Chapter 1

GENERAL INTRODUCTION

This chapter details the framework of this dissertation. It begins with an overview of the perturbations of the nitrogen cycle, from its historical perspective to the related environmental issues. The specificities of ammonia (NH$_3$) in the atmospheric context and the limitations of the global monitoring network are then discussed. Finally, the new opportunities offered by satellite infrared measurements to monitor NH$_3$ globally are presented. In this section we put emphasis on the Infrared Atmospheric Sounding Interferometer (IASI), which is central to this research.
1.1 Background

1.1.1 Reactive nitrogen in the environment

A new era, the Anthropocene, beginning with the industrial revolution, has been designated as the period when human impacts became the main driver of global environmental changes (Crutzen 2002). In addition to carbon, the nitrogen (N) cycle, central to many biogeochemistry processes, has been heavily affected by human activities (Galloway et al., 2004). The N cycle is believed to be one of the main Earth-system processes having exceeded its planetary boundaries, along with biodiversity loss and climate change (Rockström et al., 2009). These boundaries define a rather arbitrary safe operating space for humanity and are associated with the biophysical subsystems or principal processes at play. The boundary for the N cycle was defined in terms of the gaseous nitrogen fixation for human use and set to 35 Tg N per year, while the current value is largely above, around 120 Tg of N yr\(^{-1}\) (Rockström et al., 2009).

Nitrogen fixation converts nonreactive N (N\(_2\)) into a reactive form (Nr, e.g. ammonia (NH\(_3\)), nitrogen oxides (NO\(_x\) = NO + NO\(_2\)), nitrous oxide (N\(_2\)O)). Before the industrial revolution, biological nitrogen fixation and lightning were essential to life by being the only processes able to break N\(_2\) molecules. Nowadays, anthropogenic fixation of N is estimated at 210 Tg N yr\(^{-1}\), larger than the 203 Tg N yr\(^{-1}\) fixed naturally by ecosystems and has resulted in the doubling of the reactive nitrogen forms in ecosystems throughout the last century (Fowler et al., 2013). This drastic increase, in comparison with preindustrial budgets, arises from the intensification of food and energy production to sustain the world’s population (Galloway et al., 2004). While Nr creation from energy production is mainly unintentional, nutrient availability is needed to raise crops and animals to feed mankind. A key change occurred therefore in the beginning of twentieth century, when the Haber-Bosch process was discovered, allowing the industrial production of Nr from atmospheric nonreactive N\(_2\). It is estimated that around half of the actual world’s human population depends for its food on the use of nitrogen fertilizers from this industrial process (Erisman et al., 2008).

The production of reactive nitrogen has also two serious drawbacks. Firstly, nitrogen explosives are thought to be responsible for 100-150 millions deaths throughout the twentieth century (Erisman et al., 2008). Secondly, due to the very low efficiency of nutrient use, a large part of the production is lost in the environment, causing large adverse environmental and societal impacts (Galloway et al., 2008, Sutton et al., 2013a). An example, Galloway et al. (2008) have estimated that while the world population has increased by 78% since 1970, the increase of Nr creation was 120%. Overall and considering the full chain, 80% of N consumed is lost in the environment (Sutton et al., 2013a). The principal effects on human health, ecosystems services, biodiversity and climate change are the following (Erisman et al., 2013):

- **Air quality.** NO\(_x\) and NH\(_3\) have direct impacts on human health when they are inhaled at very high concentrations (asthma, respiratory disorder, cancers, etc.) but the major air quality concern is indirect through the formation of particulate matter (PM). For instance in Europe, airborne particles are reducing six months of the life expectancy of at least half of the people (Sutton et al., 2011). NO\(_2\) is also responsible for increased tropospheric ozone (O\(_3\)), which affects human health through inhalation and which also reduces agriculture yields.

- **Water bodies.** Excess nitrogen in coastal water bodies results in eutrophication and related algal blooms causing dead zones and reducing biodiversity (Paerl et al., 2014). Furthermore, in Europe, it has been demonstrated that 80% of the fresh water contains more than 1.5 mg N per liter, which is the estimated tipping point for high risk to biodiversity (Sutton et al., 2011). Excess N in drinking water also poses risks to human health. Lastly, due to the decline of sulfur emissions in Europe and United-States, Nr is now the major component of atmospheric acidic deposition on aquatic ecosystems.

- **Terrestrial ecosystems.** NH\(_3\), NO\(_x\) and NH\(_4^+\) are phytotoxic and cause direct local damage to plants at local scale. High Nr deposition has also important consequences at landscape to global scale such as
reduced biodiversity and terrestrial ecosystems acidification and eutrophication (Erisman et al., 2007; EEA: European Environment Agency, 2014a).

• Climate change. The N cycle perturbation results in several indirect (e.g., PM and O₃ formation, interactions C-N cycles) warming and cooling effects, which are difficult to quantify. Current estimates tend to favor a small net cooling effect (Erisman et al., 2011). Although warming and cooling interactions between N and climate are complex, it is widely accepted that the environmental regulations on the Nr budgets should be considered for their impacts on the future climate.

Figure 1.1: Illustration of multiple pathways that a reactive atom of N can have in various compartments of the environment, once converted from its nonreactive form into Nr (from UNEP and WHRC (2007), adapted from Galloway et al. (2003)). Red dots indicate the potentialities of denitrification.

All these impacts are magnified by the fact that one single Nr atom can cycle in various forms within the ecosystems, and cause a sequence of impacts; this is known as the “Nitrogen Cascade” (Galloway et al., 2003). It results from the fact that Nr are easily transported among atmospheric, terrestrial and aquatic compartments of the environment (UNEP and WHRC, 2007). Figure 1.1 shows examples of sequential effects that a Nr atom can have while moving along its biogeochemical pathway. The only way to interrupt the cascade is converting Nr back to N₂ through denitrification (red dots in Figure 1.1) or storing it in a stable reservoir.
1.1.2 \( \text{NH}_3 \) in the atmosphere

It is commonly acknowledged that major uncertainties in the nitrogen cycles and fluxes are related to reduced nitrogen and in particular \( \text{NH}_3 \) (e.g., Erisman et al. (2007); Sutton et al. (2008, 2011); van Vuuren et al. (2011); Fowler et al. (2013)). Globally, \( \text{NH}_3 \) represents more than half of the Nr atmospheric emission (Galloway et al., 2004) and is mainly emitted by agricultural activities and biomass burning (EDGAR-Emission Database for Global Atmospheric Research, 2011). Figure 1.2 depicts the distribution of these emissions at global scale for the year 2008, pointing to Europe and Asia as main contributors, following the EDGAR v4.2 inventory.

\[ \text{Figure 1.2: } \text{NH}_3 \text{ emissions distribution (tons } \text{NH}_3 \text{ per } 0.1^\circ \times 0.1^\circ \text{ cell per year) for 2008; from EDGAR-Emission Database for Global Atmospheric Research (2011).} \]

Sutton et al. (2013b) have proposed a comprehensive estimate of all atmospheric emission sources of \( \text{NH}_3 \) for the same year, which is presented in Figure 1.3: from the total of 65.4 Tg N released in the atmosphere, 37 Tg N yr\(^{-1}\) is directly from agriculture (livestock and crops) while 8.6 Tg N yr\(^{-1}\) are emitted by oceans (and volcanoes). Biomass burning contributes for 5.5 Tg N yr\(^{-1}\). It is worth noting that these numbers are associated with uncertainties of at least \( \pm 30\% \) (Sutton et al., 2013b). Furthermore, as the amount of \( \text{NH}_3 \) lost in the atmosphere is highly dependent on environmental conditions and agricultural practices, the relative contribution of each source shows large variations at national/regional scale (Reis et al., 2009). For instance in Europe, 93.7% of total emission were attributed to the agricultural sector in 2011 (EEA-European Environment Agency, 2014b). In contrast, biomass burning contributes much more in Africa (44%) and South America (22%) (Behera et al., 2013). Locally, other sources such as traffic and/or industry can be significant (Gong et al., 2011).

\( \text{NH}_3 \) is the major atmospheric basic component and is therefore highly reactive. It rapidly neutralizes acid components such as sulfur dioxide (SO\(_2\)) or sulfuric, nitric and hydrochloric acids (respectively H\(_2\)SO\(_4\), HNO\(_3\) and HCl) to form aerosols but can also attach to existing particles (Hertel et al., 2012). \( \text{NH}_3 \) deposition (wet and dry) on terrestrial and aquatic ecosystems is also an important sink, which acts close to the sources (Hertel et al., 2012). The high reactivity and deposition rates explain the relatively short lifetime of \( \text{NH}_3 \) in the atmosphere, from a few hours to a few days (Dentener and Crutzen, 1994). Baek and Aneja (2004) report a lifetime of 0.5 to 5 days. If \( \text{NH}_3 \) is not deposited or scavenged by rain, it is converted to particulate \( \text{NH}_4^+ \), which has a longer lifetime of 5 to 10 days (Baek and Aneja, 2004). In this form, it is therefore available for longer range transport than \( \text{NH}_3 \).

Measuring gaseous \( \text{NH}_3 \) in the atmosphere is challenging due to three main reasons: (1) the high spatial and temporal variability of ambient concentrations, (2) the quick conversion from one phase to another (gas/particulate/liquid), (3) the stickiness to some observational instruments (Sutton et al., 2008; von Bobrutzki et al., 2010). The \( \text{NH}_3 \) monitoring networks at the surface are sparse and very few stations provide observations at
high temporal sampling (in fact most measurements are performed using passive sampler or denuder systems with a time resolution of several weeks). Some countries such as the Netherlands, the United States and the United Kingdom are providing long-term data sets across a large area. As far as we are aware of, only the Netherlands National Air Quality Monitoring Network (LML for “Landelijk Meetnet Luchtkwaliteit”) is providing long term observations at an hourly resolution. The available data sets for atmospheric NH$_3$ are thus strongly heterogeneous spatially, with in particular a large underrepresentation of tropical agroecosystems and more generally the Southern Hemisphere (Bouwman et al., 2002). The only network providing observations in this part of the world is the IGAC/DEBITS/AFRICA (IDAF) network (see idaf.sedoo.fr). Airborne measurements have recently started to become available (e.g., Nowak et al., 2010; Leen et al., 2013), complementing the surface measurements and providing useful information on the vertical distribution of NH$_3$. A few ship campaigns have been conducted and measured NH$_3$ over oceans (e.g., Norman and Leck, 2005; Sharma et al., 2012). Similarly, on-road measurements are being developed to measure at landscape scale (Sun et al., 2014). Lastly, NH$_3$ retrieved columns from ground-based Fourier-Transform InfraRed (FTIR) spectra are becoming available (e.g., Vigouroux et al., 2013).

The scarcity of measurements and poor temporal sampling of measuring devices is of special importance considering the large variability in time and space of NH$_3$. As its emissions are highly dependent on local environmental conditions as well as specific agricultural practices, this results in poorly known emission estimates, which are a crucial input for Chemistry-Transport Models (CTMs) (Dentener et al., 2006; Simpson et al., 2011; Fowler et al., 2013). Especially the emission seasonality at various scales is not well characterized (Gilliland et al., 2003). While the bottom-up approach, consisting of calculating nitrogen emissions using detailed data for livestock operations and mineral fertilizer use, is consistent at national to regional scale, it suffers from a lack of information on local environmental conditions and agricultural practices when it is applied at global scale in addition to not be coupled to climate (Sutton et al., 2013b). The top-down approach relies on the inversion of atmospheric observations to derive emissions. It has shown its capacity to provide constraints to emission timing and distributions at larger scale (Gilliland et al., 2006; Paulot et al., 2014) but suffers from measurement availability at global scale. Improvements of local to regional NH$_3$ modeling has recently been achieved because of progress in instrumentations, flux measurements and understanding of processes such as the bi-directional exchange of NH$_3$ between surfaces and the atmosphere (Flechard et al., 2013; Wichink Kruit et al., 2012a). Hybrid
and process-based approaches (Hamaoui-Laguel et al., 2014) include a better parameterization of the temporal evolution in emissions but are not yet applicable at global scale.

Overall, these limitations of the global monitoring network in place for NH\textsubscript{3} prevent on one hand the accurate determination of emission magnitude and distribution, which are needed to define and control national-scale policy requirements (Sutton et al., 2013b), and on the other hand efficient CTMs simulations and in particular air quality model predictions (Gilliland et al., 2003, 2006; Heald et al., 2012). The recent application of infrared satellite instruments to probe atmospheric NH\textsubscript{3} quasi-globally has opened unexpected perspectives to evaluate model outputs, to improve emission patterns using top-down approaches and to monitor the response of nitrogen on climate change (Skjøth and Geels, 2013; Sutton et al., 2013b).

1.1.3 Satellite remote sensing of NH\textsubscript{3}

Several recent publications report on the measurements of NH\textsubscript{3} using high-spectral resolution observations of infrared satellite sounders (Beer et al., 2008; Coheur et al., 2009; Clarisse et al., 2009, 2010; Shephard et al., 2011). Among the hyperspectral sounders in operation, those on meteorological platforms are providing global observations at a relatively high spatial and temporal resolution (Hilton et al., 2012). More specifically, the Infrared Atmospheric Sounding Interferometer (IASI), aboard the European MetOp polar orbiting satellites, offers the potential to provide distributions of tropospheric pollutants globally twice a day (Clerbaux et al., 2009). These capabilities stem from its scanning mode and spectral performances. In this work we focus on IASI/MetOp-A observations, consisting of NH\textsubscript{3} measurements from November 2007 up to now. Additionally, MetOp-B was successfully launched in 2012, with NH\textsubscript{3} concentrations (vertically integrated) already retrieved since March 2013. MetOp-C is planned for 2017, which means that altogether the three copies of IASI instruments aboard MetOp-A, -B and -C will provide at least 15 years of consistent measurements.

The first detection of NH\textsubscript{3} in the IASI spectra was made in the plume of a large but local fire event (Coheur et al., 2009). Shortly after, the first global distributions were obtained with IASI measurements integrated over one year (Clarisse et al., 2009). In that pioneering study, the comparison of the satellite distribution (column abundance, mg/m\textsuperscript{2} or molec/cm\textsuperscript{2}) with model simulations from the Tracer Model 5 (TM5) suggested an overestimate of NH\textsubscript{3} emissions in several regions and in particular in Central Asia. These first satellite-derived distributions were based on a simplified retrieval approach to derive the concentrations, looking at only one spectral feature of NH\textsubscript{3} using brightness temperature differences and relying on a single conversion factor of the signal to total columns (Clarisse et al., 2009). A better understanding of the sensitivity of infrared sounders to NH\textsubscript{3} was obtained in a later study by applying full radiative transfer models and inverse schemes on IASI and Tropospheric Emission Spectrometer (TES) spectra to retrieve vertical NH\textsubscript{3} profiles over California (Clarisse et al., 2010). Clarisse et al. (2010) have in particular clearly shown the dependency of the retrieval to thermal contrast, defined as the difference between the Earth’s surface temperature and the air temperature close to the surface. Using TES observations and GEOS-Chem model simulations, Shephard et al. (2011) have performed the first preliminary analyzes of the seasonality at global scale. Despite serious limitations due to the lower spatial coverage of TES (no scanning mode) for analyzing the temporality in NH\textsubscript{3}, this study highlighted underestimated modeled columns.

The TES retrieved NH\textsubscript{3} columns are based on the optimal estimation method for solving the inverse problem. The same approach is applicable to IASI spectra but is difficult to set up because of the large variability of NH\textsubscript{3} around a mean profile. Using vertical profiles retrieved in this way, furthermore revealed in particular difficulties with the averaging kernels (see Heald et al., 2012). With the goal of fully exploiting the hyperspectral character of IASI, Walker et al. (2011) have developed an alternative approach for detection only (generalized optimal estimation method) which showed, using a broader spectral range (800-1000 cm\textsuperscript{-1}), largely enhanced sensitivity to NH\textsubscript{3}. Our work is based on the expansion of this approach and uses an even larger spectral range between 800 and 1200 cm\textsuperscript{-1}, including the entire \(\nu_2\) vibrational band of NH\textsubscript{3}. As an illustration, Figure 1.4 shows NH\textsubscript{3} measurements from IASI/MetOp-A (morning overpass) over Europe and Western Russia on 4 August 2010, with an image from the Moderate Resolution Imaging Spectroradiometer (MODIS) as background.
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Figure 1.4: Four overpasses of IASI cloud-free observations over Europe and Western Russia on 4 August 2010 (background image is from the MODIS instrument the same day. The large swath observed allows to provide bi-daily quasi-global coverage. The color scale corresponds to NH$_3$ total columns (mg/m$^2$); the large values observed in Western Russia are due to biomass burning around Moscow (see further and R'Honi et al. (2013)). Variations in footprint on ground are identifiable, ranging from 113 km$^2$ to 613 km$^2$.

1.2 Aim and outline

The aim of this thesis is to assess distributions and variability in time and space of NH$_3$ using satellite data to improve our understanding of its contribution to the global N cycle and its related effects. Central in this work is the improved retrieval method for NH$_3$ applied on IASI spectra, from the development of this retrieval scheme to data comparisons and interpretations of local to global distributions and time series. The next four chapters are based on four separate peer-reviewed publications. Even though an effort was made to present them in a logical order, some concepts and introduction materials are repeated from chapter to chapter. Chapter 2 presents the IASI retrieval scheme and performance, in comparison with other methods. First multiple-years daytime and nighttime distributions are also discussed. Chapter 3 provides a first joint assessment of the IASI satellite measurements and of the LOTOS-EUROS regional model simulations. The analyses are made from four years of measured and modeled NH$_3$ distributions above Europe. A first attempt to validate the NH$_3$ retrieved columns and the difficulties associated with such an exercise in view of the NH$_3$ variability is presented in Chapter 4. Chapter 5 investigates the NH$_3$ seasonality and inter-annual variability worldwide using six full years of NH$_3$ retrievals, linking them with source processes. Concluding remarks, ongoing activities and perspectives for future work are presented in Chapter 6.
1.3 Data availability

Observations of NH$_3$ from IASI/MetOp-A and -B are available on request at ULB. The morning and evening daily observations from IASI/MetOp-A for the year 2011 are also available in the IASI section of Ether website (pole-ether.fr, open access after registration). Other years and IASI/MetOp-B will be accessible through Ether in a near future. Figure 1.5 show an example of the daily “quicklooks” for the 15 June 2011.

![Figure 1.5: 15 June 2011 daily “quicklooks” of NH$_3$ total columns for the morning and evening overpasses of IASI/MetOp-A available on Ether website (pole-ether.fr).]