposed. WRF and MM5 (free software) can be used combined with AVN/NCEP (as forcing) public weather forecasts.
- Boundary conditions: A set of boundary conditions from the MOZART and/or LMDz-INCA models is proposed as a default solution. Data are kindly provided by Max-Planck Institut, Hamburg, thanks to M. Schultz, G. Brasseur, C. Granier and D. Niehl, and IPSL/LSCE, thanks to Sophie Szopa and Didier Hauglustaine. This allows tropospheric simulations below 200 hPa. For aerosols, a set of boundary conditions based on GOCART global simulations (thanks to Mian Chin, NASA) is proposed in addition to the LMDz data.
- Land-use: CHIMERE needs input landuse information for a number of processes. The proposed land use databases are GLCF3 and GlobCover4.
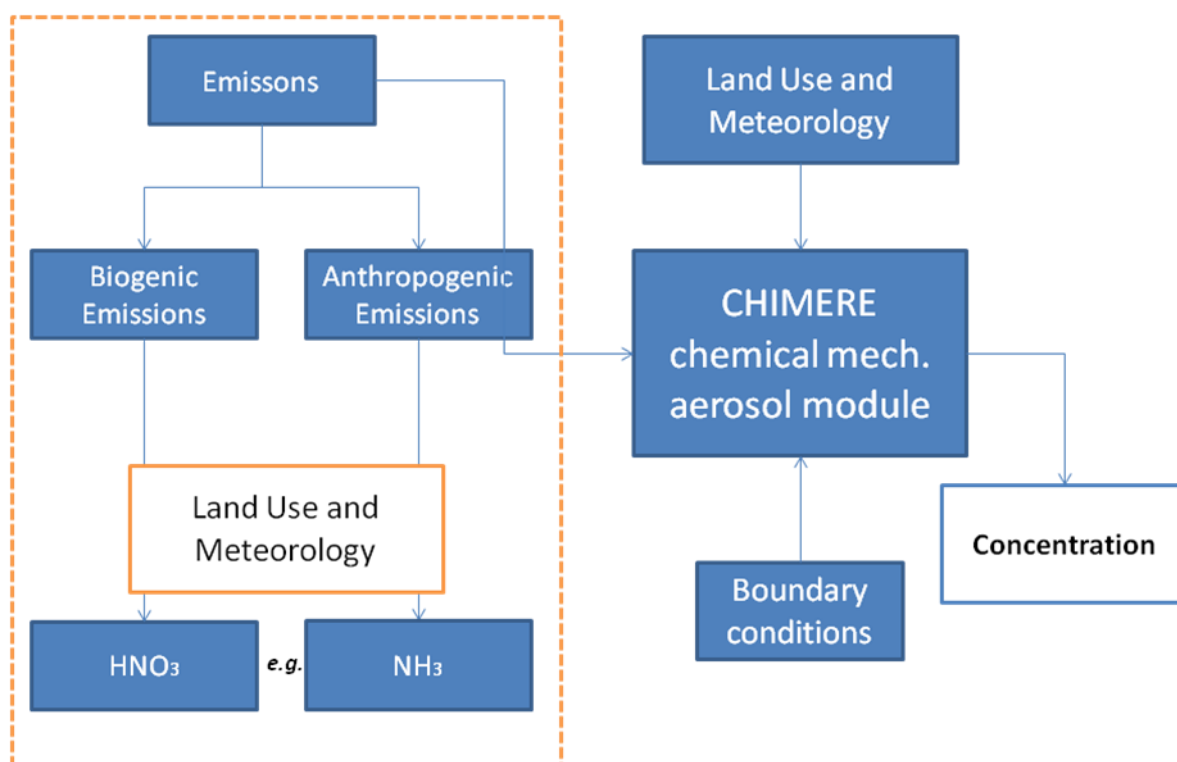

Figure 2.9 - Emissions data of the chemical species of interest for the present work into the CHIMERE model.

For better understand the mechanism involved, Figure 2.9 shows as initial inputs of CHIMERE model, the introduction of emission data from EMEP database, which consider anthropogenic emissions and other complementary models such as MEGAN which included biogenic emissions. Land use needs to be provided as well as the meteorological data calculated by a weather forecast model of compatible scale of the CHIMERE applications.

After reallocated to the CHIMERE grid domain, both horizontally and vertically, the annual emissions are affected by seasonal and hourly factors, and disaggregated into the chemical species considered by the chemical mechanism and aerosol chosen options.

2.4.3. COMPLEMENTARY MODELS INSIDE CHIMERE WITH INTEREST FOR THE PRESENT STUDY

Starting with biogenic emissions estimations, they are calculated through the MEGAN model.

MEGAN model

MEGAN uses canopy-scale emission factors based on leaf area index obtained from the standard MEGAN LAIv database. The MEGAN modelling effort (Guenther *et al*., 2006) has combined a global scale model with high spatial resolution (1 km) suitable for regional modelling. The intent of the MEGAN effort is to incorporate all available regional information into a global model that is widely available. MEGAN currently includes the most recent information from North America and the tropics, besides Europe (Startelet *et al*., 2012; Monks *et al*., 2009).

The MEGAN model estimates the net emission rate of isoprene (described in detail in Guenter *et al*., 2006) and more five CHIMERE species: *α*-pinene, *β*-pinene, limonene, ocimene and NO.

$$ER_i = EF_i \times \gamma_i \, (T, PPFD, LAI) \times \rho_i$$

(2.5)

where,

ER_i ($\mu g \cdot m^{-2} \cdot h^{-1}$) is the estimation rate of species I;

EF_i ($\mu g \cdot m^{-2} \cdot h^{-1}$) is the emission factor at the canopy standard conditions;

γ_i (not dimensional) is an emission activity factor that accounts for deviations from canopy standard conditions;

ρ_i is a factor that accounts for production/loss within the canopy (assume to be = 1 inside the canopy);

Standard conditions in the canopy are defined as

   T - temperature = 303 K (~ 30 º C);

   PPFD – photosynthetic photon flux density = 1500 µmol. m^{-2}. s^{-1} (at the top of the canopy);

   LAI – leaf area index = 5 $m^2.m^{-2}$

the canopy is considered to have 10 % old foliage, 10 % is growing and 80 % of it is mature.

The emission factors are provided and fixed, the LAI data is given as monthly means of the MODIS product (MODIS, 2013). For hourly emissions calculations, the MEGAN model need information on 2-m temperature and short-wave radiation. These are calculated in a pre-processor using the meteorological data of the weather forecast model (also previously runned). The MODIS product is given one km^2 on horizontal resolution, hence the biogenic emissions will be regridded to the grid dimensions of the CHIMERE defined domain.

ISORROPIA model.

Aerosols include organic and inorganic material, however, the latest is the major contributor to particulate matter. Inorganic aerosol is dominated by ammonium, sulfates and nitrates. The thermodynamic equilibrium model ISORROPIA (Nenes *et al.*, 1998), is used to determine the particle/gas partitioning (of semi-volatile inorganic species. The possible species are the following (CHIMERE, 2012):

- Gas phase : NH_3, HNO_3, HCl, H_2O;

- Liquid phase : NH_4^+, Na^+, H^+, Cl^-, NO_3^-, SO_4^{2-}, HSO_4^-, OH^-, H_2O, $HNO_3(aq)$, $HCl(aq)$, $NH_3(aq)$, $H_2SO_4(aq)$;

- Solid phase : $(NH_4)_2SO_4$, NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, NH_4NO_3, NH_4Cl, $NaCl$, $NaNO_3$, $NaHSO_4$, Na_2SO_4.

In ISORROPIA, the solid/liquid phase transition is solved by computing the deliquescent relative humidities. After a series of sensitivity tests it was proved that this thermodynamical equilibrium may be implemented on the basis of pre-calculated look-up table interpolation values.

The points covered in this literature review were chosen regarding the possible implications of the emitted pollutants by the agriculture sector, especially ammonia, on the concentration calculations of air pollutants by a CTM, particularly the CHIMERE model. Details on other emissions estimations inside CHIMERE, as well as the gas phase chemical mechanism and secondary organic aerosols implementations may be found in CHIMERE 2012.

3. METHODS AND DATA

This chapter starts with a brief characterisation of the climate over the region where filed measurements on rice paddies were carried out. Details on the field campaigns performed in the aim of the project *"Trace gas emissions from Portuguese irrigated rice fields in contrasting soils, by the influence of crop management, climate and increase concentration of CO$_2$ in the atmosphere"* are provided and, finally, a description of the CHIMERE model application.

3.1. CLIMATE CONDITIONS IN THE REGION OF INTEREST

Air quality modelling

External processes like solar variability, terrestrial orbital variations, pole wandering (continental drift), tectonic results, sea level alteration, atmospheric composition and mass (except CO$_2$, H$_2$O, O$_3$ and other pollutants) and also volcanic activity and stratospheric aerosols production influence the climate system. As internal processes the mechanism between atmosphere-ocean-cryosphere-biosphere-lithosphere as well as its individual variation have implications on de system development. Land use, thermal pollution, gases, aerosols, manager by human activities and the climatic fluctuation add to external and internal processes along time form characteristic climate systems (adapted from Ferreira, 2012).
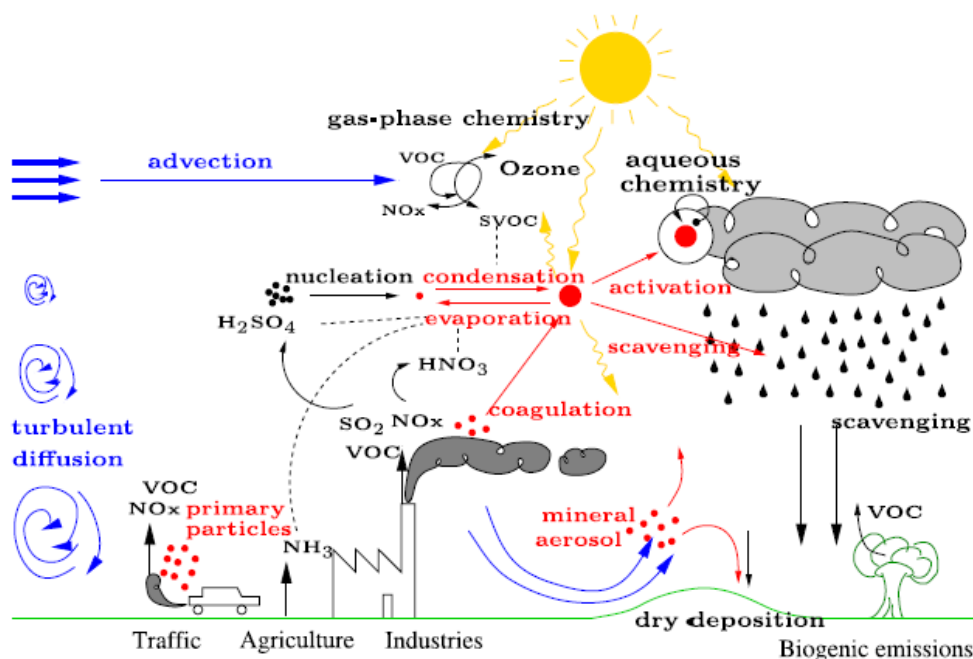

Figure 3.1 - Atmospheric mechanisms in air quality (Sportisse, 2010).

Air quality transcends all scales with in the atmosphere from the local to the global with handovers and feedbacks at each scale interaction (Monks *et al.*, 2009). Temporal scales of atmospheric transport, from continental with 1 week and stratospheric to tropospheric changes between one and two years. Also depending on their composition, elements present different residence time on the atmosphere. It is represented by the mean time of a species existing in the atmosphere, i.e. between its emission into the air and its removal by chemical transformation or deposition. Regarding not the global atmosphere but an atmospheric box, also the transport time (between importation and exportation) determines the box residence time. Mathematically, we can define the residence time as the arithmetic mean of individual life time of all particles of a trace species (Ferreira, 2012; Moller, 2004).

The residence time depends from time and space, i.e. is not being constant in the atmosphere due to varying conditions for chemical reactions and deposition processes (Moller, 2004). In this way it is important to understand and define special and temporal scales, in order to define the best model available for each study case.

Regional model - Eulerian Model (Box Model) is considered in this study.

Many advances have been made in recent years, in what concerns emission inventories, but much remains to be done. Spatial resolution has in general improved but spatial and temporal variability still needs further quantification. There has been overall a reasonable correlation between trends in emissions and in measured concentrations, although very recently discrepancies have been noted in NOx trends in urban areas, where concentrations in some areas, notably roadside locations, do not appear to have been reducing as quickly as emission inventories would predict (Monks *et al.*, 2009).

According to 2.1.2 Chapter, the nitrogen cycle influence factors of N emissions include meteorological conditions such as temperature, air humidity, wind speed and precipitation.
The nearest meteorological station to Salvaterra de Magos with climate normals available is Santarém. Figure 3.2 presents the values of the latest climate normal available (provisional) by the "Instituto Português do Mar e da Atmosfera" (http://www.ipma.pt/en/index.html) and the differences of the meteorological parameters concerning temperature and precipitation between the climate normals of 1971-2000 and 1981-2010.
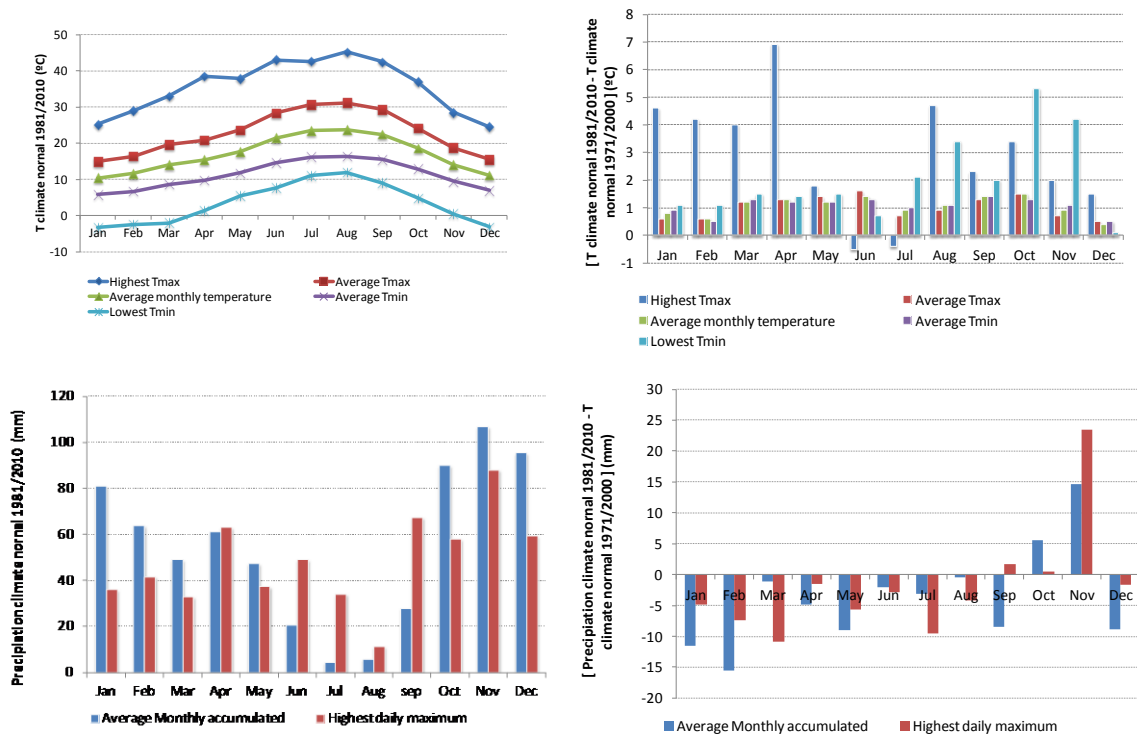
Figure 3.2 - Temperature and precipitation climate normals in Santarém for the 1981-2010 (provisional) - left column; differential values between climate normal 1981/2010 and 1971/2000 (adapted from IPMA, 2013).

In Figure 3.2, the features that suffer more changes between the two temperature climate normals are the daily extreme values registered in a given month, both minimum and maximum temperature values. Maximum daily temperature values above 40 ºC were recorded in June and July during the climate normal of 1971-2000, whereas in the recent climate normal, maximum daily values above 40 ºC were observed between June and September.

Averages for maximum, minimum and monthly averages temperatures increased more than 1 ºC in March, April, May, June, September and October, but all the parameters suffer increases (except for the maximum daily registered temperature in June and July). Opposite tendency is observed between the two climate normals for precipitation, where total monthly precipitation amounts and maximum daily precipitation decreases from 1971/2000 to 1981/2010 climate normals. January and February experienced less 10 -15 mm in monthly total amount. However, for October and November the monthly totals increased in recent years between 5 and 15 mm, respectively. The month of November also shows enhancement of the daily amounts greater than 20 mm.

The above information is reflecting that, in Santarém, the temperature parameters are increased and precipitation have decreased from 1971-2000 to 1981-2010 climate normal's, namely during the period of the rice cultural operations (between March and September).

Meteorological conditions on field were analyzed using two different sources, from *Sistema Nacional de Informação de Recursos Hídricos* (SNIRH) by monitored grid stations and from local weather monitoring station in Salvaterra de Magos, data provided by *Associação de Regantes e Beneficiários do Vale da Sorraia* (ARBVS).

Two main stations were considered in the case of SNIRH data which are São Julião Tojal (Sj TOJAL (20C/01C) and Barragem de Magos (BMAGOS (20E/01C) (Table 3.1 indicates information on SNIRH stations location characteristics and classification).

Table 3.1 - Station characteristics (SNIRH, 2012).

Code	Name	Latitude	Longitude	Altitude	Bacia	District	Concelho	Freguesia	Sation type
20e/01c	Barragem de Magos	38.99	-8.694	43	Tejo	Santarém	Salvaterra de Magos	Foros de Salvaterra	Climatologic
20c/01c	São Julião do Tojal	38.843	-9.123	6	Tejo	Lisboa	Loures	São Julião do Tojal	Climatologic
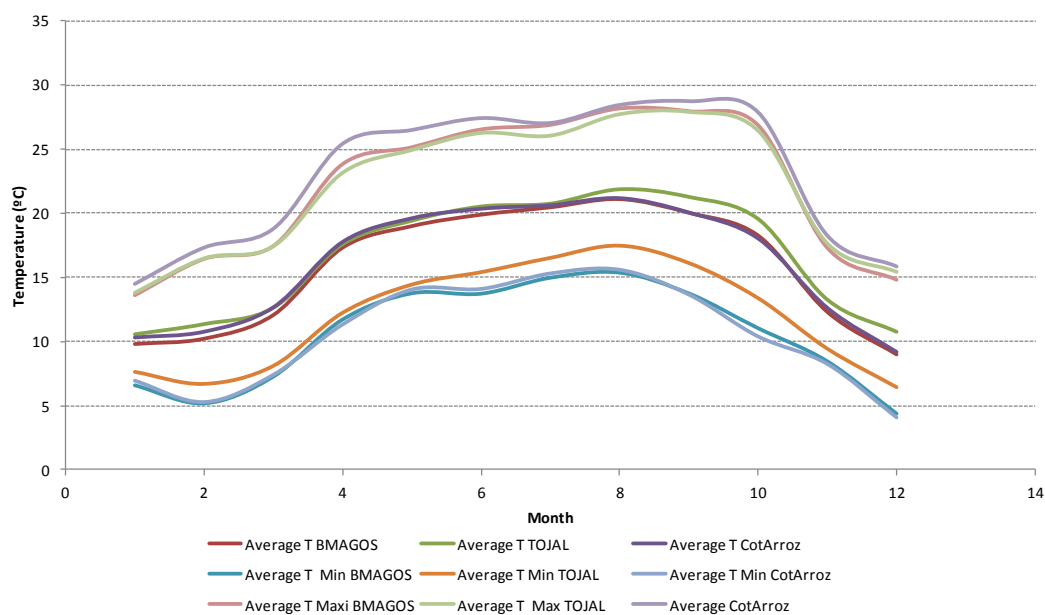
Figure 3.3 - Monthly averages of daily temperature maximum, minimum and daily averages temperature in 2011 (SNIRH, 2012; ARBVS, 2012).

The data in Figure 3.3 regards the climatological stations of the SNIRH database located near the rice field experiment. These climatological stations are usually located near dams, water reservoirs and are used to assess watershed. Since the CotArroz field experiment are near the Tejo River, the three meteorological stations may be considered as measuring conditions at the

same watershed. Higher minimum temperature averages are observed in Tojal, Tojal also presents higher daily temperature averages in between July and December. However, the data measured in CotaArroz shows the higher maximum temperatures averages in the region. The patterns of the temperature maxim and daily averages are similar for all the stations. Regarding meteorological field variables, the data of the three stations may be used to characterise the weather over the region of interest.

During the one month period between 11th May and 10th June, which includes the period of fertilization, and the three days simulation period by CHIMERE, the temperature recorded in the region may in all the three stations present the highest daily maximum (32.2-33.4 ºC) and daily average temperature (23.4-24 ºC) (Figure 3.4). This period of high temperatures was proceeded and followed by two rainy ones, 17-20 and 27-31 of May, respectively. These high temperatures during the fertilization period may be responsible for higher volatilization rates.
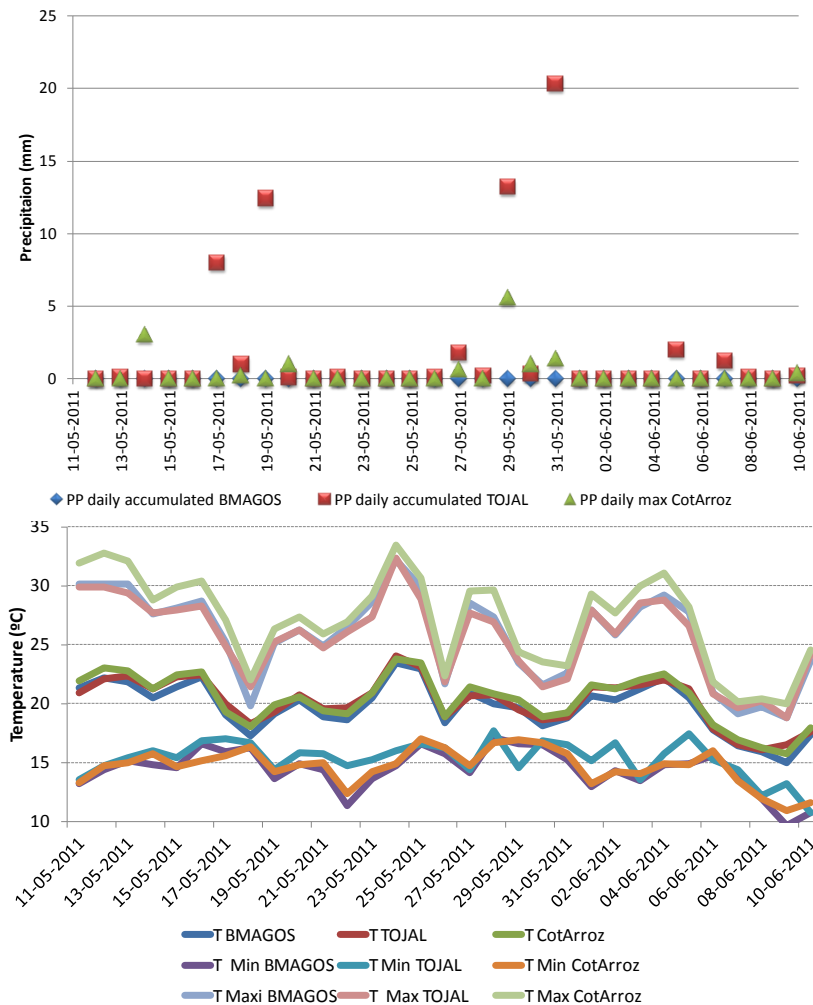

Figure 3.4 - Daily values of temperature and precipitation recorded between the 11th May and 10th June 2010 (SNIRH, 2012; ARBVS, 2012).

3.2. COTARROZ DATA

The gas emissions by the culture of *Oriza sativa L. Ariete* measurements were focused mainly on N compounds, CH_4, NMVOC´s, CO_2. Nitrogen compounds were measured and analysed by Figueiredo, (2011) and the INIAV team members. These compounds were measured in irrigated rice fields at CotArroz, Salvaterra de Magos (Lisboa e Vale do Tejo region, Portugal) under different conditions:

a) *open field*, loamy sand and silty clay soils;

b) *open chambers*, silty clay soil, increasing temperature with and without enhanced CO_2 concentrations.

Figure 3.5 - Location of CotArroz soil A and soil B.

The open chambers pretend to recreate future climate conditions. Temperature and CO_2 were the parameters that contributed for it. Measured parameters are potential mineralizable N, Soil plant analysis development (SPAD), Productivity, N concentration and exportation.

Table 3.2 presents the calendar of cultural operations placed on field that occurred in 2011, the precise days of fertilization and by which method was carried out.

Table 3.2 - Cultural operations calendar of 2011 (adapted from Figueiredo, 2011).

2011 Year		
Cultural Operations	**Date**	**Fertilizer application type**
1	11th April	-
2	18th April	-
3	24th May	Manual and aerial
4	27th May	Manual and aerial
5	14th June	Manual and aerial
6	6th July	Aeria
7	11th July	Manual and aerial

## 3.3. CHIMERE MODEL APPLICATION

As it will be described latter on in this chapter two types of emissions are considered by the CHIMERE model:

- Anthropogenic emissions; these are pre-processed based on the grid EMEP data.
- Biogenic emissions: are automatically calculated by the CHIMERE pre-processor using landuse data and a priory meteorological fields results from a numerical weather prediction model.

The CHIMERE model was applied in order to evaluate the sensitivity of chemical species concentrations to changes in NH_3 agricultural emissions in specific locations, namely the ones in Portugal identified as rice crops. The model's sensitivity to the chemical species concentrations was verified over two locations, near the CotArroz field experiment and over Lisbon.

The first step was to identify the Portuguese regions were rice production is a dominant crop. For that purpose the European Environment Agency Corine Land Cover (CLC) (http://www.eea.europa.eu/data-and-maps/data/corine-land-cover-2006-raster.html) 2006 data base was used.

The next three figures, Figure 3.6, Figure 3.7 and Figure 3.8 consider rice fields as land prepared for rice cultivation, flat surfaces with irrigation channels and surfaces periodically flooded (CLC, 1999). Other categories were consider for better understand the main differences.
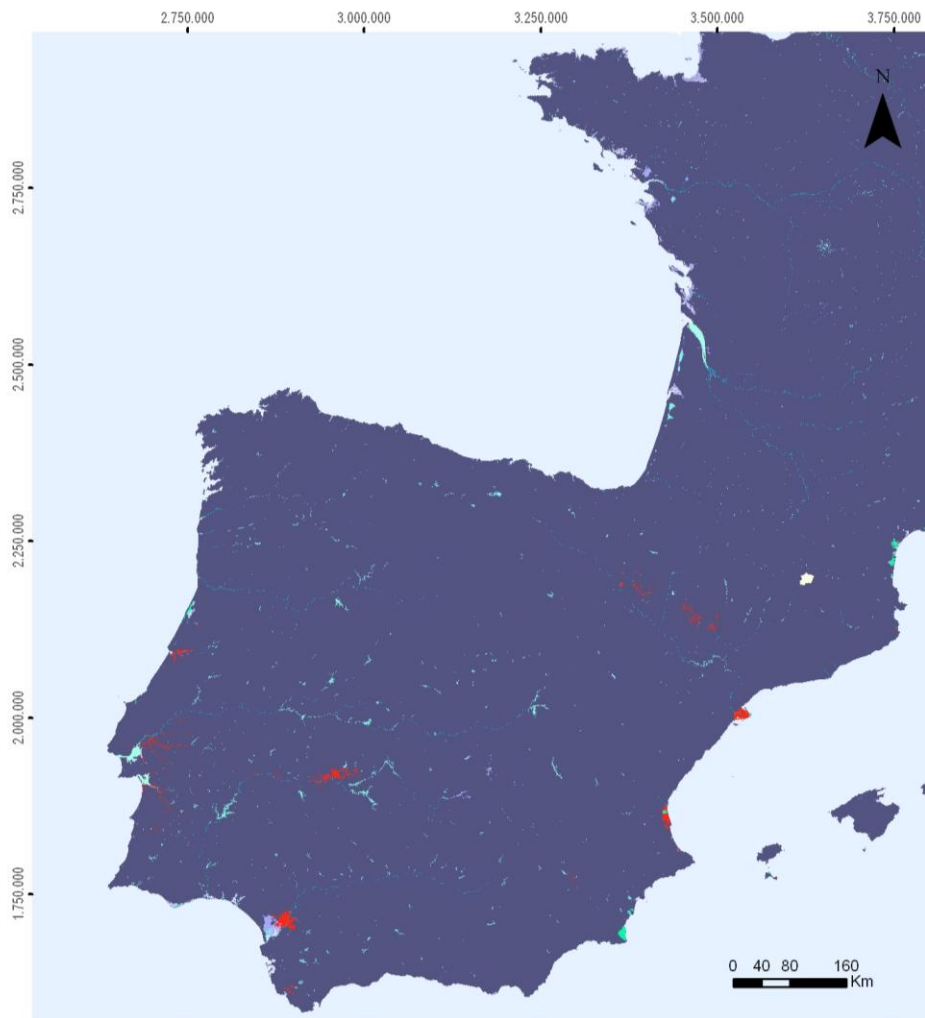
Figure 3.6 - Rice fields location in Iberian Peninsula.
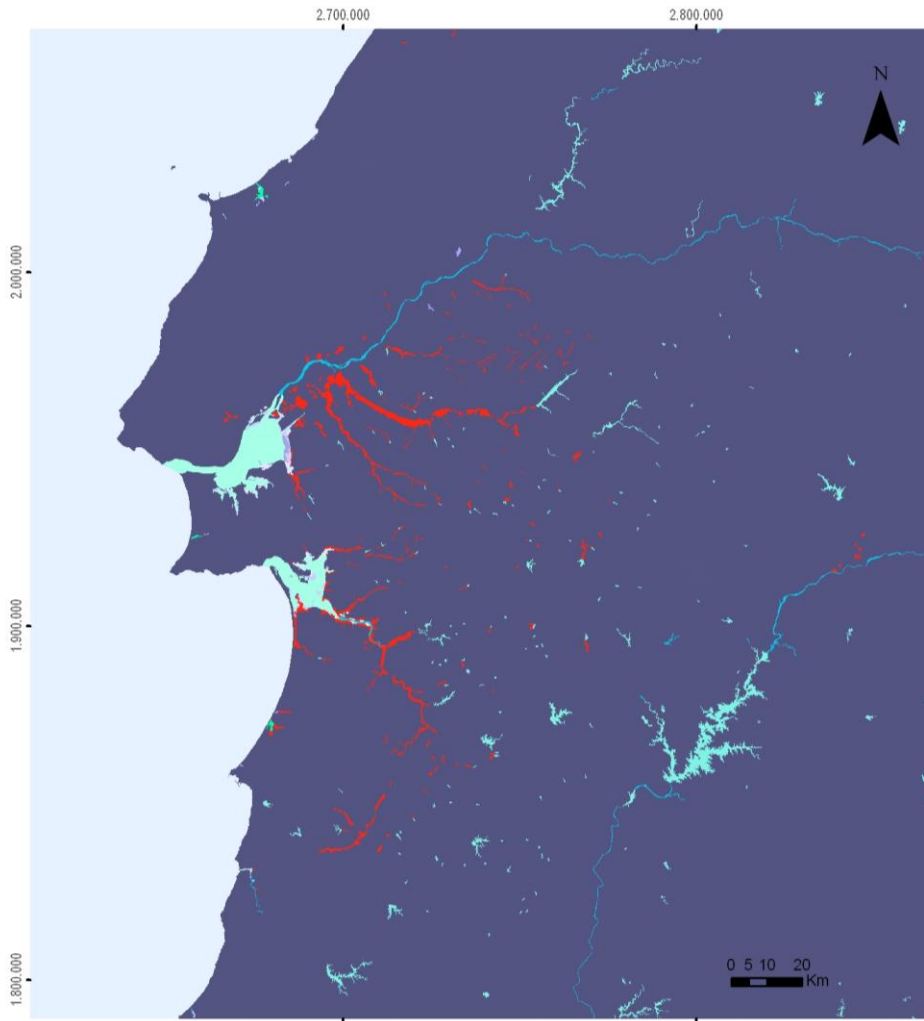
Figure 3.7 - Location of Tejo and Sado rivers rice fields.

Tejo and Sado rivers represents the portuguese south rice fields. In what concerns Sado river, the region of Alcácer do Sal gets the main characteristics to the rice culture development, which includes water availability. In an area of 6 000 hectares, rice producers of Sado Estuary represent the main agriculture activity of this region.
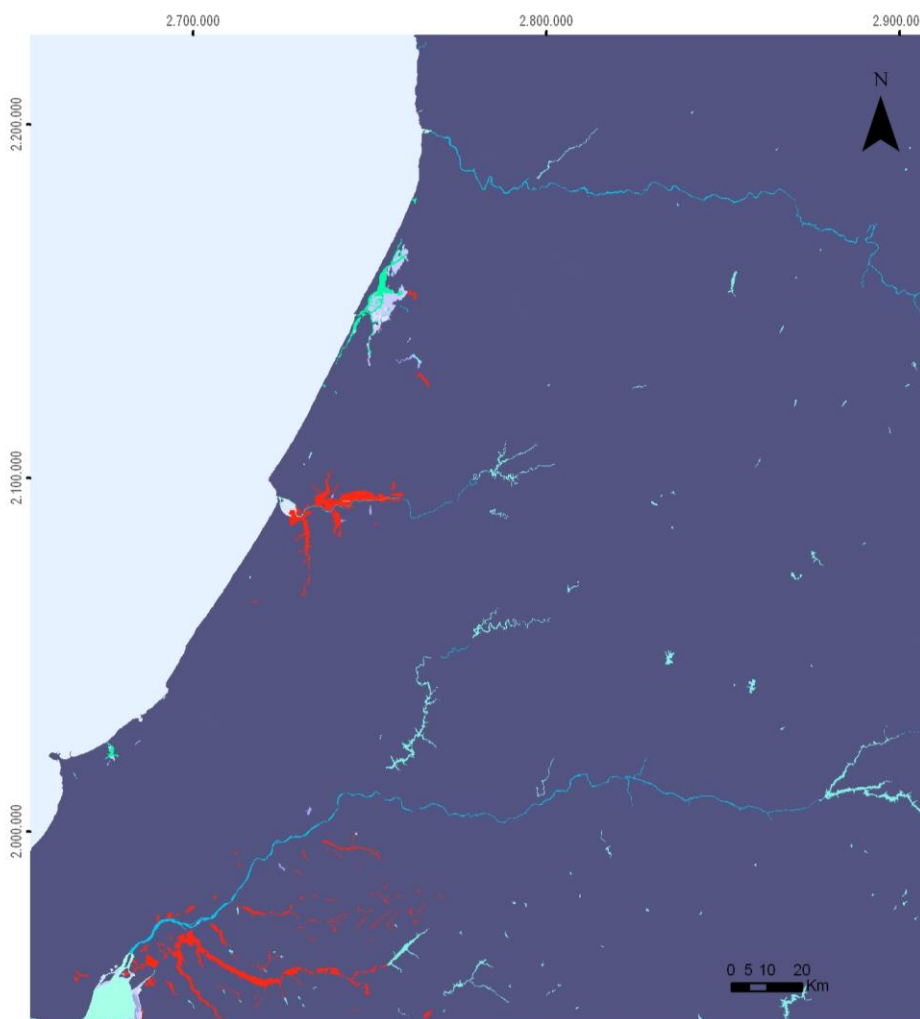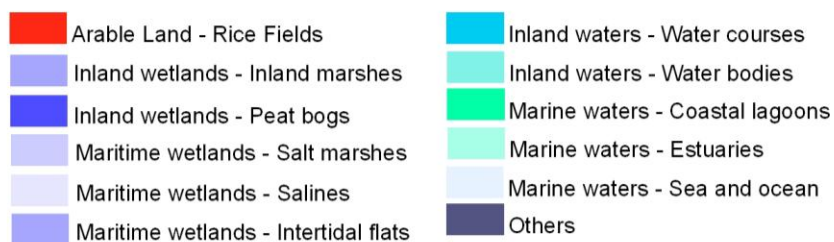
Figure 3.8 - Location of Low Mondego Valley rice fields.

Low Mondego Valley is located in Litoral Beira region (Figure 3.8) and considers a large plain included in between Coimbra and Figueira da Foz cities. This is the local of production of Carolin Rice of Low Mondego Valley.

The second step was to match the above indentified regions EMEP grid emissions cells for subsequent changes on NH_3 annual total emissions values before the application of the CHIMERE anthropogenic emission pre-processor.

As discussed in the literature review, the fertilization procedure in the rice cultural operation is one of the major contributors to the anthropogenic emissions of NH_3 from the agriculture sector.

Due to the short term period for the execution of the presented work, and the time necessary to run the models, only a period of fertilization application was chosen for the subsequent CTM application. A CHIMERE run was made including the 24th May 2011, where both manual and aerial fertilization was applied. On both soils, 250 kg ha^{-1} of ternery fertilizar (20-20-0) was applied manually allowing availability, in each hectare of soil, of 50 kg of nitrogen, 50 kg phosphorus and no potassium. Aerial fertilization was applied in a dose of 60 kg N ha^{-1}.

The CHIMERE model was applied over the Iberian Peninsula in a horizontal grid resolution of 25 km x 25 km. Since horizontal advection is contributing to the chemical species concentration in the air, and the resolution is coarse, it is important to have a domain were the sensitivity analysis is all inside the domain, and not disturbed by the imposed model boundary conditions.

Input data required and used in the study:

o **Meteorology**: as Meteo data is not provided on the server and CHIMERE proposes interfaces for the WRF and MM5 mesoscale model, WRF was chosen in this simulation. The meteorological fields were calculated by the WRF model during a period representing the meteorological conditions verified during the fertilizer application, i.e. in May 2011; the simulation period was 3 days. The WRF meteorological model was forced to run by the GFS global model every 6 hours. The hourly meteorological variables calculated by the WRF model were interpolated horizontally and vertically between the WRF grid and the CHIMERE model grid. The meteorological fields were also used *a priori* to calculate the biogenic emissions, which mostly depending on radiation, temperature, wind speed and stability, according to the chemical species emitted.

o **Boundary conditions**: A set of boundary conditions from the MOZART and/or LMDz-INCA models is proposed as a default solution. In the present simulation the concentrations admitted at the model boundaries were adequate to the climatology of the period under analysis, and given by the global chemical transport model LMDZ-INCA (http://lmdz.lmd.jussieu.fr/) for gas species. For aerosols, a set of boundary conditions based on GOCART global simulations (thanks to Mian Chin, NASA) is proposed in addition to the LMDz data. In the present case GOCART model for aerosol particles was used (http://acd-ext.gsfc.nasa.gov/People/Chin/gocartinfo.html).

- o **Land-use**: CHIMERE needs input landuse information for a number of processes. The proposed land use databases are GLCF3 and GlobCover4. MODIS was used in this case, Modis Sensor, measure land use beyond other characteristics.

- o **Emissions:** The biogenic emissions were estimated using the MEGAN model (Guenther *et al.*, 2006). Also, the estimations of dust emissions and particulate matter ressuspension are dependent on *a priori* knowledge of the meteorological fields.

  The anthropogenic emissions were recalculated for the defined CHIMERE domain based on the EMEP emission grid available at *http: http://www.ceip.at/webdab-emission-database/emissions-as-used-in-emep-models/* and reallocated according to the MODIS land use database (1 km resolution, *http: http://glcf.umd.edu/data/* aggregated to the CHIMERE domain grid resolution. The more recent EMEP anthropogenic emissions available reflect the emissions of 2010 and were updated in 2012. The chemical mechanism used was the reduced MELCHIOR2, which considers 120 reactions and 44 species; the option for chemically active aerosols was set on, the number of aerosol sections was 9, dust was included, and the secondary organic aerosol scheme chosen was the medium scheme. All these choices were made having in mind the model performance, and the time necessary to run the simulation period for the planned sensitivity test on the NH_3 EMEP emissions.

Figure 3.9 - Representative scheme of grids considered to CHIMERE mechanism.

The CHIMERE model results were saved on hourly basis. Since the simulation was made in a cold start process, a model *spin up* of 24 hours was considered, which excluded this period from the analysis. Just the second and third days simulation were taken in to account for the results and discussion.

Weather pattern during the simulation period:
During the simulation period Portugal was under fair weather conditions with synoptic winds blowing from the East, normally associated with dry air masses and higher than average temperatures (from the end of May to the beginning of June) and low wind speeds. These conditions may differ locally according to the land use where measurements are taken.
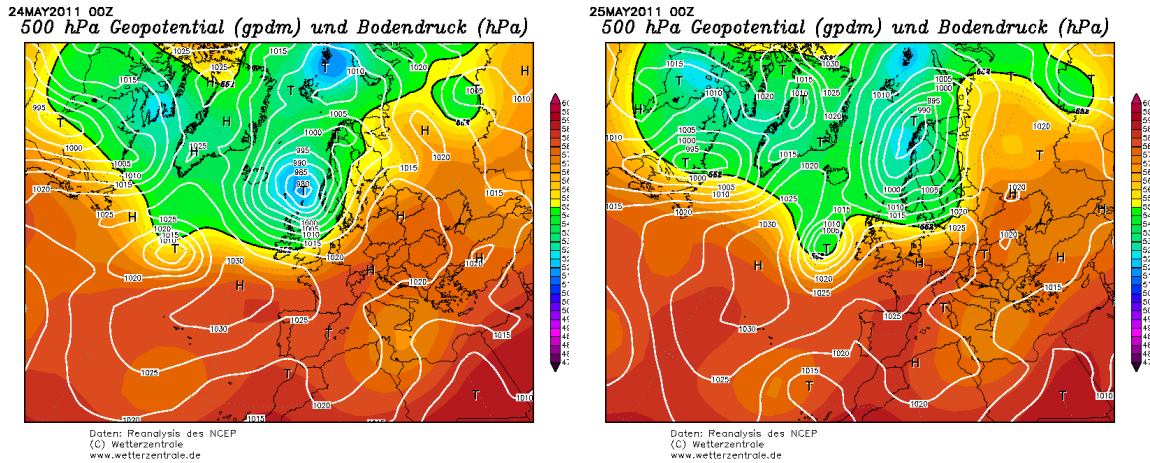
Figure 3.10 - Mean sea level pressure fields (white contour lines) over Europe for the 24 (left panel) and 25 of May (right panel) 2011 (http://www.wetterzentrale.de/topkarten/fsreaeur.html).

Sensitivity analysis of the concentrations obtained by the model

Three model runs were performed:

1) a control run with emissions as provided by EMEP 2010;

2) a second run where the original 2010 EMEP NH_3 emissions from the agriculture sector were divided by two; and

3) a third run where the original EMEP NH_3 emissions from the agriculture sector were multiplied by a factor of two (inspired in the work of Hamaoui-Laguel *et al.*, 2012).

In total, changes were performed in only 12 EMEP original cells, over rice crop fields in river contiguous areas: Mondego (4 cells), Tejo (4 cells) and Sado (4 cells).

Gas Emissions on Rice Culture and its importance on air quality

4. RESULTS AND DISCUSSION

Firstly, the time evolution of the EMEP emissions is observed as well as the obtained results on the CotArroz field measurements. Nitrogen agricultural emissions impact on the concentration of the air chemical species calculated by the CHIMERE model was analysed. The period of simulation was of three days in May 2011: 23rd, 24th and 25th, as a representation of the fertilization processes, according to culture operations in CotArroz. The 23rd of May was excluded for analyses due to the *spin up* effect of the simulation model. The resulting concentrations were assessed over two locations; over the local irrigation fields near the Tejo river and over Lisbon city. The purpose was to verify if there is any impact of the irrigated fields emissions on the air pollutants concentration over Lisbon region, which in this particular period is downwind of the fertilized field experiment.

4.1. EMEP DATA BASE AND COTARROZ FIELD MEASUREMENTS

The primary analysis to the EMEP emissions for Portugal and EMEP grid cell where CotArroz field experiment is located was performed, in order to have in insight of what is the proportion of the ammonia emissions of the agriculture sector regarding other sectors and other pollutants. Figure 4.1 represents the time evolution of the emissions of all pollutants from agriculture sector (S10).

Figure 4.1 - EMEP Compounds emission evolution from 1998 to 2010 and total emissions in sector S10 (from T1 in Annexes).

A general tendency of decrease of all pollutants along the years is presented in the Figure 4.1. Although, it is important to note the emissions e. g. of the NH_3 in 2009 and 2010 years which are approximately about 4.23×10^6 Gg.

The CotArroz field experiment was identified over the European EMEP grid emission (cell i =53, j = 6). Time series of total emissions, NH_3 and NOx annual emissions from the agriculture sector (S10) over this cell were analyzed and are shown in Figure 4.2. The time span covers the period between 1996 and 2012. Both NO_x and NH_3 emissions of this sector presents a clear tendency of decrease. Since 2005, the total emissions and the ammonia emissions have stabilized around 30 %.
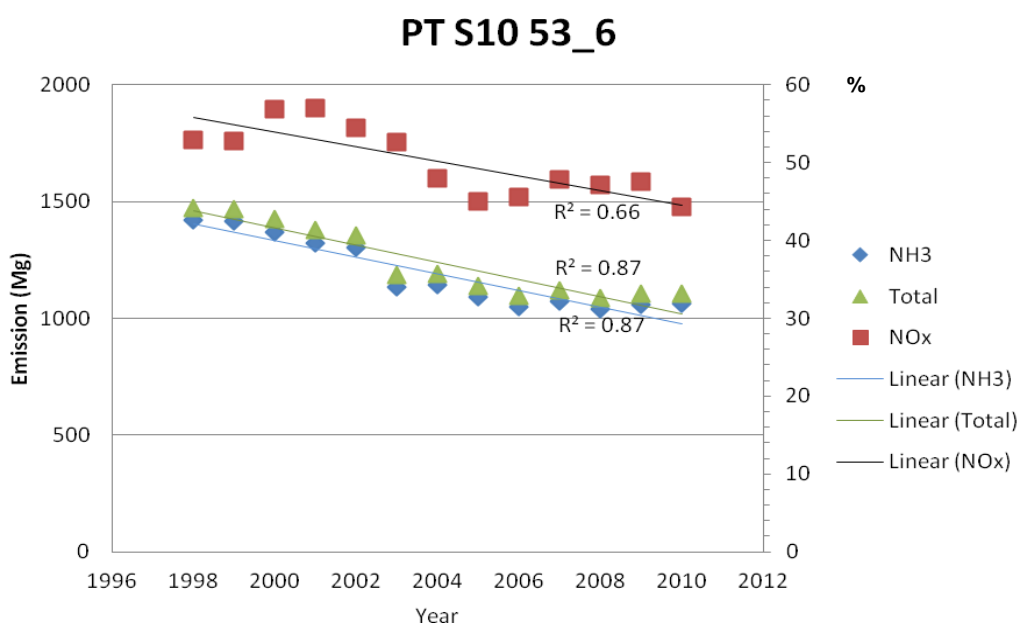
Figure 4.2 - Pollutants NH_3 and NOx (Mg) emissions evolution from 1996-2012 in the agriculture sector (S10) over EMEP grid cell 56/6 (EMEP database in: http://www.ceip.at/webdab-emission-database).

Linear regression of NH_3 and total emission are approximately 0.87 which represent good correlation between emission along the years. Decrease tendency of NOx is less representative with 0,66 of correlation but still is representative.
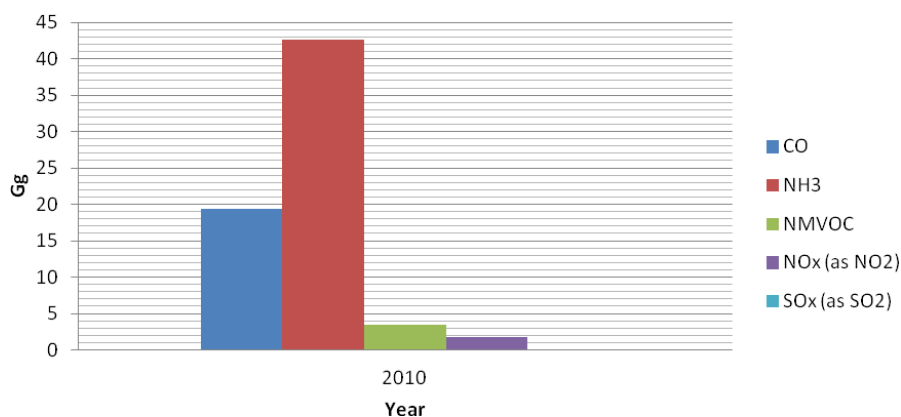
Figure 4.3 - Pollutant emissions in 2010 from S10 sector – Agriculture, for Portugal.

As may be observed in Figure 4.3, and already noted in the literature review, NH_3 is the major contributor to the agricultural sector emissions.

Standard Emissions of NH_3 provided by EMEP were applied on the CHIMERE Model. According to the Table 4.1 mean of NH_3 emission used as input of the simulation shows 16,3 g/ha.d which represents in N compounds 227,5 g/ha.d average. These are de emission values which can be compared with local field measurements, in CotArroz rice paddies.

Table 4.1 - Standard emissions of N-NH_3 of the two days, used in the simulation.

	N-NH_3 emissions
	(g/ha.d)
Day 2	227.5
Day 3	227.4
Mean	227.5

From the third report of the project PTDC/AGR-AAM/102529/2008, Carranca *et al.*, (2013), emissions of NH_3 were measured in two types of soil and the result shows a range between 0-1000 g N-NH_3/ha.d, except one day of measurement in which the peak value is approximately 8000 g N-NH_3/ha.d.

In 2010 and 2011 measurements by Figueiredo (from internal data of measured compounds by Nuno Figueiredo during two rice cycles) had taken part on field of Salvaterra de Magos rice paddies. In the first year of rice cycle, 2010, two types of soil (A and B) were considered and measurements of 3 depths: 0-20, 20-40, 40-60 cm, were taken in eight days of sampling (1-8). Vertical axis of the Figure 4.6 and Figure 4.7 represents quantity of N-NH_4^+ and N-NO_3^- and its variability among depths and 8 samples (horizontal axis).

Figure 4.4 - N-NH$_4^+$ in two different soils in 2010 (adapted from Figueiredo, 2011).

Figure 4.5 - N-NO$_3^-$ in two different soils in 2010 (adapted from Figueiredo, 2011).

There is a clear relation between N-NH$_4^+$ and N-NO$_3^-$ (mg/kg) and the three depths.

The second rice cycle was measured in 2011, two types of soil (A and B) were considered and measurements in 3 depths: 0-20, 20-40, 40-60 cm, were taken in eight days of sampling (1-8). In this year soil B was divided by three types of treatment which include: T1 – atmospheric air; T2 – CO$_2$ and temperature increasing and T3 – increase of temperature. Vertical axis of Figure 4.8 and Figure 4.7 represents quantity of N-NH$_4^+$ and N-NO$_3^-$ and its variability among depths and 8 samples (horizontal axis).
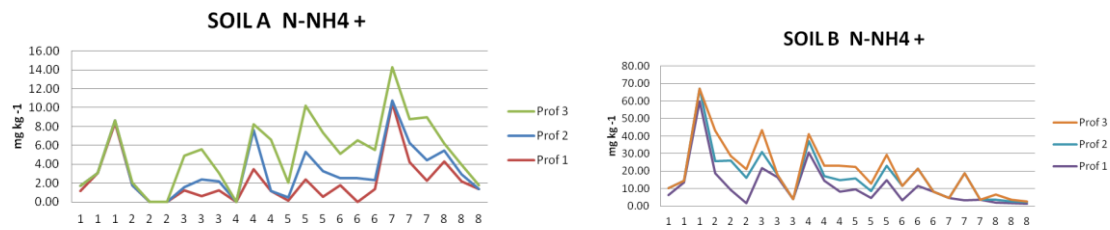

Figure 4.6 - N-NH$_4^+$ in two different soils in 2011 (adapted from Figueiredo, 2011).
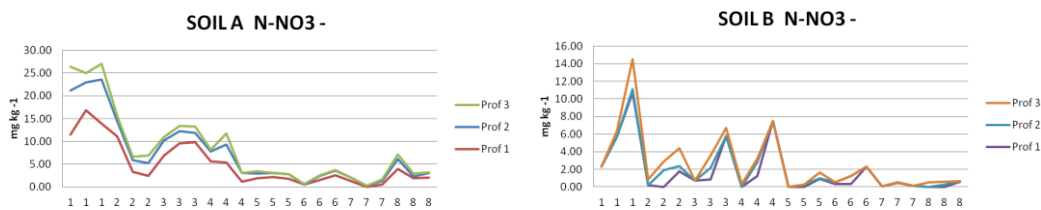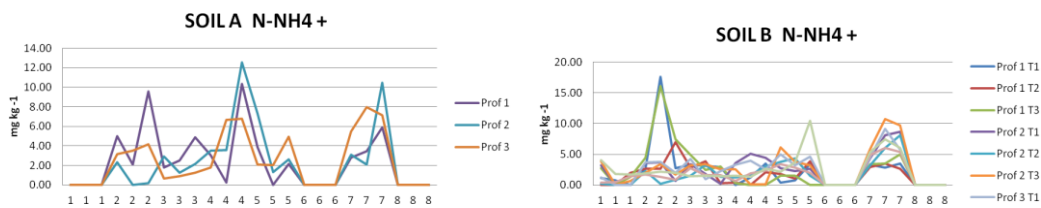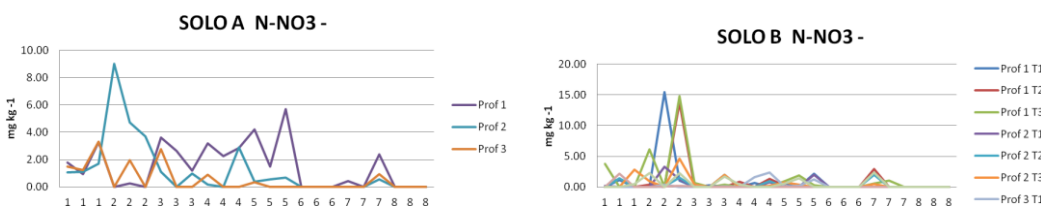

Figure 4.7 - N-NO$_3^-$ in two different soils in 2011 (adapted from Figueiredo, 2011).

It is not so clear the relationship N-NH$_4^+$ and N-NO$_3^-$ (mg/kg) and the three depths and the three considered treatments.

4.2.   TEJO AND LISBON CHIMERE MODEL RESULTS

The chemical species simulation concentration results more interesting for the present study are the ones formed due to the NH$_3$ emissions via the ISORROPIA aerosol chemical mechanism. Hence, the time evolution of NH$_3$ at gas phase, NH$_3$ at liquid phase and in the particulate matter (representing the sum of the NH$_4^+$ ion, NH$_3$ liquid and NH$_4$NO$_3$ solid, i.e. the model species pNH$_3$), were analysed. Since the ammonia reacts with nitric and sulphuric acids and HNO$_3$ is involved in photochemical reactions, it was also considered to follow the evolution of HNO$_3$ and NO$_y$ concentrations. The time series were taken in two model grid cell, which represent the modelled atmospheric chemical of two places of interest: 1) the model cell over the CotArroz field experiment and 2) Lisbon city, downwind of CotArroz in this particular model application.

The following figures compare the three simulations performed: Time series over Tejo, i.e the grid cell in the model which contains the region of the CotArroz field rice experiment, and Lisbon were simulated and analysed for HNO$_{3aq}$, HNO$_3$, NH$_{3aq}$, NH$_3$, NO$_Y$, pHNO$_3$, and pNH$_3$ compounds.
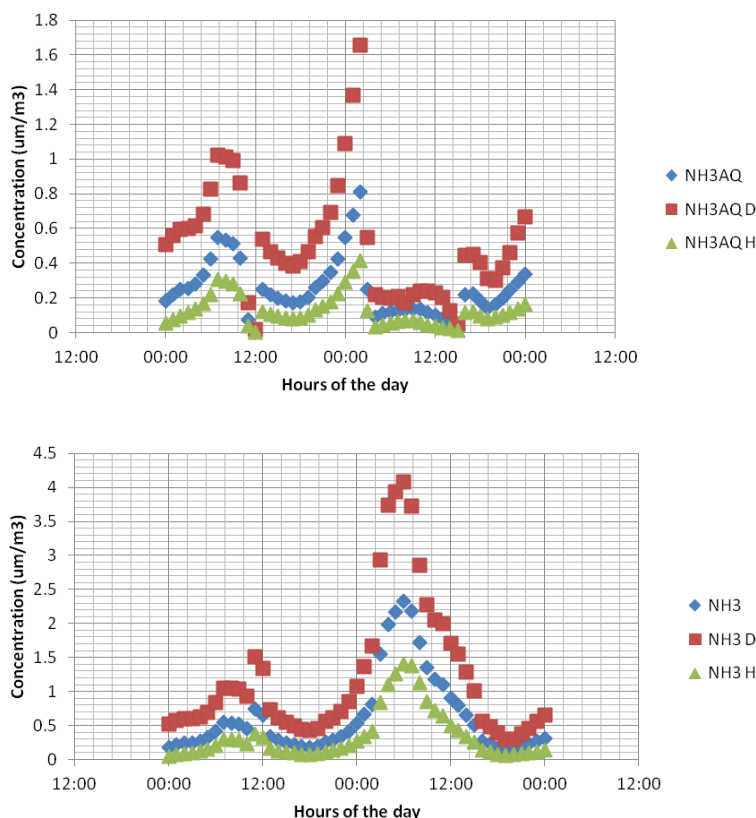

Figure 4.8 - NH$_{3aq}$ and NH$_3$ time series over Tejo.

From Figure 4.8 to Figure 4.15 the representations show concentrations in µm/m^3, of the different compounds, as y variable, and hours of the day as x variable. In what concerns days, three days were measured, starting on 12 a.m. of the first day and ending on 12 a.m. of the third day.

Representations on the following figures take in account the original concentration of each measured compound, the double emissions (D) and the reduction emissions (H) of all compounds, as referred on the § 3.3. The compound state was distinguished between aqueous (aq) and non-aqueous. In the particular case of Figure 4.8, the description presents:

NH_3 – as the [original] control run provided by EMEP 2010;
NH_3 D – as the [double] emissions were double 50%;
NH_3 H – as the [half] emissions were reduced by 50%.

In general, as reported by Hamaoui Lague *et al.*, (2012), the diurnal variations depend on meteorological conditions, especially soil temperature and wind speed. When the soil temperature increases, the dissolved ammonia present in the soil water is more effectively transferred to the gas phase.
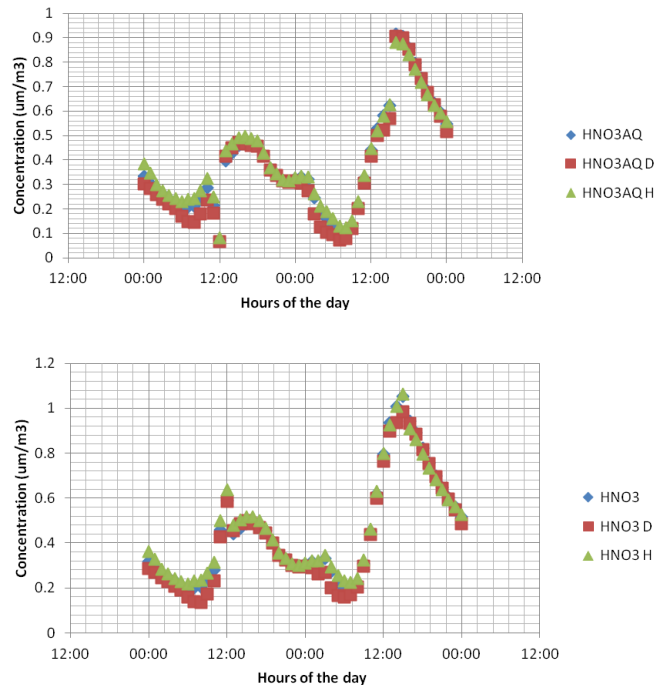
Figure 4.9 - HNO$_{3aq}$ and HNO$_3$ time series over Tejo.

This effect is observed in Figure 4.8 where the meteorological effects may be inferred. Figure 4.8 also shows that synergetic effect of doubling the ammonia emissions and the meteorology on the ammonia concentration is different in the two days presented. It must be kept in mind that the amount emitted, although varying between the three tested simulations, is nearly constant between days of simulations, for each run. Maximum values of ammonia in gas phase are found near 10 a.m. in the morning, when the atmosphere has heated near the ground. The concentration in liquid phase is determined by the gaseous concentration, by the air temperature and humidity which may explain the behaviour of the liquid ammonia.
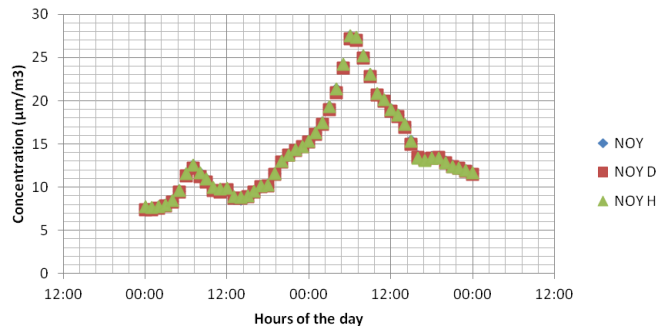
Figure 4.10 - NO_y time series over Tejo.
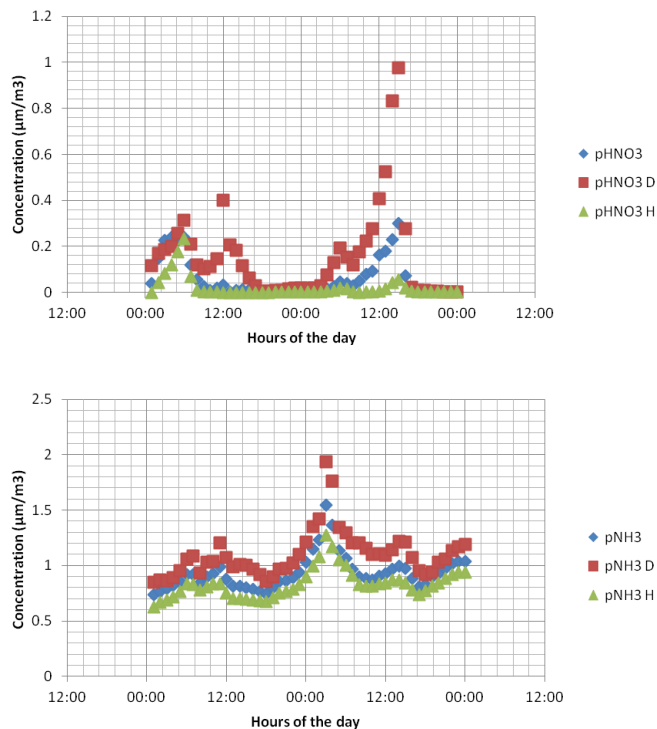
Figure 4.11 - pNO_3 and pNH_3 time series over Tejo.

In Figure 4.9, it is possible to compare HNO_3 aqueous with HNO_3 gas phase. The tendency is similar, presenting the first peak around midday of the 24th May and after midday of the 25th May. HNO_3 in the gas phase is produce by NO_x oxidation (CHIMERE, 2011), but is also consumed in photolytic reactions. It is the reason why its concentration decreases in the afternoon.

Regarding NO_y concentration (Figure 4.10), the model is not showing sensitivity this variable to the NH_3 emissions over the Tejo region. This fact may be explained by the eventual dominance of NO and NO_x to the NO_y concentration.

Figure 4.12 to Figure 4.15 show the Lisbon region time series of HNO_{3aq}, HNO_3, NH_{3aq}, NH_3, NO_Y, $pHNO_3$, and pNH_3 compounds.
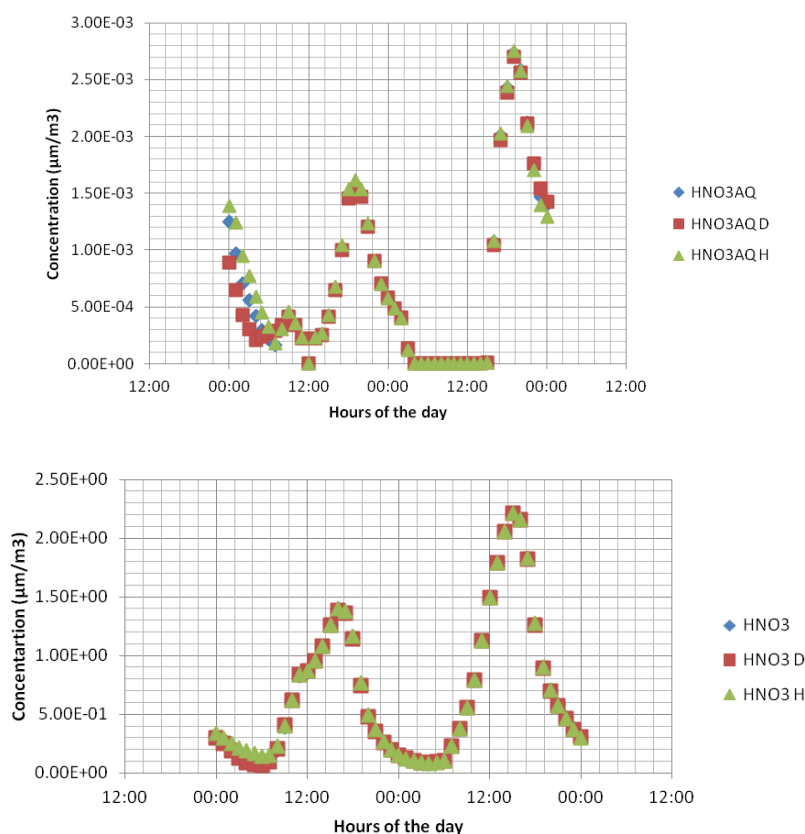
Figure 4.12 - HNO_{3aq} and HNO_3 time series over Lisbon.
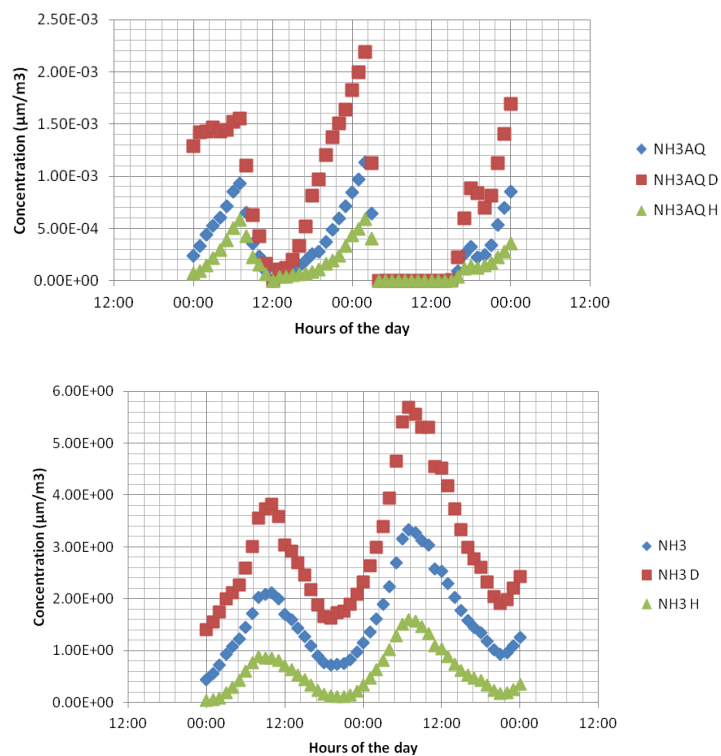
Figure 4.13 - NH_{3aq} and NH_3 time series over Lisbon.
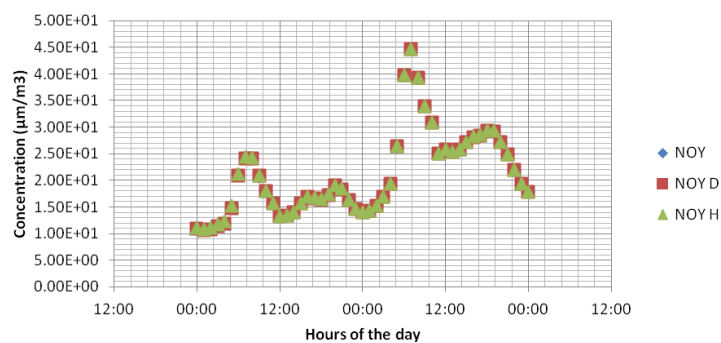
Figure 4.14 - NOy time series over Lisbon.

These figures also show that the chemical species resolved by the model which are more sensitive to the changes on NH_3 emissions from agriculture fields of Tejo, and eventually of Sado, are NH_3 in gas, liquid and in particulate matter forms, the ion nitrate in particulate matter (Figure 4.15) also varies in its concentration, particularly in the first day, although the nitrous acid show approximately the same concentration in the three simulations (Figure 4.12).
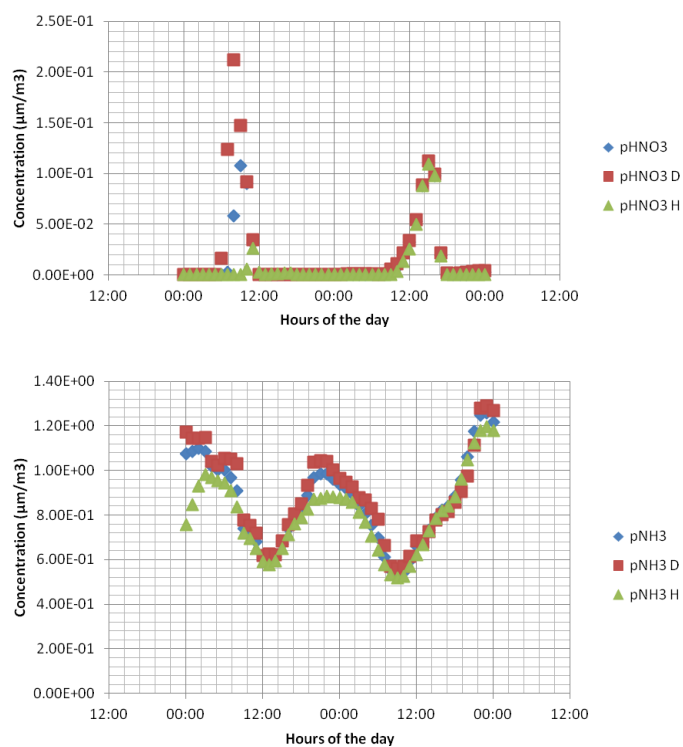
Figure 4.15 - pNO$_3$ and pNH$_3$ time series over Lisbon.

The PM$_{10}$ and PM$_{2.5}$ model sensitivity was analyzed regarding the changes made on the S10 NH$_3$ EMEP emissions. Time evolution of PM$_{10}$ associated to anthropogenic total emissions and PM$_{10}$ are depicted in Figure 4.16, for Tejo region and Lisbon. Doubling the agricultural NH$_3$ emissions has a small impact in Lisbon.

Small increases are perceived during the morning hours, around 10 a.m. Over Tejo region, the impact of changes on the emissions is more visible. However, it must be noticed that the behavior over the two locations is dependent on the meteorological conditions, which determinates the photolytic reactions, temperature and humidity for the reactions that are dependent on them, namely the partitioning of phases on the ISORROPIA aerosol module, transport and hence determines differences in the concentrations in the two days.
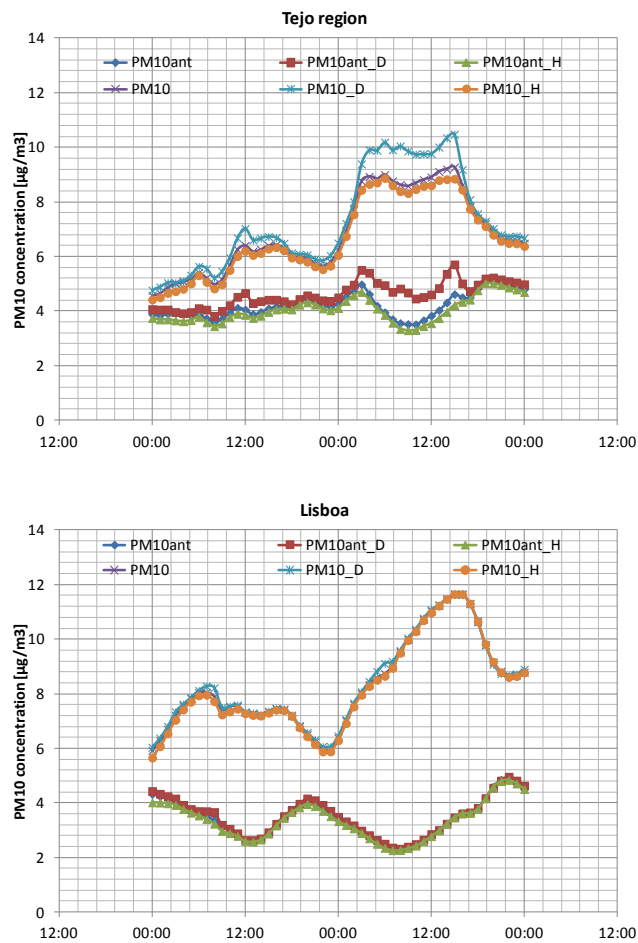
Figure 4.16 - Time evolution of CHIMERE results on PM_{10} total and PM_{10} due to anthropogenic sources over Lisbon and Tejo region.

Over both regions the model is calculating almost all the fraction of $PM_{2.5}$ as $PM_{2.5}$. The time evolution over the two sites is similar between PM_{10} and $PM_{2.5}$ (when comparing Figure 4.16 and Figure 4.17).

Interesting features from the both Figure 4.16 and Figure 4.17 is that in Lisbon higher values of the PM_{10} and $PM_{2.5}$ totals are not in phase. Total PM_{10} and $PM_{2.5}$ show daily maximum values in the morning and in the afternoon, whereas maximum values due to anthropogenic sources are seen at 10 p.m. and 11 p.m., i.e. suffers accumulation during the afternoon and are consumed during the night period.
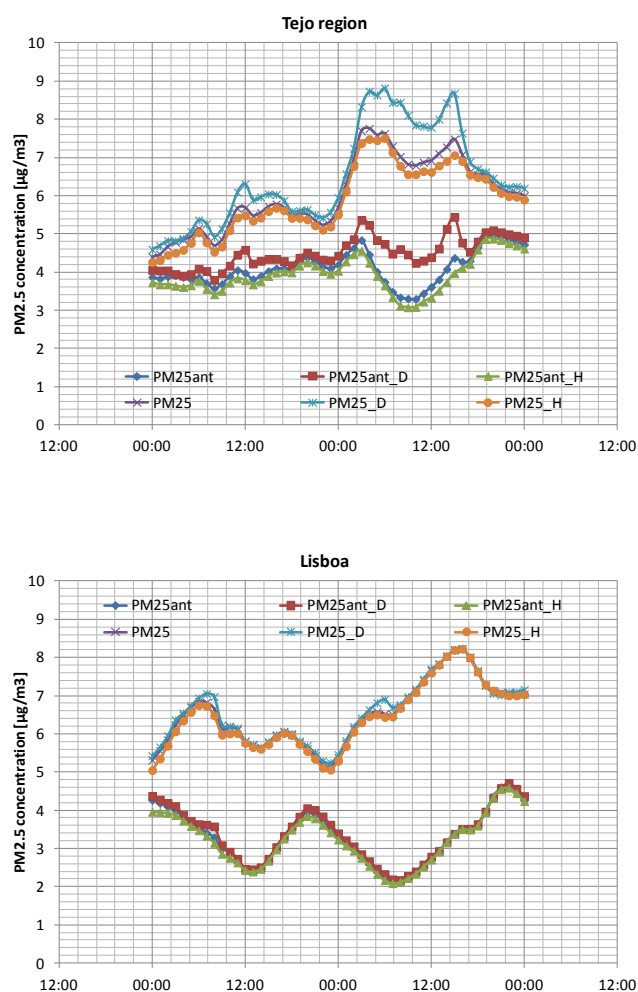
Figure 4.17 - Time evolution of CHIMERE results on PM$_{2.5}$ total and PM$_{2.5}$ due to anthropogenic sources over Lisbon and Tejo region.

The ratios between the PM$_{10}$ and PM$_{2.5}$ due to anthropogenic sources and total concentration of PM$_{10}$ and PM$_{2.5}$ were calculated in both locations. The ratio of the particulate matter from anthropogenic source varies according to the meteorological conditions and between locations. Anthropogenic contribution sources for particulate matter are less dominant on total particulate matter during the afternoon, i.e, during the period of higher insulation and higher temperatures.

The amount of the emissions to the concentration values is felt near the region where changes were introduced, over the Tejo region. In this region, as expected when the emission of NH$_3$ doubles the anthropogenic contribution is higher, observe Figure 4.18 during the second day in the early morning, noon and after noon.
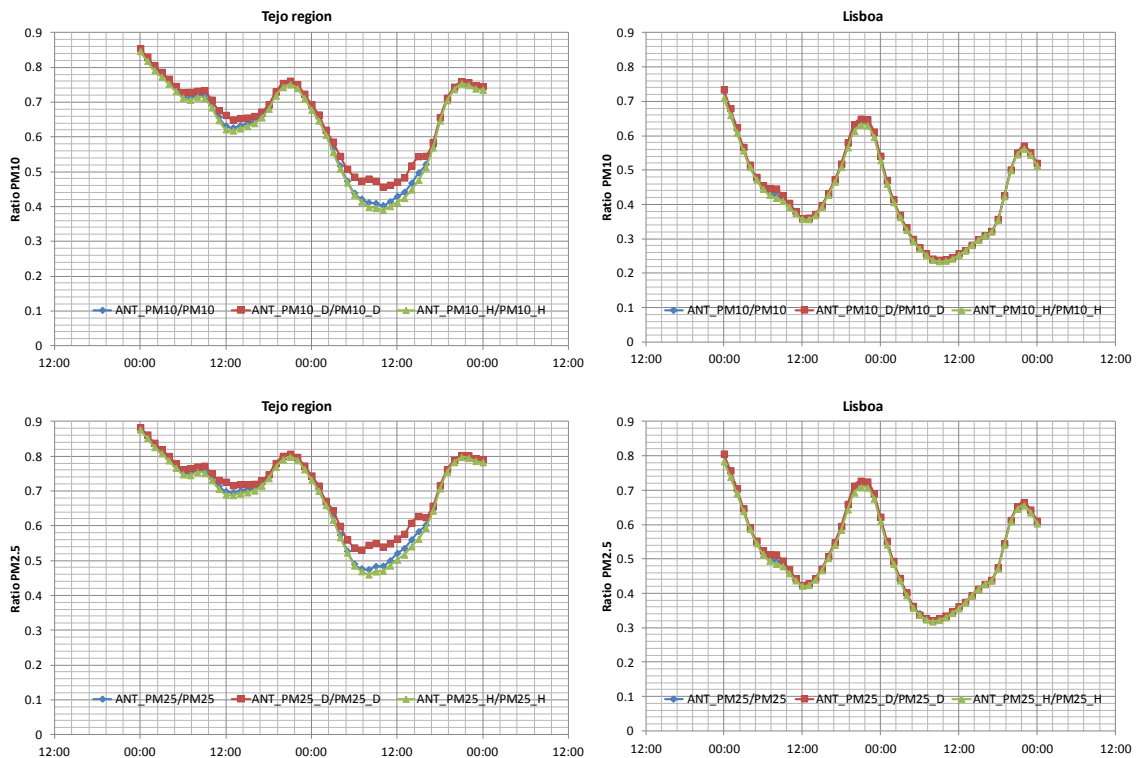
Figure 4.18 - Time evolution of CHIMERE results on the ratios of (i) anthropogenic PM_{10} to total PM_{10} concentrations over Lisbon and Tejo region (left panel) (ii) anthropogenic $PM_{2.5}$ to total $PM_{2.5}$ concentrations over Lisbon and Tejo region (right panel).

Average observed by EMEP, (2012a), of annual average of the PM_{10} concentration of all sites was 15.5 µg/m^3, which means Tejo and Lisbon is approximately 36.7 % and 36.8 % of estimated global value. The high altitude high altitude global site in Switzerland is ranging from 2.2 µg/m^3 to 30.4 µg/m^3 near the level sea in Cyprus. The average of 5.7 µg/m^3 for Tejo and Lisbon is included on this range.

In other study provided by Startelet *et al.*, (2012) different emission inventories were used in four simulations conducted over Europe. In one of them the methodology is the same of this work: anthropogenic emissions measured by EMEP database and biogenic emissions measured by MEGAN. Concentration of PM_{10} and $PM_{2.5}$ were concluded. Over Europe it shows average concentration of 23.2 µm/m^3 of PM_{10} and 13.3 µm/m^3 of $PM_{2.5}$. Comparing with our results, the variation is not so high the achieved values.

We conclude the average value achieved for the two sites – Tejo and Lisbon are lower than the average estimated for other places such as global sites over Europe, high and low altitudes sites.

4.3. AVERAGE AND SURFACE CONCENTRATION SCENARIOS

The model results sensitivity to the changes applied on the NH_3 emissions from agricultural sector were also analysed as averaged time surface concentration fields of NH_3 (both in gas and in particulate matter), PM_{10} and $PM_{2.5}$ due to anthropogenic and total sources (i.e, including also biogenic and secondary organic aerosol formation on the CHIMERE model). The average procedure excluded, as in the time series analyses, the first day of simulation, due to the cold start of the model. The averaged concentration fields were overlapped with wind field information also averaged for the same period. In this way it is possible to understand the mean transport conditions over the simulated domain, the Iberian Peninsula, both in wind speed and direction.

During this period the winds show low speed in the central part of the Iberian Peninsula, with a counter clock wise movement (see, e.g Figure 4.20). This movement brings the dry and hot air masses measured in the three meteorological stations (Figure 3.2 to Figure 3.4 for the meteorological data recorded).

It is not detected major discrepancies between the two days averages fields and the hourly fields, as an example, NH_3 (gas) and wind vectors surface fields at noon, on day 24th May are also depicted in Figure 4.19. As it may be observed the transport characteristics are the same. The first implication is that the concentration plumes are transported mainly over the sea.

Another noticeable feature that is observed in Figure 4.19, is a hot spot of higher NH_3 gas concentrations near Aveiro's region. These are also possible due to the industrial sector of Estarreja (APA, 2011), adding to the ones emitted by the agricultural sector over this region. This figure also gives the first impression on how the concentration fields changes in concentration values, according to the changes made on indicial NH_3 agricultural emissions.
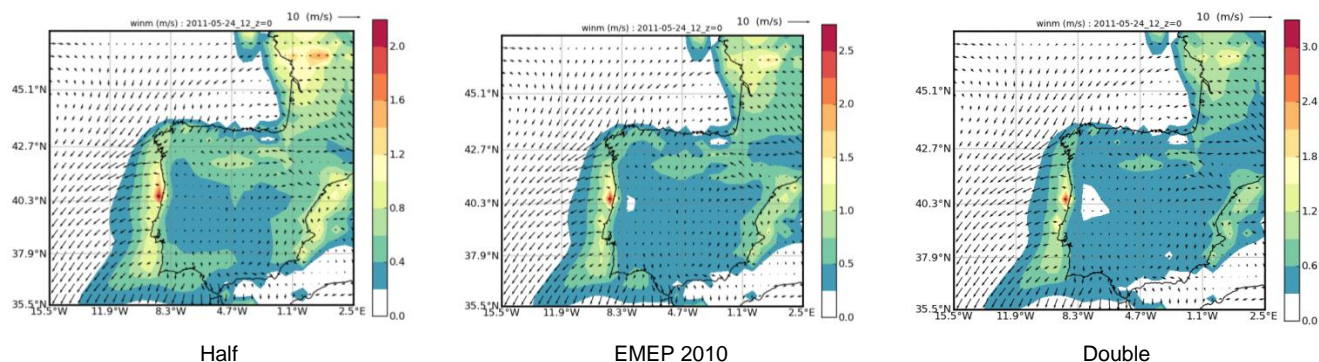

| Half | EMEP 2010 | Double |

Figure 4.19 - Surface concentration fields of NH_3 in gas phase ($\mu m/m^3$) over the Iberian Peninsula at 12H00 UTC.

Half   EMEP 2010   Double
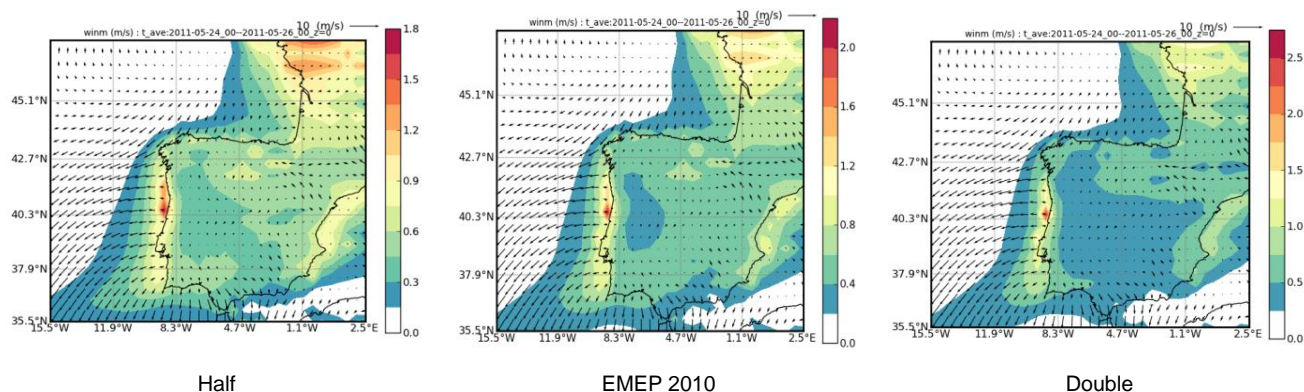
Figure 4.20 - Time average surface concentration fields of NH$_3$ in particulate matter (µm/m^3) over the Iberian Peninsula, with time average wind field overlapped.

Large values of NH$_3$ in particulate matter occur over Iberian Peninsula coast, Particularly over NW of Portugal, reflecting the NH$_3$ present in gas form as seen in Figure 4.19. It is located in Beira Litoral region and considers a large plain included in Coimbra and Figueira da Foz cities. This is the local of production of Carolin Rice of Low Mondego Valley.

The higher average values of NH$_3$ in particulate matter are between approximately 1.8 µg m^{-3} in this region for the EMEP 2010 emission inventory. Reducing or increasing the inventory by 50 % show impact on the highest concentrations simulated by the CHIMERE model in this region.

The tendency of PM$_{10}$ concentrations due to anthropogenic sources follows NH$_3$ in particulate matter which suggests the inclusion of pNH$_3$ particulate in it. In general observation by PM$_{10}$ and PM$_{10}$ Anthropogenic suggest large influence of winds from south in the case of PM$_{10}$ total so the major average occurs in south of Portugal. From that PM$_{10}$ Anthropogenic reveals not so influenced by wind factor. The exact some relation is expected to happen in the PM$_{2.5}$/ PM$_{2.5}$ Anthropogenic, and it is proved by Figure 4.22.

Particulate Matter (PM) is both a primary and a secondary air pollutant. It is released into the atmosphere directly from a specific source, secondary PM is produced in the atmosphere in the form of ammonium nitrate (NH$_4$NO$_3$) and ammonium sulfate ((NH$_4$)$_2$SO$_4$). Secondary PM is the fraction known as PM$_{2.5}$, particulate matter with aerodynamic diameter smaller than 2.5 µm or less (Beychok and Hogan, 2012; EPA, 2001a). NH$_4$NO$_3$ ammonium nitrate is limited by the availability of HNO$_3$ nitric acid and also depends on meteorological conditions, thus reducing the impact of modified NH$_3$ emissions on aerosol loads (Hamaoui-Laguel *et al.*, 2012).

Regarding the above and having the possibility to distinguished between the anthropogenic contribution and the total concentration of PM_{10} and $PM_{2.5}$, the average surface concentration fields were compared through Figure 4.16 and Figure 4.17.

Observation of anthropogenic driven average concentration fields of PM10 and $PM_{2.5}$ and the total concentration of these compounds, produced by CHIMERE, helps to understand that biogenic emissions are transported from the southern part of the domain to the Iberian Peninsula, raising the levels of particulate matter in the southern part of Portugal and Spain.

These results points to a possible Sahara dust event contribution on particulate matter that is not properly simulated by the model: this reason is that the domain is not extended to the northern part of Africa, hence the biogenic dust emissions are not calculated for the present meteorological conditions, but are considered in the boundary conditions as monthly climatologic.

The fact that the surface wind vectors are pointing to south is counteracting the influence of a larger synoptic transport, which in fact has helped to diminish the influence of the Sahara outbreak influence over the Iberian Peninsula.

Although the detected contribution of the dust to the particulate matter concentration is possible to observe, that changes on the agriculture sector emissions over the three sites (Mondego, Tejo and Sado) have an visible impact on the $PM_{2.5}$ concentration, due to the anthropogenic sources, increasing the concentration gradient from the coast to the interior part of the country (Figure 4.17). This feature is also seen on PM_{10} average concentration fields (Figure 4.16).

PM_{10} Anthropogenic represents a part of composition on particulate matter of NH_3. In the PM_{10} universe of biogenic and anthropogenic emissions, PM_{10} Anthropogenic represents a part of composition on particulate matter of the total one, which means some quantity of PM10 are provided by biogenic emissions.

As already shown in Chapter 4, the standard emissions of NH_3 provided by EMEP were applied on the CHIMERE Model. The daily emissions allocated over the CHIMERE cell, that include the CotArroz field experiment, were calculated as $N-NH_3$ (previously shown in Table 4.1).

In average the value was of 227.5 g $N-NH_3$ ha^{-1} d^{-1}. Recent results from the project "*Trace gas emissions from Portuguese irrigated rice fields in contrasting soils, by the influence of crop management, climate and increase concentration of CO$_2$ in the atmosphere*" (Carranca *et al.*, 2013) show that these values may be underestimated during the fertilization application period. They may be highly underestimated during the day of fertilizer application for

sandy loam soils, since values around 8000 g $N\text{-}NH_3$ ha^{-1} d^{-1} were measured. The impacts of this new data on NH_3 emissions on PM_{10} and $PM_{2.5}$ due to anthropogenic sources may be done in the future.
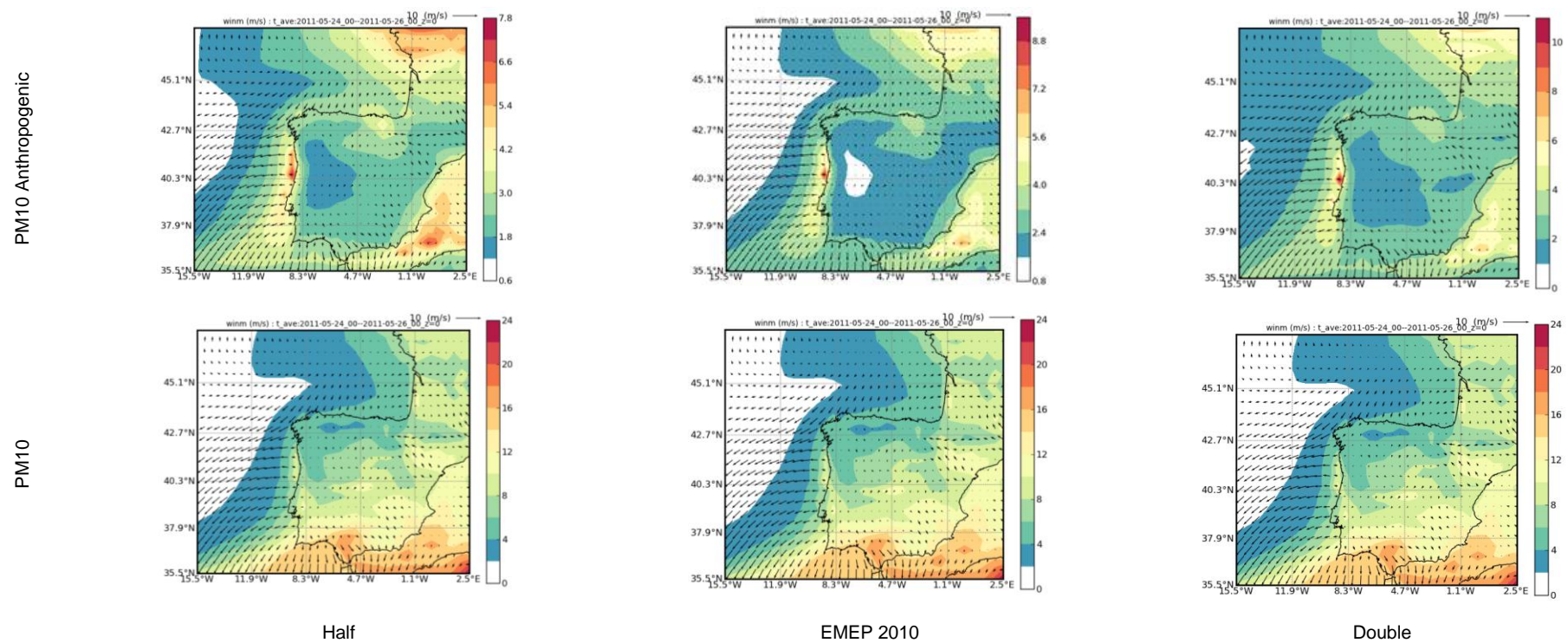
Figure 4.21 - Time average surface concentration fields of anthropogenic PM_{10} (upper line) and PM_{10} (lower line), µm/m^3, over the Iberian Peninsula, with time average wind field overlapped.
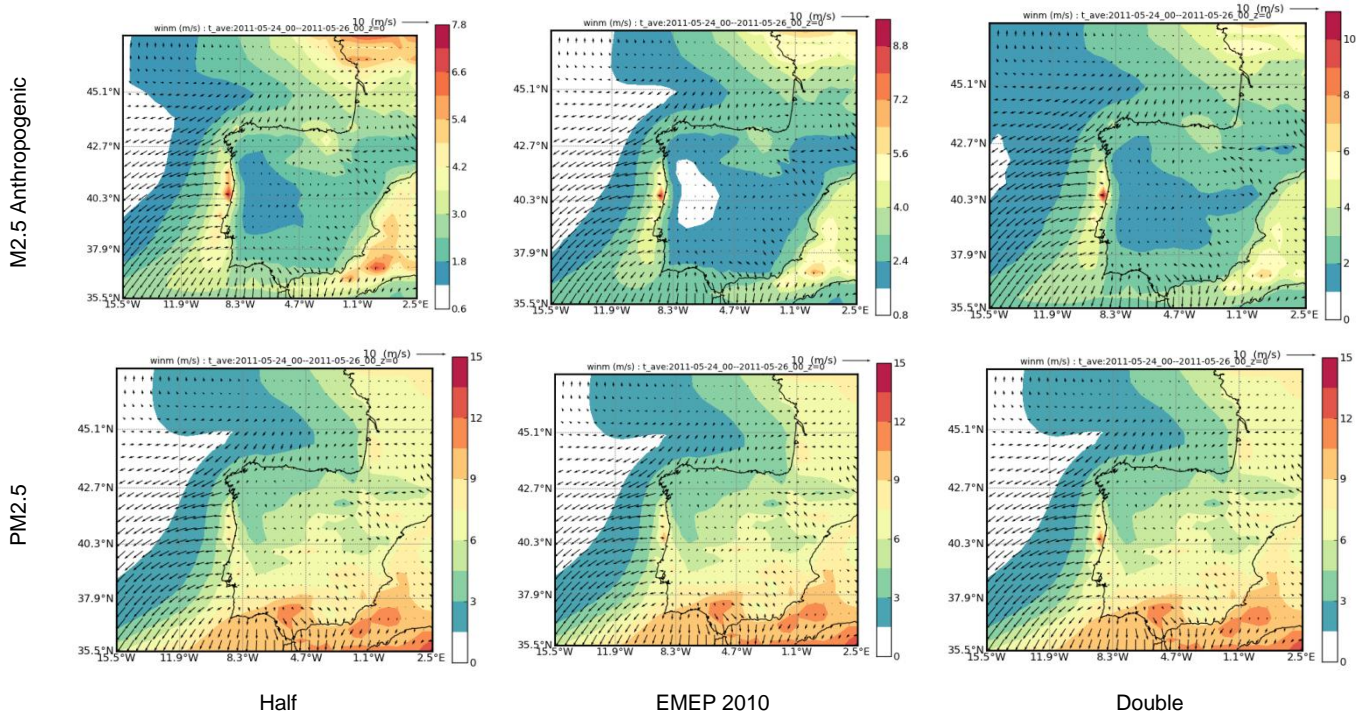
Figure 4.22 - Time average surface concentration fields of anthropogenic $PM_{2.5}$ (upper line) and $PM_{2.5}$ (lower line), $\mu m/m^3$, over the Iberian Peninsula, with time average wind field overlapped.

Gas Emissions on Rice Culture and its importance on air quality

5. CONCLUSIONS

According to this study air quality scenarios can contribute for the analyses of emission compounds and their impact on air quality. The emission inventories of the agriculture sector are less explored in what concerns land use and specific identified compounds. The relationship between agriculture emission and consequent released pollutants concentration in the air is not linear and must be explored.

In this work, the importance of the emissions of the agricultural sector used as inputs on air quality models were acknowledged, focus was given to the NH_3 emissions, classified as anthropogenic emissions by the EMEP programme.

In the present study, the regional Eulerian chemical transport CHIMERE model was used. This model is forced by global concentrations at its lateral and top boundaries, meteorological fields (including information on temperature, wind, cloudiness, radiation, relative humidity, among others), air pollutants emissions, orography, land use, with the objective to produce atmospheric concentration species. These concentrations were calculated in time updating all the variations in the above mentioned factors. Sensitivity tests to the model concentration results were done by changes on the NH_3 emissions from the agricultural sector.

The EMEP emission inventory data base was used for all the anthropogenic activity sectors classified in this programme. The EMEP emissions inventory, as a policy driven programme for international co-operation to solve transboundary air pollution problems is the reference for this study in what concerns the emission considered by CTM model. The emission data are reported by countries members on pollutants such as CO, NH_3, NMVOC, NO_X, SO_X PMcoarse and $PM_{2.5}$, from 11 activity sectors.

Due to the relevance of the NH_3 emissions factors in the present work, the annual emissions of the agriculture sector were analysed between 1998 and 2010. These emissions have decrease between 1997 and 2003, showing small variations between 2006 and 2010, around 48 Gg of NH_3 emitted at the national level.

In this work, the NH_3 EMEP emissions from agriculture sector (S10) were considered by the CHIMERE model in three modes: (i) as it is the original grid EMEP inventory (version of 2012, referring to emissions estimation of 2010); having the previous amounts as reference quantities, the following changes were performed (ii) multiplying by a factor of two the NH_3 emitted over the three main regions indentified as major rice producer in Portugal; (iii) and dividing by a factor of two the reference emitted quantities over the same regions. These regions were identified

previously trough the Corine Land cover product (version of 2006). The locations founded were the ones of irrigated rice fields in the basins of Mondego, Tejo and Sado rivers, in Continental Portugal.

The model's sensitivity to the chemical species concentrations was verified in time over two locations, near the CotArroz field experiment and over Lisbon. Based on the description of the chemical mechanism and the aerosol mode of CHIMERE model, the chemical species under analysis were NH_3 (aq), NH_3, HNO_3 (aq), HNO_3, NOy, $pHNO_3$, pNH_3, PM_{10}, PM_{10} anthropogenic, $PM_{2.5}$, $PM_{2.5}$ anthropogenic. The model result show to be more sensitive to changes in NH_3 emissions of the agriculture sector in all the phases of the NH_3 concentration, which includes the particulate matter. This is the reason why anthropogenic particulate matter, both PM_{10} and $PM_{2.5}$ are affected by changes in the considered emissions.

Based on this *a priori* knowledge time average concentration fields over the domain of simulation were compared permitting to detect that maximum and minimum values over the domain are sensitive to the emissions changes. This result is more evident over the NH_3 concentration fields and PM_{10} and $PM_{2.5}$ from anthropogenic emissions.

Collected data from field measurements of the research project "*Trace gas emissions from Portuguese irrigated rice fields in contrasting soils, by the influence of crop management, climate and increase concentration of CO$_2$ in the atmosphere*" on NH_3 emissions from rice fields were compared to the ones considered by the model. During the day of fertilization the NH_3 emissions were found to be around 8000 g N-NH_3 ha^{-1} d^{-1}, whereas the model uses the estimation of 227.5 g N-NH_3 ha^{-1} d^{-1}. According to the obtained results, these emissions estimation values suggests that during fertilization days the NH_3 volatilization may have an increase impact on the particulate matter formed in the atmosphere.

Chemical transport models, as CHIMERE, represent an important tool to achieve such relation between emissions and concentrations. It allows comparing emissions measured on field with the ones used as input of the model, from the referred inventories, permitting to evaluated and tune the diagnose and forecast of chemical species to the emissions data measured through experimental field work and correct the emissions inventories considered by the CTMs.

Future investigations:

− use of the NH_3 emission measured on field as input of a CHIMERE simulation in order to conclude if final concentration is similar with the one tested here;
− testing the 3 years of rice cycle compare if results from each year are significant.

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ANNEXES

T1 - Compounds evolution from 1998 year to 2010, in Gg, and total emissions of S10 sector (EMEP database).

Year	CO	NH$_3$	NMVOC	NOx	SOx	Total
1998	1.61	5.02	2.74	0.02	0.00	9.40
1999	1.61	5.01	2.70	0.19	0.00	9.51
2000	2.73	5.32	0.37	0.23	0.00	8.65
2001	2.76	5.14	0.37	0.23	0.00	8.50
2002	2.55	5.06	0.37	0.22	0.00	8.21
2003	2.42	4.52	0.37	0.21	0.00	7.53
2004	2.06	4.56	0.37	0.19	0.00	7.18
2005	1.83	4.37	0.35	0.18	0.00	6.73
2006	1.91	4.20	0.35	0.18	0.00	6.65
2007	2.15	4.29	0.35	0.19	0.00	6.98
2008	2.13	4.18	0.35	0.19	0.00	6.85
2009	2.21	4.25	0.35	0.19	0.00	6.99
2010	1.94	4.26	0.35	0.18	0.00	6.73

F1 - NH$_3$ emissions in 2009 by EMEP.
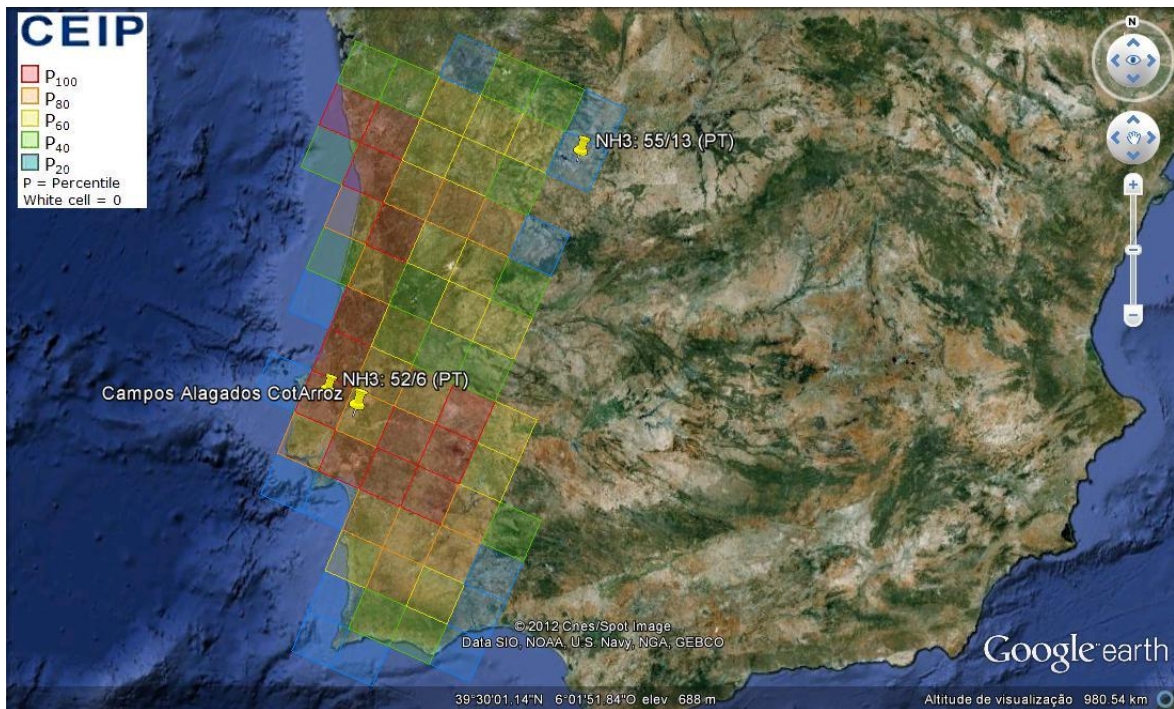
F2 - NH$_3$ emissions in 2010 by EMEP.

F3 - NOx as (NO$_2$) in 2009 by EMEP
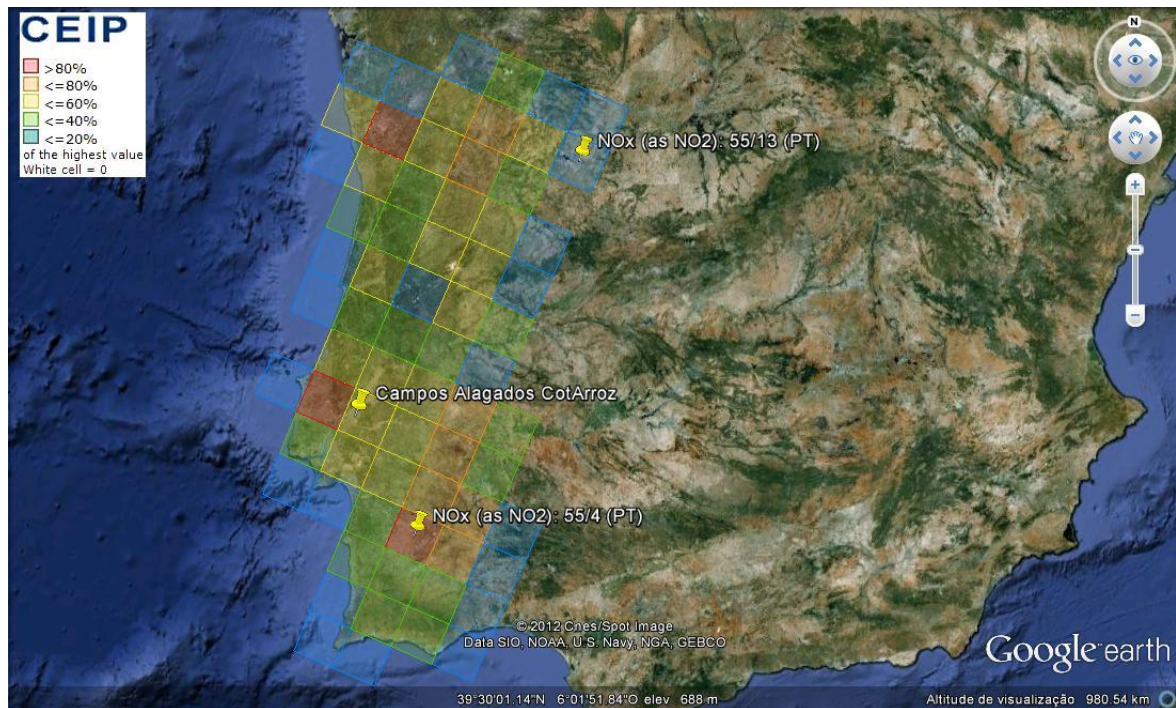
F4 - NOx as (NO$_2$) in 2010 by EMEP.