

# Remote sensing of atmospheric boundary layer composition using infrared satellite observations

Thèse présentée en vue de l'obtention du grade de Docteur en Sciences

## Sophie Bauduin



Promoteur Professeur Pierre-François Coheur

Service Service de Chimie quantique et Photophysique (CQP) Années académiques 2012 - 2016

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"Personne ne sait comment sont exactement les choses quand on ne les regarde pas." Hubert Reeves

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#### Abstract

Measuring the composition of the planetary boundary layer is essential for monitoring pollutants and for understanding their impact on environment and health. Nadir satellite remote sensing is particularly appealing to sound this part of the atmosphere, but is however challenging because pollutants concentrations are generally weak and confined in a small part of the atmospheric column. Among the sounders currently in orbit, those operating in the thermal infrared have usually their maximum sensitivity in the mid-troposphere, and are thought to be inadequate to measure the near-surface atmospheric composition. Their sensitivity to this part of the atmosphere is indeed generally limited by low temperature contrast (called thermal contrast) between the ground and the air above it. Shortly before the beginning of this PhD, this has however been challenged with different studies, which have shown the possibility to measure air pollution with thermal infrared sounders in case of high thermal contrast conditions. This was especially demonstrated with the measurement of ammonia global distribution using the Infrared Atmospheric Sounding Interferometer (IASI).

This work aims at fully exploring the capabilities of thermal infrared sounders to sound the nearsurface atmospheric composition. It mainly focuses on the observations of the IASI instrument, and addresses the following questions: where and when is IASI sensitive to the near-surface atmosphere? How large and how variable is the sensitivity to near-surface pollutants? What are the parameters that drive this variability? The answers to these questions are looked at for two pollutants: sulphur dioxide (SO<sub>2</sub>) and carbon monoxide (CO), and are obtained through a series of different analyses.

 $SO_2$  is the first constituent on which this work focuses. The retrieval of its near-surface concentration is first of all attempted in an area surrounding the industrial area of Norilsk. This region, well-known for the extraction of heavy metals and its extremely high levels of pollution, encounters large temperature inversions in winter, which trap  $SO_2$  close to the ground. By exploiting these (corresponding to high negative thermal contrast), we show that it is possible to retrieve the surface  $SO_2$  concentrations in the region. This is done using a simplified version of the optimal estimation method, based on the use of a total measurement error covariance matrix. Further, we show that the surface  $SO_2$  concentration retrieval using the  $\nu_3$  band is limited, in addition to thermal contrast, by the strong water (H<sub>2</sub>O) absorption, which renders the lowest atmosphere opaque in this spectral range in case of large humidity. Two conditions are therefore shown to be required to monitor near-surface  $SO_2$  in the  $\nu_3$  band: large thermal contrast and low surface humidity.

These findings are confirmed with the retrieval of SO<sub>2</sub> at global scale, performed using a newly developed retrieval scheme based on the conversion of radiance indexes into SO<sub>2</sub> columns using look-up-tables. It is composed of two successive steps: 1) the determination of the altitude of SO<sub>2</sub> and the selection of low plumes (below 4 km), 2) for the selected observations, the conversion of radiance indexes into integrated SO<sub>2</sub> 0–4 km columns. The distributions and time series so obtained are used to better characterise the variability of IASI sensitivity to surface SO<sub>2</sub> in the  $\nu_3$  band at the global scale, and more particularly, in terms of thermal contrast strength and total column of H<sub>2</sub>O.

The characterisation of IASI sensitivity to CO is realised in a second part of the work. Radiative transfer simulations are conducted first to determine the possibility to detect enhancement in CO near-surface concentrations with IASI. The framework of the optimal estimation is then used to investigate the capability of IASI to decorrelate, as a function of thermal contrast, the CO concentration in the low troposphere from that in the high troposphere. Finally, comparisons of IASI CO observations with co-located aircraft and ground-based measurements are shown to confirm with real data how IASI sensitivity to near-surface CO varies in terms of thermal contrast conditions, and to which extent it allows determining the CO abundance in case of high pollution.

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# List of acronyms

ACE-FTS	Atmospheric Chemistry Experiment-Fourier Transform			
	Spectrometer			
AIRS	Atmospheric Infrared Sounder			
$\mathbf{AMF}$	Air Mass Factor 114			
AVK	Averaging Kernel			
BIRA	Belgian Institute for Space Aeronomy			
$\operatorname{BT}$	Brightness Temperature			
BTD	Brightness Temperature Difference			
CNES	Centre National d'Études Spatiales			
DOAS	Differential Optical Absorption Spectroscopy			
DOFS	Degree Of Freedom for Signal			
$\mathrm{DU}$	Dobson Unit			
$\mathbf{EEA}$	European Environment Agency 16			
EUMETSAT	European Organisation for the Exploitation of Meteorolog-			
	ical Satellites			
FORLI	Fast Optimal Retrievals on Layers for IASI			
FWHM	Full Width at Half Maximum65			
GEO	Geostationary Orbit			
GOME	Global Ozone Monitoring Experiment			
HRI	Hyperspectral Range Index			
HWHM	Half Width at Half Maximum			
IASI	Infrared Atmospheric Sounding Interferometer			
ILS	Instrumental Line Shape			
LEO	Low Earth Orbit			
$\mathbf{LTE}$	Local Thermodynamic Equilibrium			
$\mathbf{LUT}$	Look-Up-Table			
MAP	Maximum A Posteriori			
MOPITT	Measurements Of Pollution In The Troposphere			
MOZAIC	Measurement of Ozone, water vapour, carbon monoxide			
	and nitrogen oxides by Airbus Inservice Aircraft 139			
NASA	National Aeronautics and Space Administration			
OEM	Optimal Estimation Method			
OMI	Ozone Monitoring Instrument			
PBL	Planetary Boundary Layer 18			
PDF	Probability Density Function			
PPF	Product Processing Facility			
RAMA	Red Automática de Monitoreo Atmosférico 144			
RMS	Root Mean Square			
SCD	Slant Column Density			
TES	Tropospheric Emission Spectrometer			
TC	Thermal Contrast			
TIR	Thermal Infrared			
TOA	Top Of the Atmosphere40			
UV	Ultraviolet			
VCD	Vertical Column Density			
$\mathbf{VMR}$	Volume Mixing Ratio9			
VOC	Volatile Organic Compound 17			

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#### GENERAL INTRODUCTION AND OBJECTIVES

Air pollution has become a major concern worldwide, especially in large populated areas. Since the industrial revolution, anthropogenic activities and fuel combustion have released a large number of pollutants in the atmosphere. These pollutants, mainly emitted close to the surface can, by direct exposure, be harmful to both health and environment above certain concentration thresholds. Through their transport, they can affect air quality many hundreds of kilometres away from their sources, but also the global atmospheric system. Monitoring their concentrations in the atmosphere is therefore crucial to quantify their emissions, to determine their transport pathways and especially to understand their impact on environment and health.

Because air pollution affects mainly the lowest layers of the atmosphere, concentrations of pollutants can be measured well from ground-based monitoring stations. However, the horizontal coverage of such surface measurements is then limited to the station surrounding areas and this is not sufficient to understand the temporal/spatial evolution of pollution plumes. Nadir satellite remote sensing offers an appealing solution for monitoring such plumes on larger time and spatial scales. Thanks to their higher horizontal coverage, satellites allow acquiring the geographical distributions of different pollutants simultaneously, and with their regular overpasses, they enable following their temporal evolution (Martin, 2008). Sounding the near-surface atmosphere with satellites is however challenging because the concentrations of pollutants are generally small and confined to a small part of the entire atmospheric column. Ultraviolet-visible sounders have already shown their ability to measure air pollution, and more particularly nitrogen dioxide and sulphur dioxide concentrations (e.g., Richter et al., 2005; Fioletov et al., 2013). On the contrary, although they are independent on the solar radiation availability, thermal infrared satellite instruments are considered being less suited for probing the composition of the lowest part of the atmosphere. This is due to the fact that their sensitivity is limited by low temperature contrast (called thermal contrast) between the ground and the air above it which appear to be frequent. However, before the beginning of this PhD, thermal infrared sounders were found capable of measuring the boundary layer composition in case of high thermal contrast. The retrieval of ammonia distributions at global scale was the most convincing demonstration of this (Clarisse et al., 2009). The results obtained during our Master thesis (Bauduin, 2012) have provided additional evidence that thermal infrared measurements, taken in high thermal contrast conditions, are carrying useful information on near-surface concentrations of trace species. This was especially shown for sulphur dioxide emitted in the Norilsk industrial region that encounters large temperature inversions during the winter.

In this context, this work has the principal objective to revisit the capabilities of thermal

infrared sounders to measure the composition of the near-surface atmosphere. It focuses especially on the observations of the Infrared Atmospheric Sounding Interferometer (IASI). This instrument appears to be an excellent candidate for the goal of our research. Owing to its quasi global coverage, IASI provides a large dataset for our analyses, including measurements recorded in different regions of the world at various meteorological conditions. The bi-daily overpass times of IASI offer also the possibility to investigate sensitivity differences between day and night measurements. In parallel to the choice of the IASI instrument, two specific pollutants, presenting specific challenges for their near-surface monitoring, have been targeted: sulphur dioxide  $(SO_2)$  and carbon monoxide (CO). Due to its short lifetime,  $SO_2$  mainly stays confined in the boundary layer, but spectrally interfere with the strong water vapour absorption. CO, less impacted by water vapour, is on its hand distributed in the whole troposphere, and provides a good case study for which the near-surface concentration needs to be decorrelated from that in the higher atmospheric layers. Although there was already clear evidence at the beginning of the PhD that thermal infrared sounders can measure these gases in the near-surface atmosphere, the exact influence of thermal contrast and other variables on their capabilities were mostly qualitatively investigated. Moreover, mostly the range of positive thermal contrast was considered, and less attention was given to the gain in sensitivity brought by negative values (temperature inversions). In this thesis, we investigate in a more systematic way the influence of the thermal contrast on the sensitivity of IASI to near-surface  $SO_2$  and CO. More particularly, our main goal is to assess which geophysical conditions, and specifically which thermal contrast values, are needed to probe concentration variations of these two gases in the lowest part of the atmosphere.

For our purpose, a series of different analyses have been performed and specific methodologies have also been set up. After a first part dedicated to the explanation of the required theoretical background, these analyses are presented separately for  $SO_2$  (part II) and for CO (part III). Each part starts with an introductory chapter, describing the main objectives, and ends with a chapter of conclusions. The chapters in between present the analyses performed for each targeted gas. The last chapter of the thesis concludes this PhD work, identifies and discusses perspectives for further work and for using better the thermal infrared sounders for measuring air pollution.

# Part I

# Sounding the Earth's atmosphere using satellites

# CHAPTER 1

#### A FEW REMINDERS

#### 1.1 The Earth's atmosphere

The atmosphere of the Earth is the gaseous envelope that surrounds the planet. It played a crucial role in the development of life and is still essential nowadays. For instance, it is a reservoir of oxygen for all the living species and thanks to the ozone layer, which filters out the harmful ultraviolet (UV) radiation coming from the Sun, it protects life on the planet. Although it is very thin compared to the Earth radius, the atmosphere encounters different important processes, which control the weather and the climate that we know today. Its composition results from permanent exchanges of matter with oceans and soils and from its rich chemistry.

In this section, we briefly review the Earth's atmosphere in terms of its vertical structure and chemical composition. The general motions of air masses that occur in the atmosphere, and which drive the mean mixing time for the chemical species, are also briefly described.

#### 1.1.1 Vertical structure

#### 1.1.1.1 Temperature

The atmosphere can be divided into different horizontal layers according to the change of the temperature gradient. We can distinguish 4 layers (see Figure 1.1.1):

#### • The troposphere

The troposphere is the lowest layer of the atmosphere and contains around 90% of the total molecular mass of the atmosphere. It extends from ground to the tropopause, its upper limit. The height of the latter is 11 km on average, but varies with the latitude. Above polar regions, it is about 8 km and above equatorial regions, it can reach 16 km. This height varies also seasonally; it is generally higher during the summer than during the winter for all latitudes. In the troposphere, the temperature usually decreases; it drops from on average 288 K at the surface to 220–190 K at the tropopause, from polar to equatorial regions. The rate of this decrease is called the *lapse rate* and is of 6.5 K km<sup>-1</sup> on average. Occasionally, the air temperature inversion. This phenomenon generally occurs near the surface during winter and/or night, and leads

to a very stable atmosphere below the thermal inversion, with weak turbulence (see subsections 1.1.3.2 and 1.2.2). This notably contributes to the build-up of pollutants in the near-surface atmosphere (and possibly to extreme air quality degradation) and are of particular interest for this work.



Figure 1.1.1: Vertical structure of the Earth's atmosphere. The different layers are defined according to the change of the temperature gradient. The presented vertical profile of temperature is taken from the US Standard 1976 model (Anderson et al., 1986).

#### • The stratosphere

Above the tropopause starts the stratosphere, which extends to around 50 km, corresponding to the stratopause. In this layer, after being constant up to 20 km, the temperature starts to increase and rises up to 270 K above 40 km. This increase in air temperature produces a very stable atmospheric state. Hence, the inversion layer and the underneath isothermal layer tend to keep the vertical currents of the troposphere from spreading in the stratosphere. Also, the vertical motions in the stratosphere itself are reduced due to the inversion layer; the stratosphere is therefore a stratified layer. The reason of the increase of air temperature with height comes from the absorption of UV radiation by the ozone  $(O_3)$  layer, located between 20 km and 30 km.

#### • The mesosphere

The mesosphere extends from the stratopause to around 85–90 km of height. The gradient of the temperature is negative, as in the troposphere. At the top of the layer, the coldest temperature of the atmosphere is reached, around 170 K. The mesosphere ends up with the mesopause, where the temperature starts rising again.

#### • The thermosphere

The thermosphere is the "hot" layer above the mesosphere. It spreads from the mesopause to around 500 km of height. In this atmospheric region, the molecular

densities are very low and the temperature rises with altitude, owing to the absorption of solar UV radiation by atomic and molecular oxygen. Above 500 km of height, temperature reaches very high values which makes the escape of the lighter species possible. This exosphere represents the upper limit of our atmosphere and has no real physical boundary.

#### 1.1.1.2 Pressure and air density

The air density,  $\rho_{air}$ , is defined as the number of air molecules per unit volume. It can be also expressed in units of grams per cubic meters; it is in this case the mass of the air molecules per unit volume,  $\rho_{air}^m$  (see also subsection 1.1.2). The air density can be calculated using the ideal gas law:

$$P = \rho_{air} k_B T = \rho_{air}^m \frac{R}{M_{air}} T, \qquad (1.1.1)$$

where P is the atmospheric pressure,  $k_B$  is the Boltzmann constant  $(1.381 \times 10^{-23} \text{ J K}^{-1})$ , R is the ideal gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>),  $M_{air}$  is the molar mass of the air, and T is the atmospheric temperature.

The atmospheric pressure P is defined as the force exerted by the atmosphere on a unit area of surface. Let's consider P(z) the pressure at altitude z and an air volume of infinitesimal thickness dz and area S. If we assume the hydrostatic equilibrium, there is a balance between the different exerted forces: the one due to the atmospheric pressure difference and the one due to gravitation (see Figure 1.1.2, left). Therefore, we can write

$$[P(z + dz) - P(z)]S + \rho_{air}^m Sg \, dz = 0, \qquad (1.1.2)$$

with g the gravitational acceleration, which can be computed at altitude z according to

$$g = \left(\frac{R_t}{R_t + z}\right)^2 g_0, \tag{1.1.3}$$

where  $R_t$  is the radius of the Earth ( $\approx 6400 \text{ km}$ ) and  $g_0$  is the gravitational acceleration at the ground (9.806 m s<sup>-2</sup>). Rearranging equation (1.1.2) leads to the hydrostatic equation

$$\frac{\mathrm{d}P}{\mathrm{d}z} = -\rho_{air}^m g. \tag{1.1.4}$$

If we integrate equation (1.1.4) between the ground and z, we obtain

$$P(z) = P(0) \exp\left(-\int_0^z \frac{M_{air}(z')g(z')}{RT(z')} \,\mathrm{d}z'\right),$$
(1.1.5)

where P(0) is the pressure at the ground (at sea level, the standard value for atmospheric pressure is 1013.25 mb). Considering that the temperature, the molar mass of the air and the gravitational acceleration are constant with height, we can finally express the pressure at altitude z as

$$P(z) = P(0) \exp\left(-\frac{z}{H}\right)$$
 with  $H = \frac{RT}{M_{air}g}$ . (1.1.6)

This equation is called the *barometric law*, which expresses that the pressure exponentially decreases with height. This decrease also corresponds to a reduction of the air density as shown in Figure 1.1.2 (right). H is the scale height and represents the increase in altitude for which the atmospheric pressure decreases of a factor e. For a mean tropospheric temperature of 250 K, H is around 7.4 km.



Figure 1.1.2: (Left) Balance between the forces due to pressure and gravitation on an air volume of thickness dz and area S. Figure taken from Sportisse (2010). (Right) Pressure (in mb) as a function of altitude. The percentage indicated for four different levels represents the percentage of the total number of atmospheric molecules located below each level. Figure taken from Ahrens (2001).

### 1.1.2 Chemical composition

#### 1.1.2.1 Variables and units at play

Different variables can be used to describe the composition of the atmosphere. In this work, we have principally used the number density, the column and the volume mixing ratio to express the quantity of molecular species.

#### 1. Number density

The number density of a gas X,  $\rho_X$ , is the number of molecules of X per unit volume of air. It has the units of molecules cm<sup>-3</sup>. The number density is particularly used for studying reactions kinetics in the atmosphere. It is also the relevant quantity to calculate the partial/total columns of molecular species.

#### 2. Partial/total columns

The column of a gas X,  $C_X$ , is defined as the number of molecules of X included in an air column, whose basis has a unit area. The column can be partial (calculated between two defined altitudes) or total (calculated over the whole atmospheric height). It has the units of molecules cm<sup>-2</sup> and, considering a vertical column extending from ground to the altitude z, is calculated as

$$C_X = \int_0^z \rho_X \, \mathrm{d}z'. \tag{1.1.7}$$

The notion of column is very important in remote sensing, because it determines the efficiency with which an optically active gas absorbs radiation in the atmosphere. Indeed, the degree of absorption depends on the number of molecules of gas present along the path of the radiation beam. This will be described in more details in chapter 2. For clarity, partial columns will be written as PC and total columns as C.

#### 3. Volume mixing ratio

The volume mixing ratio (VMR) of a gas X,  $q_X$ , is defined as the number of moles of X,  $n_X$ , per mole of air,  $n_{air}$ . It can also be calculated as the ratio of the number of molecules of X per the number of molecules of air:

$$q_X = \frac{n_X}{n_{air}} = \frac{\rho_X}{\rho_{air}}.$$
(1.1.8)

It is expressed in mol/mol units (or V/V). More generally, it is expressed in parts per million volume (ppmv or simply ppm, 1 ppmv =  $10^{-6}$  mol/mol), in parts per billion volume (ppbv or ppb, 1 ppbv =  $10^{-9}$  mol/mol) and in parts per trillion volume (pptv or ppt, 1 pptv =  $10^{-12}$  mol/mol). For simplicity, the letter "v" will be omitted in the following. Note that using equation (1.1.8), the calculated VMR is level dependent, i.e., it is defined for a certain altitude. However, it can be also calculated in an integrated way using

$$q_X = \frac{C_X}{C_{air}},\tag{1.1.9}$$

where  $C_{air}$  is the air column. In this case, it is layer dependent, i.e., defined between two certain altitudes, and represents a layer-averaged value of the VMR.

#### 1.1.2.2 General composition

The Earth's atmosphere is mainly composed of nitrogen  $(N_2)$  and oxygen  $(O_2)$ , accounting respectively for 78% and 21% of the total of molecules in the atmosphere. Argon (Ar) is the third most abundant gas, with a VMR of 0.0093 mol/mol. The remaining species are called *trace species*. Table 1.1 gives a summary of averaged VMRs for different atmospheric gases located at near-ground altitude. These VMRs are calculated for regions not directly affected by surface sources and in dry air. Water vapour (H<sub>2</sub>O) is indeed a particular case because it presents a highly variable VMR in the atmosphere, which ranges from  $10^{-6}$  mol/mol to  $10^{-2}$  mol/mol. Note that the VMRs of carbon monoxide (CO) and sulphur dioxide (SO<sub>2</sub>), which are the two pollutants in which we are interested in this work, are respectively below 0.1 ppm and below 1 ppb in case of no pollution.

The composition of the Earth's atmosphere is not identical everywhere on the globe and at anytime. It varies according to different factors, such as

- The altitude; e.g., SO<sub>2</sub> height location and amount strongly depend on its source. SO<sub>2</sub> will be found close to ground in small concentrations in case of anthropogenic emissions, but can be injected at high altitudes in large amount in case of volcanic eruption.
- The latitude; e.g., CO is more abundant in the Northern Hemisphere, where the number of sources is largest.
- The period of the day or of the year; e.g., CO presents seasonal variations of its quantity, which are different according to the regions.
- The region which is concerned (sea or land, city or countryside).

In atmospheric sciences, to represent the atmosphere, climatologies are generally used. They represent a certain spatially averaged state of the atmosphere, including the vertical profiles of temperature, pressure, and of different gases. They can be built for different regions of the world, for different time periods,... In this work, we have mainly used the

Gas	VMR (ppm)
N <sub>2</sub>	$78 \times 10^{4}$
$O_2$	$21{ imes}10^4$
Ar	$93 \times 10^{2}$
Carbon dioxide $(CO_2)$	380
Methane $(CH_4)$	1.8
Nitrous oxide $(N_2O)$	0.3
CO	< 0.1
$SO_2$	$< 10^{-3}$

Table 1.1: VMRs of different atmospheric gases, calculated in dry air (Bliefert and Perraud, 2009).

climatologies reported by Anderson et al. (1986), describing with a few standard models the atmosphere for different regions (Arctic, mid-latitudes and tropical regions) and for two different seasons (summer and winter). In the following, the chosen models are specified when needed. For some gases, vertical profiles have been adapted to take into account current VMRs. Details about these changes are also specified if needed.

#### 1.1.3 General circulation

Air motions play a key role in the distribution of chemical species in the atmosphere. These motions are controlled by three main forces: the pressure-gradient force, the gravity and the Coriolis force. In this section, we briefly recall what these forces are and how they affect air masses. Horizontal and vertical motions are discussed separately. We invite the reader looking for more details about the circulation to consult the book of Jacob (1999), from which most of the following concepts are taken.

#### 1.1.3.1 Horizontal motions

In the horizontal direction, air motions are driven by the Coriolis force and by the horizontal pressure-gradient force.

#### • Coriolis force

The latitudinal gradient of the translational speed of the Earth is at the origin of the Coriolis force. It is a fictitious force, which is however needed to describe the air motions from the viewpoint of an observer in a rotating frame of reference. The Coriolis force applies in a similar way for both latitudinal and longitudinal motions. For latitudinal motions (see Figure 1.1.3, left), it is the conservation of the angular momentum that causes a deflection of air masses. Indeed, an air mass travelling from the Equator to the North Pole loses angular momentum because of decreasing translational velocity of the Earth for increasing latitudes. To conserve the angular momentum, the air mass acquires an eastward velocity relative to the rotating Earth. From the perspective of an observer located at the Equator, the air mass is deflected to the right compared to the direction of movement. This results from the Coriolis force. The same applies for an air mass travelling from the North Pole to the Equator (deviation to the right compared to the direction of motion). Along the longitude, it is the variation of the centrifugal force that is at the origin of the deviation. For an air mass at rest and for an observer located at the Earth's surface, there is a balance between the centrifugal force, the gravity and the reaction at the surface (see Figure 1.1.3, right). When moving from west to east in the Northern Hemisphere, the air mass has its angular velocity that increases. As a result, the exerted centrifugal force increases. The balance between the forces is broken and the air mass is deflected towards the Equator. Conversely, an air mass travelling from east to west experienced a decrease in its angular velocity, which results in a decrease in the centrifugal force; the air mass is deflected towards the North. In general, the Coriolis force deflects air masses to the right from the direction of the motion in the Northern Hemisphere, and to the left in the Southern Hemisphere. The Coriolis force is equal to 0 at the Equator and as well as for an air mass at rest. It increases with increasing latitude.



Figure 1.1.3: (Left) Deflection of an air mass travelling in the latitudinal direction due to the Coriolis force. (Right) Forces exerted on an air mass travelling in the longitudinal direction. The observer is considered located at the Earth's surface. Figures taken from Jacob (1999).

#### • Pressure-gradient force

A pressure gradient in the atmosphere generates a pressure-gradient force on air masses. This force is oriented along the pressure gradient and leads air masses to move from high to low pressure areas.

The combined effect of the Coriolis force and pressure-gradient force is shown in Figure 1.1.4 (top). In the Northern Hemisphere, an air parcel initially at rest is subjected to the pressure-gradient force  $(\gamma_p)$  and starts flowing from high pressure to low pressure zones. As it is acquiring speed, the Coriolis force  $(\gamma_c)$  increases and causes the air parcel to be deflected to the right. A balance between the two forces can be reached and this results in a steady flow perpendicular to the pressure gradient, which is called *the geostrophic flow*. In the Northern hemisphere, the geostrophic flow is such that air motion around a high pressure area is clockwise, and around a low pressure zone is counter-clockwise (contrary in the Southern Hemisphere). The center of high pressure is called an anticyclone or a *High* and the center of low pressure is called a cyclone or a *Low* (see also top of Figure 1.1.5).

Close to the surface, an additional friction force  $(\gamma_f)$  has to be taken into account to describe the loss of momentum of the air mass due to obstacles (e.g. trees, buildings,...) and orography. This force is exerted in the opposite direction of the motion, and leads to a slowdown of the air parcel and thus to a decrease in the Coriolis force. This is represented in Figure 1.1.4 (bottom). As a result, the air is deflected towards the region of low pressure and this is valid for both hemispheres. Therefore, in a region of high pressure, the air parcel is deflected away from the High, and towards the Low in a region of low pressure. These deflections generate vertical motions to compensate the air divergence or convergence (respectively for the High and the Low) occurring at the surface (mass conservation). For



Figure 1.1.4: (Top) Combined effect of the Coriolis force  $(\gamma_c)$  and the pressure-gradient force  $(\gamma_p)$ . (Bottom) Additional effect of the friction force  $(\gamma_f)$  at the surface on the air mass. Figures taken from Jacob (1999).

high pressure zones, sinking flow is generated, called *subsidence*; rising flow is produced for low pressure zones, and called *upwelling*. This is shown in the top panel of Figure 1.1.5.

In the 18<sup>th</sup> century, Hadley proposed the first model to describe the general circulation of the atmosphere. Based on the temperature contrast between the Equator and the poles, Hadley saw this circulation as a large cell, with upwelling air at the Equator that then flows towards the poles, where it sinks. This model however does not take into account the Coriolis force, but remains mainly valid to describe the tropical atmosphere circulation (see bottom panel of Figure 1.1.5). In brief, in the so-called Hadley cell, air masses that have been rising to the tropopause at the Equator flow towards the poles, are then deflected towards the East and accelerated by the Coriolis force. This flow finally breaks down into an unstable flow around  $30^{\circ}$  of latitude; the air is pushed down and this produces the subtropical high-pressure belts. Further poleward transport is difficult because the Coriolis force tends to balance the pressure-gradient force and thus to produce a geostrophic flow. To further move polewards, air masses have to lose momentum, and this is generated by the friction force at the surface. It is worth pointing that, in the region of the Equator, a ribbon of the atmosphere of a few kilometres wide experiences persistent convergence. This ribbon is called the InterTropical Convergence Zone and forms a barrier for interhemispheric transport.

The general circulation described above can be translated to averaged time scales for the horizontal transport of air masses and chemical species in the troposphere. They are summarised in Table 1.2. The longitudinal transport is the fastest, with averaged wind speeds of the order of 10 m s<sup>-1</sup> corresponding to the geostrophic flow. Continental transport and intercontinental exchange in a given latitude band are the order of 1 and 2 weeks respectively. The transport is slower in the latitudinal direction, with wind speeds around 1 m s<sup>-1</sup>. Transport from mid-latitudes to the Equator and the poles takes 1 or 2 months. Finally, because of the InterTropical Convergence Zone, the interhemispheric transport is very slow and takes around 1 year. Of course on shorter time scales and locally, different



Figure 1.1.5: (Top) Air motions around high and low pressure centers. (Bottom) Global horizontal air motions and Hadley cell. Figures taken from Jacob (1999).

transport patterns occur and produce mixing times that can be significantly different from those listed in Table 1.2.

Spatial scale	Time for transport
Continental (longitudinal)	1 week
Intercontinental (longitudinal)	2 weeks
Mid-latitudes to Equator	1-2 months
Mid-latitudes to poles	1-2 months
Interhemispheric	1 year

Table 1.2: Typical time scales for the horizontal transport of air masses and chemical species.

#### 1.1.3.2 Vertical motions

As mentioned in the previous section, convergence and divergence of air close to the surface due to the friction force produce vertical motions. However, the associated wind speeds are very small, of the order of 0.001-0.01 m s<sup>-1</sup> (to be compared with 1–10 m s<sup>-1</sup> for the horizontal transport). If the vertical transport was dependent on these motions only, it would take about 3 months for an air parcel to reach the tropopause. Faster vertical transport takes place with *buoyancy*. The buoyancy is the net force exerted on an object immersed in a fluid. It corresponds to the difference between the gravity and the pressure-gradient force (Archimedes' principle), the latter resulting from the pressure difference between the top and the bottom of the object.

Buoyancy in the atmosphere is determined by the vertical temperature gradient. More particularly, it depends on the relative magnitude of the atmospheric temperature lapse

rate,  $-\frac{dT_{\text{ATM}}}{dz}$  (see subsection 1.1.1.1), and the adiabatic<sup>1</sup> temperature lapse rate,  $-\frac{dT_{\text{A}}}{dz}$  (see Figure 1.1.6). Indeed, during its ascent, an air parcel expands and cools. There can be two general cases:

1.  $-\frac{\mathrm{d}T_{\mathrm{ATM}}}{\mathrm{d}z} > -\frac{\mathrm{d}T_{\mathrm{A}}}{\mathrm{d}z}$ 

After rising, the temperature of the surrounding air is smaller than that of the air parcel. The density of the latter is thus smaller than that of the surrounding atmosphere. As a result, the air parcel is accelerated upward by buoyancy. The atmosphere is *unstable* with respect to vertical motion; any initial push upward on the air parcel will be amplified by buoyancy. This kind of motion is called *convection*. Note that a push downward on the air parcel will be also amplified by buoyancy.

2. 
$$-\frac{\mathrm{d}T_{\mathrm{ATM}}}{\mathrm{d}z} < -\frac{\mathrm{d}T_{\mathrm{A}}}{\mathrm{d}z}$$

After rising, the surrounding air is warmer than the air parcel. The density of the latter is larger and the air parcel therefore sinks back to its initial position. The vertical motions in that case are suppressed and the atmosphere is *stable*. Atmospheric stability is important especially when there is temperature inversions (e.g., stratosphere).

Note that in case  $-\frac{dT_{ATM}}{dz} = -\frac{dT_A}{dz}$ , the atmosphere is said *neutral*. The stability of the atmosphere is a local property, which depends on the local lapse rate of the atmospheric temperature. The atmosphere can then be stable for a certain altitude region and unstable in another part.



Figure 1.1.6: Atmospheric temperature profile  $(T_{\text{ATM}})$  and adiabatic temperature profile  $(T_{\text{A}})$ . The latter is calculated considering an adiabatic rise of an air parcel. This example corresponds to an unstable atmosphere. Figures taken from Jacob (1999).

The adiabatic lapse rate is estimated to be  $9.8 \text{ K km}^{-1}$ . However, in a humid atmosphere, adiabatic expansion is no more valid. Indeed, condensation of H<sub>2</sub>O is an exothermic process, releasing *latent heat*. The formation of clouds in a rising air parcel provides therefore an internal source of heat that partly compensates for the cooling of the air parcel while expanding. Cloud formation increases buoyancy; the motions generated by clouds formation are called *wet convection*. The wet adiabatic lapse rate has typical values ranging between 2 K km<sup>-1</sup> and 7 K km<sup>-1</sup>, depending on the H<sub>2</sub>O condensation rate.

According to the above, and similarly to what has been done for horizontal motions, we can define typical average time scales for the vertical transport. As already mentioned, the buoyancy in an unstable atmosphere accelerates both upward and downward motions.

<sup>&</sup>lt;sup>1</sup>The adiabatic temperature profile is calculated assuming an adiabatic rise of the air parcel (without heat exchange with its surrounding): as the air parcel is rising, it expands (decreasing pressure) and cools (decreasing temperature).

There is thus no preferred direction of motion. These irregularities in the vertical flow of atmospheric air masses causes *turbulence*. Using *turbulent diffusion coefficients* (see Jacob (1999) for more details), the time scales of the vertical transport can be evaluated. They are summarised in Table 1.3. It can be shown that it takes around 1 month for an air parcel to mix from the ground to the tropopause. Mixing in the planetary boundary layer (1-3 km) needs 1 or 2 days, and the transport to the mid-troposphere (5 km) takes around 1 week. Because of the temperature inversion at the stratopause, which renders this part of the atmosphere very stable, the exchange of air between the troposphere and the stratosphere to the stratosphere, and 1–2 years for air in the stratosphere to be transported down to the troposphere. Again on smaller scales faster transport happens (e.g., stratospheric intrusion).

Table 1.3: Typical time scales for the vertical transport of air masses and chemical species, calculated from the surface.

Vertical scale	Time for transport
Top of the planetary boundary layer (1–3 km)	1-2 days
Free troposphere $(5 \text{ km})$	1 week
Tropopause	1 month
Troposphere-stratosphere	5–10 years
Stratosphere-troposphere	1-2 years

## 1.2 Pollution and planetary boundary layer

Since the industrial revolution, anthropogenic activities and fuel combustion have released a large number of pollutants in the atmosphere. By direct exposure and if present in a certain quantity, these gases can be harmful to health and environment. In this section, we describe what air pollution is and discuss the principal pollutant sources. We focus especially on CO and SO<sub>2</sub>, the targeted gases of this work. As pollution mainly affects the atmosphere close to the surface, and because this part of the atmosphere is of particular interest for this work, the definition of the *planetary boundary layer* is also presented.

### 1.2.1 Air pollution

Nowadays, air pollution has become a major concern worldwide, mainly because of local and regional anthropogenic emissions. It is during the 1950s that the global nature of air pollution became obvious, notably because of the advent of atmospheric testing of nuclear weapons and the subsequent radioactive fallout occurring at global scale. Acid rains and the influence of the chlorofluorocarbons (CFCs) on the  $O_3$  layer are other examples that have provided clear and dramatic evidence that pollutants emitted in one place can have adverse effects many hundreds of kilometres away and even more.

A pollutant is a chemical compound that "*is present in the wrong place, at the wrong time and in the wrong amounts*"<sup>2</sup>. In other words, a pollutant is a species that causes damage to human health and ecosystems if it is present above a certain amount, which is of course different from a compound to another. Pollutants can be either *primary*, when they

<sup>&</sup>lt;sup>2</sup>Metcalfe and Derwent (2005).

are directly emitted in the atmosphere (e.g.,  $SO_2$ ), or *secondary*, when they are formed in the atmosphere through chemical reactions (e.g.,  $O_3$ ).

Note that some pollutants can be both primary and secondary. For example, nitrogen dioxide  $(NO_2)$  is a primary pollutant when it is emitted by motor vehicles, but is a secondary pollutant when formed through the reaction between  $O_3$  and nitric oxide (NO). Emission sources of primary pollutants can be classified into 2 categories:

- The *anthropogenic sources*, which are induced by human activities (e.g., transport, industries,...).
- The *natural sources*, which are related to natural processes (e.g., volcanic eruptions).

Attempts to regulate anthropogenic emissions of pollutants have been settled from national to international levels. In the European Union for example, a European Environment Agency (EEA, http://www.eea.europa.eu/) has been established in 1990 and has been working since 1994. Its goal is to provide independent information on the environment for people involved in developing and adopting environmental policy (e.g., EEA, 2015). It works then closely with the European Commission, the European Parliament and the Council, and plays a key role in the adoption of European directives by these institutions. These directives consist in a number of environmental objectives that member states have to reach in a certain time. They define limit values and alert thresholds for the protection of human health and ecosystems for different pollutants. The limit values consist in fixed concentration levels of pollutants, defined within a given period of time, that cannot be exceeded once attained and cannot be reached more than a certain number of time during a year. The alert thresholds indicate pollutant concentrations beyond which there is a risk for human health in case of brief exposure and for which immediate regulation measures have to be taken by the member states. For example, for  $NO_2$ , within a period of one hour, the surface concentration should not exceed 200  $\mu g m^{-3}$  more than 18 times in a calendar year and its annual mean concentration has to be below 40  $\mu g m^{-3}$ . The alert level for NO<sub>2</sub> is set at 400  $\mu g m^{-3}$  (EU, 2008). The limit and alert values are given for SO<sub>2</sub> and CO in the next two subsections.

#### 1.2.1.1 Sulphur dioxide

Sulphur (S) is present in the atmosphere in a variety of compounds, from reduced form, such as the dimethyl sulphide (DMS,  $(CH_3)_2S$ ) emitted by the oceans, to oxidised form, such as SO<sub>2</sub>. Sulphur species have both anthropogenic and natural sources. Current estimates are that anthropogenic emissions account for about 70% of all sulphur emissions, with 60-100 Tg of S emitted in the atmosphere per year (Stevenson et al., 2003). The main sulphur compound that enters in the atmosphere is SO<sub>2</sub>. It is mostly emitted by anthropogenic sources, with the major contribution coming from combustion of sulphur-rich fuels, such as coal and oil (Smith et al., 2011). Volcanic emissions are the largest natural contributors to tropospheric and stratospheric SO<sub>2</sub>, and account for 7.5-10.5 Tg of S per year on average (Halmer et al., 2002).

In the atmosphere,  $SO_2$  undergoes oxidation reactions, in both gas and aqueous phases. In the gas phase,  $SO_2$  is oxidised in sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) by the hydroxyl radical (OH), following the reactions

 $SO_2 + OH + M \longrightarrow HOSO_2 + M$ 

$$HOSO_2 + O_2 \longrightarrow SO_3 + HO_2$$

$$SO_3 + H_2O + M \longrightarrow H_2SO_4 + M.$$

 $H_2SO_4$  then rapidly condenses, and either forms new aerosols or adds to existing ones. A part of SO<sub>2</sub> gas enters the aqueous phase (cloud droplets or aerosols), where it reacts with dissolved hydrogen peroxide ( $H_2O_2$ ) or  $O_3$  to form sulphate ( $SO_4^{2-}$ ) according to the chemical reactions

$$\begin{split} \mathrm{SO}_2 + \mathrm{H}_2\mathrm{O} \rightleftharpoons \mathrm{H}^+ + \mathrm{HSO}_3^- \\ \mathrm{HSO}_3^- \rightleftharpoons \mathrm{H}^+ + \mathrm{SO}_3^{2-} \\ \mathrm{HSO}_3^- + \mathrm{H}_2\mathrm{O}_2 \longrightarrow \mathrm{H}^+ + \mathrm{SO}_4^{2-} + \mathrm{H}_2\mathrm{O} \\ \mathrm{HSO}_3^- + \mathrm{O}_3 \longrightarrow \mathrm{H}^+ + \mathrm{SO}_4^{2-} + \mathrm{O}_2 \\ \mathrm{SO}_3^{2-} + \mathrm{O}_3 \longrightarrow \mathrm{SO}_4^{2-} + \mathrm{O}_2. \end{split}$$

These reactions are at the basis of *acid rain*, which can have devastating effects on ecosystems. They are for instance responsible for the acidification of lakes, which leads to the death of fish populations (e.g., Haines, 1981). Acid rains also cause damages to forests and vegetations (loss of leafs,...) (e.g., Likens et al., 1996; Tutubalina and Rees, 2001). SO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> have also damaging effects on human health. By their acid nature, they irritate mucous. For concentration larger than 1 mg m<sup>-3</sup>, the first symptoms of intoxication can already be detected: suffocation, inflammation of respiratory organs,... For continuous breathing of SO<sub>2</sub>, other symptoms start to appear, e.g., a loss of taste, oedema, heart failure,... To prevent such large SO<sub>2</sub> concentrations, regulation measures have been taken. The limit values for surface concentrations for human health defined by European directives (EU, 2008) are the following:

- 1. 350  $\mu$ g m<sup>-3</sup> within a period of one hour, which should not be exceeded more than 24 times per calendar year,
- 2. 125  $\mu$ g m<sup>-3</sup> within a period of one day, which should not be exceeded more than 3 times per calendar year.

An alert threshold is also fixed at 500  $\mu g m^{-3}$ .

#### 1.2.1.2 Carbon monoxide

CO is both a primary and secondary pollutant. It is emitted at the surface by different sources (Duncan et al., 2007), both anthropogenic and natural, such as the incomplete combustion of fossil fuels and biomass burning. It is commonly estimated that around 60% of the total CO emissions come from anthropogenic activities. CO is also formed in the atmosphere by the reactions of volatile organic compounds (VOCs) with the OH radical, and especially by the oxidation of CH<sub>4</sub> (Bliefert and Perraud, 2009):

$$CH_4 + 2O_2 + 2NO \longrightarrow HCHO + H_2O + 2NO_2$$

$$\mathrm{HCHO} + \mathrm{2O}_2 \xrightarrow{h\nu} \mathrm{CO} + \mathrm{H}_2\mathrm{O} + \mathrm{O}_3.$$

In the atmosphere, the oxidation of CO leads to the formation of  $O_3$  (in the presence of  $NO_x$ ) and  $CO_2$  and, by involving the OH radical, has a direct impact on the oxidation capacity of the atmosphere (Duncan and Logan, 2008). This oxidation can take two different pathways (Bliefert and Perraud, 2009), depending on the ratio between the concentration of NO and  $O_3$  ([NO]/[O<sub>3</sub>]). If [NO]/[O<sub>3</sub>] > 1/5000, the destruction of CO leads to the formation of O<sub>3</sub> according to the following chemical reactions:

 $\begin{array}{l} \mathrm{CO} + \mathrm{OH} \longrightarrow \mathrm{CO}_2 + \mathrm{H} \\ \\ \mathrm{H} + \mathrm{O}_2 + \mathrm{M} \longrightarrow \mathrm{HO}_2 + \mathrm{M} \\ \\ \mathrm{HO}_2 + \mathrm{NO} \longrightarrow \mathrm{NO}_2 + \mathrm{OH} \\ \\ \mathrm{NO}_2 \xrightarrow{h\nu} \mathrm{NO}_2 \longrightarrow \mathrm{NO} + \mathrm{O} \\ \hline \lambda < 420 \ \mathrm{nm} \end{array}$ 

If  $[NO]/[O_3] < 1/5000$ , another reaction pathway leads to the formation of CO<sub>2</sub> and O<sub>2</sub>, but the destruction of O<sub>3</sub>:

 $CO + OH \longrightarrow CO_2 + H$  $H + O_2 + M \longrightarrow HO_2 + M$  $HO_2 + O_3 \longrightarrow OH + 2O_2$ 

Because of its higher affinity with haemoglobin compared to  $O_2$ , CO is dangerous for human health. It can indeed replace  $O_2$  in blood and, thus, prevent the transport of the latter in the human body. It is estimated that death occurs when 60% of haemoglobin are linked to CO instead of  $O_2$  (Bliefert and Perraud, 2009). The limit value for CO defined by European directives consists in a maximum daily 8-hour mean of 10 mg m<sup>-3</sup> that cannot be exceeded (EU, 2008).

#### 1.2.2 Planetary boundary layer

In simple words, the planetary boundary layer (PBL) is defined as the part of the lower atmosphere that is sensitive to the varying conditions at the Earth's surface in a short period of time (typically in a few hours). It is therefore the part of the atmosphere that is directly impacted by pollution. Determining its height is of particular importance to analyse the dispersion and removal of pollutants. Despite its importance, the PBL height is difficult to estimate because of the occurrence of different complex processes. Moreover, the estimation is performed differently, depending on the type of the PBL, which is determined
by the atmospheric stability in the layer (see subsection 1.1.3.2). We distinguish therefore the unstable and the stable PBL, which are discussed separately in the following.

#### • Unstable PBL

The unstable PBL is generally encountered during daytime, when the temperature profile in the lowest part of the atmosphere is decreasing with height and generates unstable mixing. It is generally characterised by a *subsidence inversion* at its top (at around 1-3 km of height). This subsidence inversion corresponds to a small thermal inversion formed by the confluence of air convecting from the surface and warmer subsiding air from high altitudes (see Figure 1.2.1). We indeed saw in subsection 1.1.3 that an air parcel located at high altitudes can subside to respect the mass conservation at the surface; while subsiding, the temperature of the air parcel increases following the dry adiabatic lapse rate. Determining the base of this subsidence inversion is one of the possible methods to estimate the height of an unstable PBL (Seidel et al., 2010).



Figure 1.2.1: Subsidence thermal inversion formed by the confluence of air convecting from the surface and warmer subsiding air from higher altitudes. This subsidence inversion defines the PBL.  $\Gamma$  and  $\Gamma_W$  correspond respectively to the dry and wet adiabatic lapse rates. Figure taken from Jacob (1999).

The determination of the PBL height can also be based on the vertical profiles of potential temperature and/or of H<sub>2</sub>O (see Figure 1.2.2). The potential temperature,  $\theta$ , of an air parcel at pressure P is the temperature that the parcel would acquire if it was adiabatically brought to a standard reference pressure  $P_0$ , taken generally at 1000 hPa. It is calculated according to the following expression:

$$\theta = T \left(\frac{P_0}{P}\right)^{\frac{R}{c_p}},\tag{1.2.1}$$

where  $c_p$  is the specific heat capacity of air. It can be shown that  $\frac{d\theta}{dz} = 0$  when  $-\frac{dT_{ATM}}{dz} = -\frac{dT_A}{dz}$  and  $\frac{d\theta}{dz} > 0$  when the atmosphere is stable. The potential temperature is therefore a convenient indicator of the stability of the atmosphere. Determining the height where  $\frac{d\theta}{dz}$  is maximum is another method to estimate the thickness of the PBL, because it indicates the transition between the unstable conditions of the PBL and the more stable region above (Seidel et al., 2010). This is shown in Figure 1.2.2.

Because of vertical mixing,  $H_2O$  is relatively well-mixed in the PBL<sup>3</sup>. A sharp decrease is however observed above and reflects the thermal inversion barrier for the vertical

<sup>&</sup>lt;sup>3</sup>Note that the PBL height can be considered as the top of the mixing layer (Seidel et al., 2010), in which gases are mixed.

transport (Figure 1.2.2). Thus, the PBL height can also be defined as the altitude where the humidity decrease rate is maximum (Seidel et al., 2010). Note that other methods exist to determine the altitude of the PBL, based on profiles of refractivity, virtual potential temperature<sup>4</sup> and aerosols. These are discussed in Seidel et al. (2010) and Luo et al. (2014).



Figure 1.2.2: Vertical profiles of temperature, potential temperature,  $H_2O$  (dew point) and ozone measured by aircraft in August in the early afternoon over Canada. Figure taken from Jacob (1999).

• Stable PBL

The stable PBL is usually encountered at night or in winter, when the Earth's surface is not heated by the Sun. It is characterised by a temperature inversion at the surface, with the temperature of the ground colder than the temperature of the air above it. The stable atmospheric conditions that result generally lead to the build up of pollutants. The top of this surface-based thermal inversion can define in this case the PBL height (Seidel et al., 2010). More details are also given in Hyun et al. (2005).

Note that a neutral PBL can also be defined, and its height is determined by using the same methods as those presented for the unstable PBL.

In this work, notably because of a lack of vertical resolution in the temperature and humidity profiles that have been used, the PBL was not defined according to the above descriptions. We have considered the PBL more as a layer of near-surface atmosphere. Depending on the case under study, we have taken its thickness to be 1 km, 2 km or 4 km. The assumptions made are mentioned for each application.

# 1.3 Lifetime and its relationship with the atmospheric transport

The lifetime  $\tau$  of an atmospheric species X is defined as the average time that the species X stays in the atmosphere (or part of it) before being removed. It is an important concept in atmospheric science. By comparing it with time scales of transport (subsection 1.1.3), it allows us to evaluate the impact of this chemical compound on the atmospheric system.

<sup>&</sup>lt;sup>4</sup>Theoretical potential temperature of a dry parcel of air that would have the same density as moist air.

A simple one-box model can be used to express the lifetime (Jacob, 1999). Such a model describes the abundance of X inside a box that represents a fixed atmospheric domain (e.g., troposphere,...). The abundance of X is described by the mass balance equation, which expresses the mass change of X as the difference between the sources and the sinks of X:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = (F_{in} - F_{out}) + (P - L), \qquad (1.3.1)$$

where m is the mass of X,  $F_{in}$  is the flow of X into the box,  $F_{out}$  is the flow out of the box, P is the production rate of X and L is the loss rate of X. The production term includes the emissions, E, of species X, both anthropogenic and natural, and the chemical reactions that produce X, CP. The loss term involves the chemical loss of X, CL, and the dry and wet deposition, D. The dry deposition corresponds to the removal of X from the atmosphere by direct reaction at or absorption by the Earth's surface (e.g., uptake of  $CO_2$  during the photosynthesis). The wet deposition involves precipitation. Based on this, the lifetime of X inside the domain considered can be defined as the ratio between its mass and sinks in the box: m m

$$\tau = \frac{m}{F_{out} + L} = \frac{m}{F_{out} + CL + D}.$$
(1.3.2)

One lifetime per sink process can also be defined. For example, the lifetime associated to chemical loss can be written as

$$\tau_{CL} = \frac{m}{CL},\tag{1.3.3}$$

and the total effective lifetime can then be rewritten as function of the individual ones as

$$\frac{1}{\tau} = \frac{1}{\tau_{out}} + \frac{1}{\tau_{CL}} + \frac{1}{\tau_D},$$
(1.3.4)

where  $\tau_{out}$ , and  $\tau_D$  are the lifetimes associated respectively to the flow out of the box, and the total deposition. If the sinks of species X are first order processes (they are proportional to the mass of X inside the box), the lifetime can be expressed as a function of the corresponding rate constants:

$$\tau = \frac{1}{k_{out} + k_{CL} + k_D} \quad \text{with} \quad \tau_{out} = \frac{1}{k_{out}}, \ \tau_{CL} = \frac{1}{k_{CL}}, \ \tau_D = \frac{1}{k_D}, \tag{1.3.5}$$

where  $k_{out}$ ,  $k_{CL}$ , and  $k_D$  are the rate constants of respectively the flow out of the box, the chemical loss reactions and the total deposition. In case a steady state is reached  $\left(\frac{dm}{dt}=0\right)$ , the rate of production of X is equal to the rate of loss, and the lifetime can be expressed similarly as a function of sources:

$$\tau = \frac{m}{F_{out} + CL + D} = \frac{m}{F_{in} + CP + E}.$$
(1.3.6)

Following the above discussion, the lifetime can vary depending on different factors, such as the injection height of species X, meteorological conditions in the considered area, surface properties,...

To illustrate the concept of lifetime, we can take the example of  $SO_2$  in which we are interested in this work. As discussed in subsection 1.2.1.1,  $SO_2$  is emitted in the atmosphere by both anthropogenic (sulphur-rich fuels combustion) and natural (volcanic activity) sources. In the atmosphere, it undergoes oxidation reactions, with different pathways depending on the phase (aqueous or gas) in which it is located.  $SO_2$  is also removed from the atmosphere by dry (Wesely, 2007) and wet (Ali-Khodja and Kebabi, 1998) depositions. According to local conditions, such as the concentrations of oxidants or the surface properties, the lifetime of  $SO_2$  varies from a few hours to several days in the lower troposphere (Lee et al., 2011).



Figure 1.3.1: Temporal (lifetime) and spatial scales associated to different atmospheric constituents. The time scales for three different transport are indicated (PBL, intrahemispheric and interhemispheric, see also subsection 1.1.3). Figure taken from Seinfeld and Pandis (2006).

Injected in the stratosphere, where it is gradually oxidised in  $H_2SO_4$  aerosols,  $SO_2$  has a much longer lifetime, of the order of weeks.

As already mentioned above, the lifetime is important because it allows evaluating the scale of impact of an atmospheric species, by comparisons with typical time scales of transport (subsection 1.1.3). This is represented in Figure 1.3.1. For example, SO<sub>2</sub> has an average lifetime of 1-2 days if it is emitted at the surface. It has thus a local direct impact, close to the source. In the vertical, it will be relatively well-mixed in the PBL. H<sub>2</sub>SO<sub>4</sub> resulting from the oxidation of SO<sub>2</sub> has a lifetime of the order of 5 days in the troposphere. The impact of acid rain is therefore continental. At the other extreme, the CFCs are very stable compounds and have a lifetime of up to 10 years. They can therefore reach the stratosphere, where they contribute to the depletion of the O<sub>3</sub> layer. They are also well mixed at global scales.

# 1.4 Sounding the atmosphere composition using satellites

The remote sensing of an object consists in acquiring information about this object from a certain distance. The remote sounding from satellite has become a widely used approach to observe the Earth's atmosphere. It relies on the interaction between electromagnetic radiation with the atmosphere. The absorption, the emission and the scattering resulting from this interaction produce changes in the spectral properties of the initial radiation, which carry information about the state of the atmosphere. In this section, we discuss some general concepts about the satellite remote sensing of the Earth's atmosphere. We explain more particularly the different observation geometries and orbits that can be used to sound the atmosphere. A specific section is also dedicated to briefly review the results of the PBL sounding by satellites obtained before the beginning of this PhD thesis.

# 1.4.1 Active and passive soundings

The instrumentation carried onboard satellites to measure the composition of the Earth's atmosphere can differ by the source of radiation that is used. We distinguish two types of sounding (top panel of Figure 1.4.1)

- **Passive sounding**: the source of radiation is natural. It can be that of the Sun, the Moon, the Earth itself or from other stars. Passive sounding is at the heart of this work.
- Active sounding: the source of radiation is provided by the instrumentation onboard the satellite.

The spectral range in which the sounder observes the atmosphere also varies from an instrument to another. In the passive mode, it is generally included in the range UV-microwave. The choice of the spectral range covered by the instrument is generally driven by the atmospheric parameters that are targeted.

# 1.4.2 Observation geometries and orbits

The observation geometry of a satellite sounder defines the direction along which the sounder observes the atmosphere. We distinguish three observation geometries (see bottom panel of Figure 1.4.1):

- Nadir: the instrument looks down from space towards the surface. The direction defined by a satellite viewing angle<sup>5</sup> of 0° is called the *nadir*. In this geometry, the sounder can measure either the solar radiation (UV, visible, near-infrared) reflected by the Earth's surface and/or backscattered by the atmospheric constituents, or the thermal emission of the Earth's surface and of the atmosphere (thermal infrared). The latter is the observing mode of the sounder used in this work.
- Limb emission: the instrument looks at the limb of the atmosphere, and while moving, observes the atmosphere at different tangent heights. In this viewing mode, the sounder measures either radiation scattered by the atmosphere (UV, visible, near-infrared) or the thermal emission of the latter (thermal infrared).
- Occultation: the instrument looks at the limb of the atmosphere during the sunset or the sunrise of the Sun, or another object (moon, star,...). As for the limb emission sounding, while moving, the sounder observes the atmosphere at different tangent heights.

In addition to different viewing mode, satellite sounders can circle the Earth on different types of orbits. There are two main types depending on altitude:

• Low Earth Orbits (LEO): on a LEO, the satellite circles the Earth at relatively low altitudes (several hundreds kilometres). This kind of orbit is generally polar, with the satellite crossing the Equator several times per day. The LEO can be Sun-synchronous, which means that the satellite always crosses the Equator at the same local time. This type of orbit corresponds to the one of the MetOp platform, which carries onboard the IASI instrument that is used in this work. More details are given in chapter 4.

 $<sup>^{5}</sup>$ Angle formed by the vertical between the ground and the satellite and the sounder line of sight.



Figure 1.4.1: (Top) Passive and active soundings. In case of passive sounding, the Sun radiation reflected at the surface or backscattered to space by the atmosphere can be used to observe the atmosphere. Thermal emission of the Earth's surface and of the atmosphere can be other radiation sources. (Bottom) Three possible observation geometries for the satellite remote sensing of the Earth's atmosphere. Figures taken from Burrows et al. (2011).

• Geostationary orbits (GEO): on a GEO, the satellite circles the Earth at very high altitudes, around 36000 km. It is characterised by a rotational speed equal to the rotational speed of the Earth and therefore the sounder always scans the same area (disk) on Earth.

Both the viewing mode and the orbit of a satellite sounder determine its observation capability. Indeed, for example, a sounder orbiting on a LEO and observing the atmosphere

in the nadir mode reaches the quasi global coverage of the Earth and has a time resolution of 12 hours (when using a broad across-track scanning). On the contrary, a GEO limits the observation to a restricted area of the Earth, but offers a higher time resolution that can reach 30-60 minutes. The limb and occultation geometries provide a better vertical resolution than nadir sounding. Indeed, in these geometries, measurements are taken at different altitudes and allow retrieving the vertical distributions of atmospheric constituents. Nadir sounding provides an integrated measure of the whole atmospheric column and the retrieval of vertical profiles is in this case challenging (see chapters 2 and 3). However, the spatial resolution offered by nadir sounders is generally better than that of limb and occultation sounders. Finally, depending on the viewing mode, different parts of the atmosphere are probed. In case of limb and occultation measurements, the atmospheric region going from the high troposphere to the mesosphere/thermosphere is generally observed, whereas nadir observations provide information on the lower part of the atmosphere, i.e., on the troposphere and stratosphere.

# 1.4.3 Sounding the PBL composition from satellites

Measuring the composition of the PBL is essential for monitoring pollutants and, using the synergy with models, for quantifying anthropogenic emissions and understanding their impacts on our environment and climate (e.g., Laj et al., 2009). Satellite remote sensing is especially appealing for monitoring PBL pollution, as it allows acquiring spatial distributions of different trace species simultaneously and enables to evaluate their temporal variations (Martin, 2008). Sensing the PBL with satellites is however challenging as the concentrations of these gases are generally weak and confined to a small part of the atmospheric column. Moreover, the sounding of the PBL composition is only feasible in the nadir geometry. Several spectral ranges can however be used to retrieve PBL concentrations, going from the UV to the thermal infrared (TIR). In the following, we briefly present the achievements in the field of PBL sounding by satellites that were realised mainly before this work. The discussion is separated per spectral range, focusing especially on UV and TIR spectral ranges. Additional information for the applications included in this thesis are provided in part II and part III.

#### 1.4.3.1 Ultraviolet

Satellite instruments operating in the UV use the solar radiation that is backscattered to space to measure the concentrations of atmospheric species. This kind of sounders have similar sensitivity to the atmospheric column down to the surface. The extent of the sensitivity depends on the surface reflectivity, and increases with increasing reflectivity (Martin, 2008). Scattering in the atmosphere is another important parameter, which either increases or decreases the sensitivity to near-surface trace gases. Indeed, for example, scattering by clouds enhances the sensitivity to gases located above the cloud and decreases the sensitivity to the region below the cloud (Martin, 2008).

UV sounders have been used to derive the tropospheric column of NO<sub>2</sub>, which plays a crucial role in the formation of tropospheric O<sub>3</sub>, and then to determine the regions with the largest emissions. Note that 1) NO<sub>2</sub> has a short lifetime, and thus the measured tropospheric column is dominated by the PBL column of NO<sub>2</sub>, 2) the highest concentrations of NO<sub>2</sub> are found above urban and industrialised areas.

Measurements of  $SO_2$  emissions from anthropogenic sources have been achieved in the UV spectral range. This has notably been possible by the development of an operational

PBL OMI<sup>6</sup> product by NASA<sup>7</sup> (Krotkov et al. (2006, 2008), and see also http://disc. sci.gsfc.nasa.gov/Aura/data-holdings/OMI/omso2\_v003.shtml) or, more recently, of a new OMI algorithm by Theys et al. (2015) at BIRA<sup>8</sup>. Emissions from smelters (heavy metal extraction), power plants and volcanic degassing have successfully been identified and quantified (e.g., Fioletov et al., 2011, 2013).

#### 1.4.3.2 Thermal infrared

Sounders operating in the TIR use the thermal emission of the Earth's surface and of the atmosphere to measure the composition of the latter. As we will see in chapter 2, this kind of sounders have limited sensitivity to the PBL, because of generally low temperature contrast (called the *thermal contrast*, TC) between the ground and the air above it. They have however the advantage of being able to observe the atmosphere during night, compared to UV sounders.

Before the beginning of this PhD, it had already been demonstrated that TIR instruments were able to measure the composition of the PBL in case of large TC. One of the most important demonstration was provided by the retrieval of ammonia (NH<sub>3</sub>) distributions at local and global scales using the observations of the IASI instrument (Clarisse et al., 2009; Van Damme et al., 2014). NH<sub>3</sub> is indeed a short-lived species, which is mainly confined in the PBL. Furthermore, the results obtained during the Master thesis (Bauduin, 2012) have confirmed that TIR measurements, taken in conditions of high TC, can be exploited to infer PBL concentrations of trace species. Especially, by taking the advantage of large thermal inversions in the industrial area of Norilsk in winter, we were able to retrieve near-surface columns of SO<sub>2</sub> in this high polluted region. These results are reviewed in chapter 5 and Appendix B. Further analyses are performed in chapter 6. Evidence that TIR sounders carry information on near-surface CO in case of high TC was also provided in a series of studies using MOPITT<sup>9</sup> (e.g., Deeter et al., 2007; Clerbaux et al., 2008c; Kar et al., 2008) and IASI (e.g., George et al., 2009) instruments. This is something that we investigate more deeply in part III, by different types of characterisation and case studies.

<sup>&</sup>lt;sup>6</sup>Ozone Monitoring Instrument.

<sup>&</sup>lt;sup>7</sup>National Aeronautics and Space Administration.

<sup>&</sup>lt;sup>8</sup>Belgian Institute for Space Aeronomy.

 $<sup>^{9}\</sup>mathrm{Measurements}$  of Pollution in the Troposphere

# CHAPTER 2

#### RADIATIVE TRANSFER IN THE THERMAL INFRARED

In the previous chapter, we have described the Earth's atmosphere in terms of its vertical structure, composition and general circulation. We have defined different concepts, such as the relationship between the lifetime of an atmospheric constituent and its spatial mixing, that are useful in atmospheric sciences. We also have presented the general concepts of satellite remote sensing and reviewed some of earlier achievements made in the remote sensing of the PBL composition. In this chapter, we go deeper in the principles of satellite remote sensing in the nadir viewing mode and in the TIR spectral range, in which we are interested. More particularly, we derive and describe the radiative transfer equation in the TIR. This equation is central to this work, because it allows us to describe how TIR radiation interacts with the atmospheric constituents. It is also the basic equation of the forward model, which allows us to simulate the spectrum recorded by the IASI instrument. After defining in a first section the main variables and concepts that are needed, we then derive the radiative transfer equation in the TIR and discuss how this equation is solved. A last section is dedicated to the vertical sensitivity and information content of nadir TIR measurements; we discuss in this section the sensitivity of TIR sounders to the PBL composition.

## 2.1 Reminders and definitions

#### 2.1.1 Flux, radiance and solid angle

The flux and the radiance (also called radiant intensity) are two different measures of the strength of an electromagnetic radiation. They are related to each other by the solid angle. The flux, F, corresponds to the total energy that is incident on or passes through a flat surface per unit time and per unit area. It is expressed in units of J m<sup>-2</sup> s<sup>-1</sup>. A monochromatic flux,  $F_{\lambda}$ , can be defined as

$$F_{\lambda} = \lim_{\Delta \lambda \to 0} \frac{F(\lambda, \lambda + \Delta \lambda)}{\Delta \lambda}, \qquad (2.1.1)$$

where  $F(\lambda, \lambda + \Delta \lambda)$  is the flux calculated between the wavelengths  $\lambda$  and  $\lambda + \Delta \lambda$ . It is expressed in this case per unit wavelength. The flux is mostly used as a broadband quantity and results from the integration of the monochromatic flux over a certain spectral range  $[\lambda_1, \lambda_2]$ :

$$F(\lambda_1, \lambda_2) = \int_{\lambda_1}^{\lambda_2} F_{\lambda} \,\mathrm{d}\lambda. \tag{2.1.2}$$

It is important to note that the flux does not include any information about where the radiation is coming from and where it is going. It is the radiance that embodies the directional information of the radiation.

As said above, flux and radiance are related by the solid angle. The solid angle is the two-dimensional angle in the three-dimensional space that an object subtends at a point. It is a measure of how much of the visual field of view of an observer located at this point is occupied by the object, and is expressed in units of steradians (sr). With this definition, the radiance, I, is the flux measured on a surface normal to the beam, per unit solid angle and travelling in a particular direction (expressed as a vector  $\hat{\Omega}$ ). It is calculated as:

$$I(\hat{\mathbf{\Omega}}) = \frac{\delta F}{\delta \omega},\tag{2.1.3}$$

where  $\delta\omega$  is the solid angle in which a small element of scene is observed, and  $\delta F$  is the radiation flux arriving from that small region (measured on a surface normal to the beam). In addition to carrying directional information on the radiation, the radiance has also the property to be conserved along the optical path (within a vacuum or another transparent medium). The radiance is the fundamental quantity used in the radiative transfer calculations, as we will see in sections 2.2 and 2.3.

#### 2.1.2 Blackbody radiation and emissivity

As we have mentioned in chapter 1, the nadir satellite remote sensing in the TIR relies on the interaction of the thermal radiation emitted by the Earth's surface and the atmosphere with the gas species. This TIR emission from the ground and the atmosphere is represented as blackbody radiation. A *blackbody* is an object that perfectly absorbs the radiation, i.e., it absorbs the totality of radiation incident on its surface. The radiation of a blackbody is given by the Planck function and depends, at a given frequency or wavelength, only on its temperature. The Planck function, expressed as a function of wavelength<sup>1</sup>, is

$$B(\lambda, T) = \frac{2hc^2}{\lambda^5 \left[ \exp\left(\frac{hc}{k_B T \lambda}\right) - 1 \right]},$$
(2.1.4)

where  $\lambda$  is the wavelength, h is the Planck constant (6.626×10<sup>-34</sup> Js), and c is the speed of light (2.998×10<sup>8</sup> m s<sup>-1</sup>).  $B(\lambda, T)$  is the radiance emitted by a blackbody at temperature T and at wavelength  $\lambda$ . It is therefore expressed in J m<sup>-2</sup> sr<sup>-1</sup> m<sup>-1</sup> s<sup>-1</sup>.

The temperature of the body determines the wavelength of maximum emission  $(\lambda_{max})$  through the Wien law:

$$\lambda_{max} = \frac{2897}{T},\tag{2.1.5}$$

where  $\lambda_{max}$  has units of  $\mu$ m. The wavelength of maximum emission therefore decreases for increasing temperature. This is illustrated in Figure 2.1.1, which shows the blackbody radiation calculated for the Earth (blue) and Venus (red, divided by 50), considering averaged temperature respectively of 290 K and 737 K. The  $\lambda_{max}$  calculated for the two planets are 9.99  $\mu$ m and 3.93  $\mu$ m respectively for Earth and Venus, and are indicated.

 $<sup>^{1}</sup>$ The expression of the Planck function takes different forms depending on whether it is expressed as a function of wavelength, frequency or wavenumber (see Appendix A.1).



Figure 2.1.1: Blackbody radiances emitted by the Earth (blue) and Venus (red). For clarity, the radiance emitted by Venus has been divided by 50.

In addition to determine the wavelength of maximum emission, the temperature of the blackbody governs the total flux  $(F_{BB})$  of radiation emitted. Increasing temperature leads to increasing flux, and this is described by the Stefan-Boltzmann law:

$$F_{BB} = \sigma T^4, \tag{2.1.6}$$

where  $\sigma$  is the Stefan-Boltzmann constant equal to  $5.67 \times 10^{-8}$  W m<sup>-2</sup> K<sup>-4</sup>.

As mentioned, a blackbody is a theoretical object. All natural objects, such as the surface of the Earth, do not exactly behave as blackbodies and have for a given temperature a lower radiance than would have a blackbody. This deviation of a real object radiance from that of a blackbody is described by the *emissivity*. The monochromatic emissivity,  $\epsilon(\lambda)$ , is the ratio between the radiance emitted by a real surface at the wavelength  $\lambda$ , and the radiance that it would emit at this same wavelength if it was a blackbody:

$$\epsilon(\lambda) = \frac{I(\lambda)}{B(\lambda, T)}.$$
(2.1.7)

Depending on the type of the surface, the deviation from the blackbody emission can be large. The emissivity of certain surfaces can also strongly vary with the wavelength and can present sharp spectral features. This is for instance the case of deserts, whose emissivity is characterised by a spectral feature in the 8–10  $\mu$ m spectral range typical of silica. This is illustrated in Figure 2.1.2. Because it gives the radiance from the light source at the beginning of the optical path, the emissivity of the Earth surface is an important parameter that has to be taken into account in radiative transfer calculations to properly simulate nadir satellite TIR observations.

As a final remark, through the Planck function, there is an unequivocal relationship between the radiance and the temperature. For some applications it may be convenient to convert measured radiances into the equivalent blackbody temperature, which is called *brightness temperature*, BT. This conversion is performed using the following relation, regardless of the source:

$$BT = \frac{hc}{k\lambda} \frac{1}{\ln\left(\frac{1}{I(\lambda)}\frac{2hc^2}{\lambda^5} + 1\right)}.$$
(2.1.8)



Figure 2.1.2: Emissivity retrieved from IASI above the Sahara desert in June (Zhou et al., 2011).

#### 2.1.3 Beer-Lambert's law and absorption coefficient

As we have already mentioned above, the satellite remote sensing in the TIR relies on the interaction between the TIR radiation (emitted as blackbody radiation by the Earth and the atmosphere) and the atmospheric constituents. This interaction includes absorption of radiation by these constituents<sup>2</sup>, and is described by the Beer-Lambert law (Petty, 2006). Let's consider a monochromatic radiation that passes through a sample constituted of one gas X homogeneously mixed, and characterised by constant temperature T and pressure P. Let's also consider that radiation crosses this sample in an infinitesimal path ds (Figure 2.1.3). The attenuation of the radiance,  $dI(\tilde{\nu})$ , due to the absorption of X, is given by

$$dI(\tilde{\nu}) = I(\tilde{\nu}, s + ds) - I(\tilde{\nu}, s) = -\alpha_X(\tilde{\nu}, T, P) I(\tilde{\nu}, s) ds, \qquad (2.1.9)$$

where  $I(\tilde{\nu}, s)$  and  $I(\tilde{\nu}, s + ds)$  are respectively the incoming and outgoing radiances, and  $\alpha_X(\tilde{\nu}, T, P)$  is the absorption coefficient (in cm<sup>-1</sup>) of X at wavenumber  $\tilde{\nu}$  (cm<sup>-1</sup>), temperature T and pressure P. Equation (2.1.9) can be rewritten as

$$\frac{\mathrm{d}I(\tilde{\nu})}{I(\tilde{\nu},s)} = -\alpha_X(\tilde{\nu},T,P)\,\mathrm{d}s,\tag{2.1.10}$$

and the total attenuation of the radiance, due to absorption in the whole sample of X, is given by integrating this new equation over the extended path  $[s_1, s_2]$ :

$$\int_{I(\tilde{\nu},s_1)}^{I(\tilde{\nu},s_2)} \frac{\mathrm{d}I(\tilde{\nu})}{I(\tilde{\nu},s)} = \int_{s_1}^{s_2} -\alpha_X(\tilde{\nu},T,P) \,\mathrm{d}s, \qquad (2.1.11)$$

which gives

$$I(\tilde{\nu}, s_2) = I(\tilde{\nu}, s_1) \exp\left[-\alpha_X(\tilde{\nu}, T, P) l\right], \qquad (2.1.12)$$

where l is the length of the path defined between  $s_1$  and  $s_2$ .

 $<sup>^{2}</sup>$ Note that emission and scattering of radiation are also part of the interaction but are neglected here. Note also that clear sky scenes have been studied in this work; the atmosphere can thus be considered as a non-scattering medium.



Figure 2.1.3: Attenuation of radiation due to the absorption of a sample of one gas X homogeneously mixed, at a constant temperature T and pressure P. Figure based on Petty (2006).

Equation (2.1.12) is Beer-Lambert's law, from which we can make some important remarks:

1. The transmittance,  $t(\tilde{\nu}, s_1, s_2)$ , of the sample of X between  $s_1$  and  $s_2$  at wavenumber  $\tilde{\nu}$  is defined as

$$t(\tilde{\nu}, s_1, s_2) = \exp\left[-\alpha_X(\tilde{\nu}, T, P) l\right].$$
(2.1.13)

It is a dimensionless quantity that represents the percentage of radiation that is transmitted by the sample between  $s_1$  and  $s_2$ . If we consider an extended sample of X $(s_1-s_N)$ , divided in several layers  $(s_1-s_2,...,s_{N-1}-s_N)$ , the total transmittance equals the product of the transmittances of each layer:

$$t(\tilde{\nu}, s_1, s_N) = \prod_{i=1}^{N-1} t(\tilde{\nu}, s_i, s_{i+1}).$$
(2.1.14)

2. The transmittance depends on the length of the sample. However, it also depends on the number of density of  $X(\rho_X)$  in the sample. This dependence is hidden in the absorption coefficient, which can be expressed as

$$\alpha_X(\tilde{\nu}, T, P) = \rho_X \,\sigma_X(\tilde{\nu}, T, P), \qquad (2.1.15)$$

where  $\sigma_X(\tilde{\nu}, T, P)$  is the absorption cross section of X (in cm<sup>2</sup> molecule<sup>-1</sup>).

In the above discussion, we have described the extinction of radiation, due to the absorption of a gas X homogeneously mixed in a sample of length l, using the Beer-Lambert law. It is worth noting that this corresponds to the simplest case of radiative transfer. Indeed, in the case of the Earth's atmosphere, we will have to take into account the variations of temperature, pressure and gases concentrations with height, to consider the absorption of several gases and to include the emission of the atmosphere. This is will be explained further in sections 2.2 and 2.3.

#### 2.1.4 Quantization of energy states and lines description

Spectroscopy studies the interaction between radiation and matter. It relies on two fundamental principles:

• The radiation can be defined as made of quantised particles, called *photons*, whose energy E is given by

$$E = h\nu = \frac{hc}{\lambda} = hc\tilde{\nu}, \qquad (2.1.16)$$

where  $\nu$  is the photon frequency (s<sup>-1</sup>).

• The internal energy in the matter is also quantised, and presents only certain permitted values, which are dependent on the molecular system. These define the energy levels of the system.

Absorption and emission of radiation by a molecular system thus involve transitions between the energy levels. Only photons that have an energy exactly equal to the energy difference between the levels of the system are absorbed (emitted). Because the energy levels are dependent on the molecular system, the interaction with the radiation is unique for each system. Registering the wavenumbers for which radiation is absorbed/emitted (i.e., measuring the spectrum of the system) allows characterising the chemical nature of the system and, measuring the strength of the absorption (emission) allows quantifying the system. This is the basis of the method employed by the satellite remote sensing to study the composition of the Earth's atmosphere. In the following sections, we develop further the notion of energy levels. We also give a thorough description of spectral lines, which will be required to solve the radiative transfer equation.

#### 2.1.4.1 Energy states

A molecule is characterised by different types of energy levels, which are illustrated in Figure 2.1.4. We distinguish the **electronic levels**, associated to the distribution of the electrons, the **vibrational levels**, associated to the vibration of the molecule, and the **rotational levels**, associated to the rotation of the molecule. As illustrated in Figure 2.1.4, one electronic level includes several vibrational levels, each including rotational levels. This implies that the energy required for the transition between two electronic states is the largest, and is the lowest for rotational transitions. Typically, UV-visible radiation is needed to allow a molecule to change of electronic states. Vibrational and rotational transitions usually require respectively IR and microwave radiations. Because this work relies entirely on the TIR remote sensing, we focus the following discussion on the vibration and rotation only.



Figure 2.1.4: Most simplified illustration of the different types of energy levels encoutered in a molecular system. One distinguishes electronic levels (green), vibrational levels (red) and rotational levels (blue).

To understand the rotation-vibration structure of the spectrum of a molecule, we need to determine the energy of vibrational and rotational states.

#### 1. Vibration

Usually, the vibration of a molecule is described using a finite set of what we call *normal modes*. Each normal mode corresponds to a particular vibrational motion and is considered independent of the others. The vibration is then described by one or a combination of normal modes. A normal mode that takes part in the vibrational motion is said *excited*. The number of normal modes defined for a molecule depends on the number of atoms N that compose the molecule. If the molecule is linear, the number of normal modes is 3N - 5 and in all the other cases, it is equal to 3N-6. For example, CO is a diatomic molecule and has only one normal mode, which corresponds to the stretch of the C-O bond. SO<sub>2</sub> is a non-linear triatomic molecule and has therefore 3 vibrational normal modes, which are illustrated in Figure 2.1.5. They correspond to the symmetric stretch of the S-O bonds ( $\nu_1$ ), the bending of the molecule ( $\nu_2$ ) and the asymmetric stretch of the S-O bonds ( $\nu_3$ ).



Figure 2.1.5: Vibrational normal modes of  $SO_2$ .

In case of a diatomic molecule (one vibrational mode), such as CO, we can show that the energy of each vibrational level,  $E_V$ , can be expressed as (Demtröder, 2010)

$$E_V = \omega \left( v + \frac{1}{2} \right) - x \left( v + \frac{1}{2} \right)^2 + \dots,$$
 (2.1.17)

where  $\omega$  is the harmonic frequency of the vibrational mode, x is its first anharmonicity correction, and v is the quantum number associated to the vibration mode. For polyatomic molecules<sup>3</sup>, the energy of a vibrational level is the sum of the energy of each vibrational normal modes excited, and is given by (Demtröder, 2010)

$$E_V = \sum_i \omega_i \left( v_i + \frac{d_i}{2} \right) + \sum_i \sum_{j \ge i} x_{ij} \left( v_i + \frac{d_i}{2} \right) \left( v_j + \frac{d_j}{2} \right) + \dots, \qquad (2.1.18)$$

where i and j refers to the normal modes, and  $d_i$  is the degeneracy of normal mode i. Each vibrational level is defined by the values of the quantum numbers associated to

 $<sup>^{3}\</sup>mathrm{We}$  consider here only non-linear molecules.

all the normal modes of the molecule; it is identified by the sequence  $(v_1 v_2 \ldots v_{3N-6})$ . For example, the first vibrational level corresponding to the excitation of the  $v_1$  mode of SO<sub>2</sub> is written (100).

From equation (2.1.18), we can calculate the energy of the transition between two vibrational states. It is called the *origin of the band*,  $\Delta E_V$ , and corresponds to the difference between the energy of the two levels:

$$\Delta E_V = E_V(v_1' \, v_2' \, \dots \, v_{3N-6}') - E_V(v_1'' \, v_2'' \, \dots \, v_{3N-6}''), \qquad (2.1.19)$$

where ' and " refer respectively to the upper and lower energy states. Vibrational transitions correspond to changes in the vibrational quantum numbers  $(\Delta v_i)$ . Vibrational bands corresponding to the change of one quantum number are called *fundamental* if  $\Delta v_i = 1$ , and *overtone* if  $\Delta v_i > 1$ . Bands corresponding to the change of more than one quantum number are called *combination bands*. If the lower level is the vibrational ground state, bands are identified using the relation  $\sum_i \Delta v_i \nu_i$ . If the band corresponds to a transition between two excited states, it is called a *hot band* and is identified using  $\sum_i \Delta v'_i \nu'_i - \sum_i \Delta v''_i \nu''_i$ .

#### 2. Rotation

In addition to vibrate, molecules also rotate and have internal energy levels of rotation. One can show that the energy of a rotational state,  $E_R$ , of a linear molecule is given by (Demtröder, 2010):

$$E_R = BJ(J+1) - DJ^2(J+1)^2 + \dots$$
 with  $B(\text{cm}^{-1}) = \frac{h}{8\pi^2 cI_m}$ , (2.1.20)

the principal rotational constant, D is the constant of centrifugal distortion, and J is the quantum number associated to the total angular momentum of the molecule. One value of J identifies each rotational level. In the expression of B,  $I_m$  is the moment of inertia of the molecule. In case of non-linear molecules, such as SO<sub>2</sub>, the expression of the energy is different, but rotational energy states remain identified among other by the quantum number J (Demtröder, 2010).

Similarly to what we have done for vibration, we can calculate the energy of the rotational transition  $(\Delta E_R)$ . It is equal to the difference between the energies of the two rotational states implied in the transition:

$$\Delta E_R = E_R(J') - E_R(J''). \tag{2.1.21}$$

Rotational transitions are associated to a variation of the quantum number J (expressed as  $\Delta J$ ).

#### 3. Vibration-rotation

In the beginning of this section, we have mentioned that IR radiation induces vibrational transitions in molecules. We have also explained that each vibrational state includes several rotational levels with a certain energy. Vibrational transitions correspond therefore to transitions between rotational states of two different levels of vibration. This is illustrated in the top panel of Figure 2.1.6. The energy of a rotational state belonging to a vibrational level  $(E_{VR})$  is given by the sum of their respective energy

$$E_{VR} = E_V(v_1 \, v_2 \, \dots \, v_{3N-6}) + E_R(J), \qquad (2.1.22)$$



Figure 2.1.6: (Top) Vibration-rotation allowed transitions. Transitions associated to a  $\Delta J = 1$  define the R-branch of the vibrational band. Those associated to a  $\Delta J = -1$  define the P-branch. A third branch, the Q-branch, may be present and is associated to  $\Delta J = 0$ . Figure taken from Liou (2002). (Bottom) 1–0 vibrational band of CO. The y-axis correspond to the integrated absorption cross section reported in *HITRAN* 2008, as defined in subsection 2.1.4.2.

and the energy of the vibration-rotation transition is given by the difference between the energy of the two vibration-rotation levels implied:

$$\Delta E_{VR} = E_V(v_1' v_2' \dots v_{3N-6}') + E_R(J') - E_V(v_1'' v_2'' \dots v_{3N-6}'') - E_R(J''). \quad (2.1.23)$$

Through equation (2.1.16),  $\Delta E_{VR}$  is related to the wavenumber; each transition is associated with a wavenumber that defines the position of the line in the spectrum (see subsection 2.1.4.2). Note also that the rotational constants vary with the vibrational state.

The vibration-rotation transitions produce a particular structure in the spectrum (see Figure 2.1.6). The vibrational band is indeed divided in different branches. Transitions associated to a change  $\Delta J = +1$  define the R-branch, which evolves from the band center towards the higher wavenumbers. Transitions associated to a change  $\Delta J = -1$  define the P-branch, which evolves in the opposite direction. Each spectral line is identified as R(J'') or P(J''). A third branch may be present in the vibrational band, and corresponds to a Q-branch defined by  $\Delta J = 0$ .

#### 2.1.4.2 Lines description

In the previous section, we have described the vibration-rotation spectrum of molecules and we have seen that the implied transitions are associated to spectral lines. These lines are described according to three parameters: their position, their shape and their intensity. These are presented hereafter (see also Demtröder (2010)):

#### 1. Line position

The position of a spectral line determines where it appears in the electromagnetic spectrum. It is expressed either in wavelength, frequency or wavenumber. In case of vibration-rotation transitions, the lines are usually in the IR part of the electromagnetic spectrum, and their positions are determined using equation (2.1.23).

In the following, for simplicity, we will consider the general case of a transition between two levels of energies  $E_i$  and  $E_j$ , such that  $E_i < E_j$ . The position of the line, in wavenumber, is in this case written  $\tilde{\nu}_{ij}$ .

#### 2. Line shape

In addition to the position, a spectral line presents a certain shape, which is characterised by the half width at half maximum (HWHM),  $\gamma$  (cm<sup>-1</sup>). Considering the transition  $E_i \rightarrow E_j$ , the natural shape<sup>4</sup> of the line located at  $\tilde{\nu}_{ij}$  presents a Lorentz profile  $f_L(\tilde{\nu} - \tilde{\nu}_{ij})$ :

$$f_L(\tilde{\nu} - \tilde{\nu}_{ij}) = \frac{1}{\pi} \frac{\gamma}{(\tilde{\nu} - \tilde{\nu}_{ij})^2 + \gamma^2},$$
 (2.1.24)

where  $\gamma$  is called the *natural width* and is related to the lifetime of the excited energy levels.

Different phenomena contribute to broaden the width of measured spectral lines beyond the natural line profile. One of these is the broadening due to molecules collisions and is therefore driven by the pressure. In this case, the line shape still shows a Lorentz-type profile (Figure 2.1.7, red) but its HWHM, now called  $\gamma_L$ , includes an additional term proportional to pressure. Moreover, the pressure broadening is also

<sup>&</sup>lt;sup>4</sup>We refer here to the shape of a line in case of no pressure and no Doppler broadening.

accompanied by a shift of the Lorentz profile,  $\Delta \tilde{\nu}$ . Taking into account these effects, equation (2.1.24) can be rewritten as

$$f_L(\tilde{\nu} - \tilde{\nu}_{ij}) = \frac{1}{\pi} \frac{\gamma_L}{(\tilde{\nu} - \tilde{\nu}_{ij} - \Delta \tilde{\nu})^2 + \gamma_L^2}.$$
(2.1.25)

For a pure sample of gas at pressure  $P, \Delta \tilde{\nu}$  is expressed as

$$\Delta \tilde{\nu} = \delta_0 P, \qquad (2.1.26)$$

where  $\delta_0$  is the pressure shift parameter (cm<sup>-1</sup> atm<sup>-1</sup>). Because in most cases the natural broadening is negligible compared with the collision broadening,  $\gamma_L$  can be expressed only as a function of pressure. In case of a pure sample of gas at pressure P,  $\gamma_L$  is given by

$$\gamma_L = \gamma_0^s P, \qquad (2.1.27)$$

where  $\gamma_0^s$  is the self-broadening parameter (cm<sup>-1</sup> atm<sup>-1</sup>). In case of a given species in a sample of air at a total pressure  $P_{tot}$ ,  $\gamma_L$  is expressed as

$$\gamma_L = \left[\gamma_0^s q + \gamma_0^{air}(1-q)\right] P_{tot}, \qquad (2.1.28)$$

where q is the VMR of the gas implied in the transition, and  $\gamma_0^{air}$  is the pressure broadening parameter of the air.

Another phenomenon that contributes to the broadening of the lines is the *Doppler effect*. At low pressure, it dominates the pressure broadening. It is related to the relative motions of molecules compared to the source: motions towards or away from the source induce a shift of the apparent wavenumber of the absorbed radiation, and contribute therefore to the broadening of the line. At thermodynamic equilibrium, the Doppler profile is described by a Gaussian function (Figure 2.1.7, blue) according to

$$f_D(\tilde{\nu} - \tilde{\nu}_{ij}) = \sqrt{\frac{\ln 2}{\pi}} \frac{1}{\gamma_D} \exp\left[-\ln 2\left(\frac{\tilde{\nu} - \tilde{\nu}_{ij}}{\gamma_D}\right)^2\right], \qquad (2.1.29)$$

where  $\gamma_D$  is the HWHM of the Doppler profile, and is given by

$$\gamma_D = 3.581 \, 10^{-7} \, \tilde{\nu}_{ij} \sqrt{\frac{T}{M}},\tag{2.1.30}$$

with M and T corresponding respectively to the molar mass and the temperature of the sample of gas.

For the Earth's atmosphere, both Doppler and pressure broadening have to be taken into account. The combined Doppler and pressure broadening gives the line a particular shape, that can be modelled by a so-called *Voigt* profile (Figure 2.1.7, green),  $f_V(\tilde{\nu} - \tilde{\nu}_{ij})$ . It is obtained by the convolution of the Lorentz (equation (2.1.25)) and Gaussian (equation (2.1.29)) functions:

$$f_V(\tilde{\nu} - \tilde{\nu}_{ij}) = f_D(\tilde{\nu}) \otimes f_L(\tilde{\nu} - \tilde{\nu}_{ij}) = \int_{-\infty}^{\infty} f_D(\tilde{\nu}') f_L(\tilde{\nu} - \tilde{\nu}_{ij} - \tilde{\nu}') \,\mathrm{d}\tilde{\nu}'.$$
(2.1.31)

There is no exact analytical expression for the HWHM  $\gamma_V$  of the Voigt profile.



Figure 2.1.7: Doppler (blue), Lorentz (red) and Voigt (green) line profiles.  $\gamma_D$  and  $\gamma_L$  have been taken equal to 1.

#### 3. Line intensity

In subsection 2.1.3, we have seen that the amount of radiation absorbed depends on the number of density of the sample. However, independently on the quantity of the gas, we can define an intensity for the spectral line. This intensity is represented through the absorption cross section  $\sigma(\tilde{\nu})$ , which depends on the wavenumber. A related useful parameter is the *integrated absorption cross section*,  $\sigma_{ij}$ , defined for each line as

$$\sigma_{ij} = \int_0^\infty \sigma(\tilde{\nu}) \,\mathrm{d}\tilde{\nu}.$$
 (2.1.32)

Considering a normalized line profile  $f(\tilde{\nu} - \tilde{\nu}_{ij})$ , we can also write

$$\sigma(\tilde{\nu}) = \sigma_{ij} f(\tilde{\nu} - \tilde{\nu}_{ij}). \tag{2.1.33}$$

 $\sigma_{ij}$  corresponds therefore to the area subtended by the line profile, and is generally referred to as the line intensity. It has units of cm<sup>2</sup> molecule<sup>-1</sup> cm<sup>-1</sup> and depends on the temperature. In the following,  $\sigma_{ij}$  will be written  $\sigma_{ij}^{int}$  to avoid confusion with the absorption cross section  $\sigma(\tilde{\nu})$ .

All the line parameters described in this section (position, pressure broadening parameters,...) are required to compute the absorption coefficient, itself needed in the radiative transfer calculations. These parameters are measured in laboratory and collected in spectroscopic databases. In this work, we have used the 2008 *HITRAN* database (Rothman et al., 2009).

# 2.2 The Schwarzschild equation

In subsection 2.1.3, we have described the absorption of radiation by a sample constituted of a well-mixed gas by the Beer-Lambert law. As we mentioned, this example is the simplest case of radiative transfer and did not take into account the emission from the sample itself.

Let's now extent the previous formulation by including the emission. For this, we consider a non-scattering layer of air in local thermodynamic equilibrium (LTE) of infinitesimal thickness ds, and an incoming radiation  $I(\tilde{\nu})$  (Petty, 2006). This layer absorbs a part of the radiation, and the reduction of the radiance,  $dI_{abs}(\tilde{\nu})$ , is obtained thanks to equation (2.1.9), and is written

$$dI_{abs}(\tilde{\nu}) = -\alpha_{tot}(\tilde{\nu}, T, P) I(\tilde{\nu}) ds, \qquad (2.2.1)$$

where  $\alpha_{tot}(\tilde{\nu}, T, P)$  is the total absorption coefficient of the air layer at temperature T and pressure P (see below). The amount of radiation  $dI_{em}(\tilde{\nu})$  emitted by the layer of air can be expressed using an *emission coefficient*,  $J(\tilde{\nu})$  (Thorne et al., 1999) as follows:

$$dI_{em}(\tilde{\nu}) = J(\tilde{\nu}) \,\mathrm{d}s. \tag{2.2.2}$$

The net change of radiance,  $dI(\tilde{\nu})$ , is then

$$dI(\tilde{\nu}) = dI_{abs}(\tilde{\nu}) + dI_{em}(\tilde{\nu}) = -\alpha_{tot}(\tilde{\nu}, T, P) \ I(\tilde{\nu}) \, ds + J(\tilde{\nu}) \, ds.$$
(2.2.3)

We can now define a new quantity called the *source function* as the ratio of the emission and absorption coefficients:

$$S(\tilde{\nu}) = \frac{J(\tilde{\nu})}{\alpha_{tot}(\tilde{\nu})}.$$
(2.2.4)

Using the source function, we can rewrite equation (2.2.3) as

$$\frac{\mathrm{d}I(\tilde{\nu})}{\mathrm{d}s} = \alpha_{tot}(\tilde{\nu}, T, P) \left[ S(\tilde{\nu}) - I(\tilde{\nu}) \right].$$
(2.2.5)

Because we consider a non-scattering medium at LTE, the source function is simply equal to the Planck function (see Appendix A), and therefore equation (2.2.5) can be rewritten as

$$\frac{\mathrm{d}I(\tilde{\nu})}{\mathrm{d}s} = \alpha_{tot}(\tilde{\nu}, T, P) \left[ B(\tilde{\nu}, T) - I(\tilde{\nu}) \right].$$
(2.2.6)

This equation is the Schwarzschild equation. It is the most fundamental radiative transfer equation, from which some important remarks can be made:

- If we consider that the incoming radiation  $I(\tilde{\nu})$  is also a blackbody radiation (emitted for example by the Sun or by the Earth), it can be expressed by a Planck function at a certain temperature  $T_{BB}$  (considering an emissivity of 1). We therefore see that if  $T = T_{BB}$ , there is no net change of radiance. The outgoing radiance is identical to the incoming radiance and, in this case, is that of a blackbody at temperature T. There is therefore no spectral lines in the outgoing spectrum for any value of the absorption coefficient. This remark will be of particular importance in subsection 2.4.4 where we will discuss the sensitivity of TIR sounders to the composition of the PBL.
- Following the previous comment, using the same example, if  $T < T_{BB}$ , the net change of the radiance is negative. The fraction of absorbed radiance is larger than the fraction emitted. This means that the outgoing radiance presents spectral lines in absorption. On the contrary, if  $T > T_{BB}$ , the net change of the radiance is positive. The fraction of emitted radiance is larger than the absorbed one and the outgoing radiance presents spectral lines in emission.
- The total absorption coefficient  $\alpha_{tot}(\tilde{\nu}, T, P)$  can be expressed as a sum of the absorption coefficients of all the gases present in the layer:

$$\alpha_{tot}(\tilde{\nu}, T, P) = \sum_{j,k} \alpha_{j,k}(\tilde{\nu}, T, P), \qquad (2.2.7)$$

where j refers to the molecular species, and k refers to the relevant absorption lines at wavenumber  $\tilde{\nu}$ . Using equations (2.1.15) and (2.1.33), we can rewrite equation (2.2.7) as

$$\alpha_{tot}(\tilde{\nu}, T, P) = \sum_{j,k} \rho_j \,\sigma_{j,k}(\tilde{\nu}) = \sum_{j,k} \rho_j \,\sigma_{j,k}^{int} \,f(\tilde{\nu} - \tilde{\nu_k}, T, P), \qquad (2.2.8)$$

where  $\tilde{\nu_k}$  is the position of the line k.

In Appendix A, the expressions of  $\alpha_{tot}(\tilde{\nu})$  and  $J(\tilde{\nu})$  as functions of the Einstein coefficients are derived for a two-level system.

# 2.3 Radiative transfer equation in the TIR

#### 2.3.1 Derivation

The Schwarzschild equation describes the radiative transfer in an infinitesimal path of the atmosphere. From this equation, we can derive the general equation of the radiative transfer through a medium of finite length such as the atmosphere (Petty, 2006). In the framework of this work, we will derive this equation for the particular case of a nadir TIR sounder, i.e., looking downward through the atmosphere at the upwelling radiance from the surface. For this, let's consider a path starting at the ground  $(s_0)$  and ending at the top of the atmosphere  $(S_{\text{TOA}})$ . Let's now introduce the optical depth between an arbitrary point *s* and  $S_{\text{TOA}}$  as

$$\tau(\tilde{\nu}, s, S_{\text{TOA}}) = \int_{s}^{S_{\text{TOA}}} \alpha_{tot}(\tilde{\nu}, s') \, \mathrm{d}s' \qquad \text{with} \qquad \alpha_{tot}(\tilde{\nu}, s') \equiv \alpha_{tot}(\tilde{\nu}, T(s'), P(s')).$$
(2.3.1)

According to this definition, we have  $\tau(\tilde{\nu}, S_{\text{TOA}}, S_{\text{TOA}}) = 0$  and we can define  $\tau(\tilde{\nu}, s_0, S_{\text{TOA}}) = \tau_0$ . For simplicity, all the dependences will be omitted in the following development. By differentiating equation (2.3.1), we have

$$\mathrm{d}\tau = -\alpha_{tot}\,\mathrm{d}s.\tag{2.3.2}$$

This equation can be substituted into the Schwarzschild's equation, and by multiplying both sides by  $\exp(-\tau)$ , we obtain

$$\exp(-\tau) \frac{\mathrm{d}I}{\mathrm{d}\tau} = \exp(-\tau) I - \exp(-\tau) B.$$
(2.3.3)

By noting that

$$\frac{\mathrm{d}}{\mathrm{d}\tau} \Big[ I \, \exp(-\tau) \Big] = \exp(-\tau) \, \frac{\mathrm{d}I}{\mathrm{d}\tau} - I \, \exp(-\tau), \tag{2.3.4}$$

we can rewrite equation (2.3.3) as

$$\frac{\mathrm{d}}{\mathrm{d}\tau} \Big[ I \, \exp(-\tau) \Big] = -B \, \exp(-\tau). \tag{2.3.5}$$

This equation can then be integrated with respect to  $\tau$  between the sensor ( $\tau = 0$ ) and the ground ( $\tau = \tau_0$ ) following

$$\int_0^{\tau_0} \frac{\mathrm{d}}{\mathrm{d}\tau} \Big[ I \, \exp(-\tau) \Big] \, \mathrm{d}\tau = -\int_0^{\tau_0} B \, \exp(-\tau) \, \mathrm{d}\tau, \tag{2.3.6}$$

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and this gives

$$I(0) = I(\tau_0) \exp(-\tau_0) + \int_0^{\tau_0} B \exp(-\tau) \,\mathrm{d}\tau.$$
 (2.3.7)

This equation is the radiative transfer equation in optical depth units. However, it is more convenient to express it in units of height. Recalling equation (2.1.13), we can write

$$t(\tilde{\nu}, s, S_{\text{TOA}}) = \exp\left[-\int_{s}^{S_{\text{TOA}}} \alpha_{tot}(\tilde{\nu}, s') \,\mathrm{d}s'\right] = \exp\left[-\tau(\tilde{\nu}, s, S_{\text{TOA}})\right],\tag{2.3.8}$$

and by noting that

$$d\tau = -\frac{dt}{t}$$
 and  $dt = \frac{dt}{ds} ds$ , (2.3.9)

we can rewrite equation (2.3.7) as

$$I(\tilde{\nu}, S_{\text{TOA}}) = I(\tilde{\nu}, s_0) t(\tilde{\nu}, s_0, S_{\text{TOA}}) + \int_{s_0}^{S_{\text{TOA}}} B(\tilde{\nu}, s) \frac{\mathrm{d}t(\tilde{\nu}, s, S_{\text{TOA}})}{\mathrm{d}s} \,\mathrm{d}s.$$
(2.3.10)

The path s between the ground and the sounder can be expressed as a function of the altitude z and of the zenith angle  $\theta$ . By doing the proper change of variable and considering that the altitudes of the ground and of the top of the atmosphere are respectively 0 and  $z_{\text{TOA}}$ , we finally obtain the radiative transfer equation as a function of height

$$I(\tilde{\nu},\theta,z_{\text{TOA}}) = I(\tilde{\nu},\theta,0) t(\tilde{\nu},\theta,0,z_{\text{TOA}}) + \int_0^{z_{\text{TOA}}} B(\tilde{\nu},T(z)) \frac{\mathrm{d}t(\tilde{\nu},\theta,z,z_{\text{TOA}})}{\mathrm{d}z} \mathrm{d}z \,, \quad (2.3.11)$$

where the transmittance  $t(\tilde{\nu}, \theta, z, z_{\text{TOA}})$  is now defined according to

$$t(\tilde{\nu}, \theta, z, z_{\text{TOA}}) = \exp\left[-\int_{z}^{z_{\text{TOA}}} \alpha_{tot}(\tilde{\nu}, z') \frac{\partial s}{\partial z'} \,\mathrm{d}z'\right].$$
(2.3.12)

The equation (2.3.11) of the radiative transfer thus describes the radiance measured by the nadir TIR sounder as the sum of two contributions:

- 1. The absorption by the atmosphere of the radiation emitted by the Earth's surface. This is represented by the first term in the right hand side of equation (2.3.11).
- 2. The thermal emission of each layer of the atmosphere, which is absorbed by the layers located above. This is represented by the integral of equation (2.3.11).

Moreover, the radiative transfer equation tells us that if a part of the atmosphere is opaque  $(t \approx 0)$ , the sounder only observes the atmosphere located above the opaque layer. A further discussion about the sensitivity of nadir TIR sounders is given in section 2.4.

#### 2.3.2 Resolution

In the beginning of this chapter, we mentioned that we need in this work to solve the radiative transfer equation to simulate IASI spectra. This means that we need to calculate the TOA radiance  $I(\tilde{\nu}, \theta, z_{\text{TOA}})$  for the observation geometry of the instrument. The first step is thus the determination of the path s of the light as a function of z and  $\theta$ , and is called the *ray tracing*. In the approximation of a plane-parallel atmosphere, s is simply expressed as

$$s = \frac{z}{\cos \theta}.\tag{2.3.13}$$

A more complete description of s takes in addition into account the radius of the curvature of the Earth and the index of refraction of air (Hurtmans et al., 2012).

Then, the atmosphere is discretised in a number N of layers, defined by N + 1 levels, for which averaged parameters are calculated. The thickness  $L_i$ , the partial column  $PC_{i,j}$ of molecular specie j, the averaged temperature  $\overline{T}_i$  and the averaged pressure  $\overline{P}_i$  of layer iare respectively computed using the following equations:

$$L_i = \int_{z_i}^{z_{i+1}} \frac{\partial s}{\partial z} \,\mathrm{d}z; \qquad (2.3.14)$$

$$PC_{i,j} = \int_{z_i}^{z_{i+1}} \rho_j(z) \frac{\partial s}{\partial z} \,\mathrm{d}z; \qquad (2.3.15)$$

$$\overline{T}_{i} = \frac{\int_{z_{i}}^{z_{i+1}} T(z) \frac{\partial s}{\partial z} dz}{\int_{z_{i}}^{z_{i+1}} \frac{\partial s}{\partial z} dz}; \qquad (2.3.16)$$

$$\overline{P}_{i} = \frac{\int_{z_{i}}^{z_{i+1}} P(z) \frac{\partial s}{\partial z} dz}{\int_{z_{i}}^{z_{i+1}} \frac{\partial s}{\partial z} dz}.$$
(2.3.17)

The upwelling radiance is then evaluated for each layer according to ( $\tilde{\nu}$ ,  $\theta$  and z dependences omitted)

$$I_i = B(\overline{T}_i) + \left(I_{i-1} - B(\overline{T}_i)\right)\overline{t}_i, \qquad (2.3.18)$$

where  $\bar{t}_i$  is the effective transmittance of layer *i* and is calculated using

$$\overline{t}_{i} = \exp\left[-\sum_{j} PC_{i,j} \sum_{j,k} \sigma_{j,k}(\widetilde{\nu}, \overline{T}_{i}, \overline{P}_{i})\right] \\
= \exp\left[-\sum_{j} PC_{i,j} \sum_{j,k} \sigma_{j,k}^{int} f_{V}(\widetilde{\nu} - \widetilde{\nu}_{k}, \overline{T}_{i}, \overline{P}_{i})\right].$$
(2.3.19)

As mentioned in subsection 2.1.4.2, the line parameters are taken from the 2008 *HITRAN* database and adapted to the temperature of the atmosphere (Herzberg, 1945). For heavy molecular species (e.g., CFCs), the spectral lines are usually not resolved in laboratory. Absorption cross sections are in this case used instead of the line parameters. If they have been measured for different couples of temperature and pressure, those closest to the atmospheric conditions in the layer are chosen. The transmittance calculation takes finally into account the continua of  $H_2O$ ,  $O_2$ ,  $N_2$  and  $CO_2$  (Clough et al., 2005).

The last term that needs to be calculated is the radiance source  $I(\tilde{\nu}, \theta, 0)$ , i.e., that of the Earth's surface. This term can be computed as

$$I(\tilde{\nu},\theta,0) = \epsilon(\tilde{\nu}) B(\tilde{\nu},T_S) + (1-\epsilon(\tilde{\nu})) I_{atm}^{\downarrow}(\tilde{\nu}) + r(\tilde{\nu},\theta) I_{sun}^{\downarrow}, \qquad (2.3.20)$$

where  $T_S$  is the temperature of the ground,  $I_{atm}^{\downarrow}(\tilde{\nu})$  is the mean radiance associated to the downward radiation flux of the atmosphere,  $r(\tilde{\nu}, \theta)$  is the effective reflectivity of the surface in the shortwave, and  $I_{sun}^{\downarrow}$  is the radiance emitted by the Sun that reaches the surface of the Earth. The source term includes therefore three contributions:

• The blackbody emission of the ground, corrected by the emissivity. This corresponds to the first term in the right hand side of equation (2.3.20).

- The reflection of the downwelling thermal radiance emitted by the atmosphere, represented by the second term of equation (2.3.20). Evaluating this term requires solving the radiative transfer equation first in the downward direction.
- The reflection of the radiance of the Sun reaching the surface, accounted for by the third term.  $I_{sun}^{\downarrow}$  is modelled by a Planck function at the temperature of the Sun (5700 K), excluding spectral lines.

Finally, the radiance measured by the TIR sounder is obtained by the convolution of the TOA radiance with the instrumental line shape (ILS):

$$I(\tilde{\nu}, \theta, z_{\text{sounder}}) = I(\tilde{\nu}, \theta, z_{\text{TOA}}) \otimes ILS(\tilde{\nu}).$$
(2.3.21)

In the following, when we refer to the TOA radiance, we will consider the radiance after the convolution with the ILS.

# 2.4 Sensitivity and vertical information content of nadir TIR spectra

# 2.4.1 Sensitivity vs information content

From the discussions above, we have seen that nadir TIR sounders collect at TOA the TIR radiation emitted/reflected at the surface of the Earth after its propagation through the whole atmosphere. It means that these instruments record the spectral signal integrated over the whole atmosphere. We can therefore ask the following questions: does the nadir TIR spectrum carry vertical information, and therefore could it be used to derive the vertical distributions of atmospheric constituents? Do these instruments have similar sensitivities to the different parts of the atmosphere in all conditions? Although these questions are fundamental for the understanding of nadir TIR measurements, it is however difficult to give them a simple answer. The first step in the understanding of these issues is to differentiate the *vertical sensitivity* of TIR measurements from their *vertical information content*:

- The sensitivity of a TIR measurement is always referred to a particular parameter (e.g., surface temperature). It describes how the TOA radiance responds to a change of the targeted parameter. This can be expressed by the derivative of the TOA radiance with respect to the parameter (see subsection 2.4.3 below). For a parameter presenting an atmospheric distribution varying with height (e.g., CO), the sensitivity can be calculated at different altitudes (e.g., sensitivity to CO in the 2–3 km layer), and an estimation of the variation of the sensitivity with the height can be obtained. This is the vertical sensitivity. The maximum vertical sensitivity is found in the part of the atmosphere where a change of the targeted parameter produces the largest response in the TOA radiance. As we will see in the next subsections, the vertical sensitivity ity depends on different parameters, such as the spectral range and the atmospheric conditions.
- The vertical information content of TIR measurements can be expressed as the number of degrees of freedom of the measurements. Considering for example the retrieval of the vertical profile of CO, it represents the number of atmospheric layers for which we can retrieve independent information about the CO concentration. We will see in part III that this number can vary from 1, meaning that only the total column of CO is retrievable (information on one layer), to 2, where in this case, two partial

columns of CO can be retrieved independently (information on two layers). The vertical information content varies according to the species considered but also to the atmospheric conditions (see below).

Despite their difference, the vertical sensitivity and the information content are intimately related. Indeed, to be able to retrieve vertical information (e.g., several partial columns), the TIR instrument has to be sensitive to the atmosphere at different heights. Moreover, changing vertical sensitivity with changing wavenumber increase the information content, and favours the decorrelation between the contributions of each layer. To get a better grip on these relations, we introduce two different functions in the following subsections: the *weighting functions* and the *Jacobians*. These functions will also help us to describe the influence of different parameters on the sensitivity and information content.

# 2.4.2 Weighting functions

Recalling equation (2.3.11) of the radiative transfer, we define the weighting function  $W(\tilde{\nu}, z)$  at wavenumber  $\tilde{\nu}$  as

$$W(\tilde{\nu}, z) = \frac{\mathrm{d}t(\tilde{\nu}, 0, z, z_{\mathrm{TOA}})}{\mathrm{d}z}.$$
(2.4.1)

This function describes how fast the transmittance is varying with height. The region of the atmosphere where  $W(\tilde{\nu}, z)$  reaches its maximal values defines the region where the transmittance varies the most rapidly. This region therefore also corresponds to the atmospheric part that is mainly sounded at  $\tilde{\nu}$ . Considering nadir view ( $\theta = 0^{\circ}$ ) and using equations (2.3.2), (2.3.8), (2.2.7) and (2.1.33), we can show that  $W(\tilde{\nu}, z)$  is equal to<sup>5</sup>

$$W(\tilde{\nu}, z) = \alpha_{tot}(\tilde{\nu}, z) t(\tilde{\nu}, 0, z, z_{\text{TOA}})$$

$$= \left[\sum_{j,k} \rho_j(z) \sigma_{j,k}(\tilde{\nu})\right] t(\tilde{\nu}, \theta, z, z_{\text{TOA}})$$

$$= \left[\sum_{j,k} \rho_j(z) \sigma_{j,k}^{int} f(\tilde{\nu} - \tilde{\nu_k}, T(z), P(z))\right] t(\tilde{\nu}, 0, z, z_{\text{TOA}}),$$
(2.4.2)

where all spectral lines (of different species if the case occurs) that contribute to the absorption coefficient and the transmittance at  $\tilde{\nu}$  are taken into account. Based on this equation, we can make several important statements:

- 1.  $W(\tilde{\nu}, z)$  is equal to 0 if the atmosphere is opaque  $(t \approx 0)$  or if it is transparent (t = 1), because  $\alpha_{tot} = 0$ .
- 2. The altitude of the maximal value of  $W(\tilde{\nu}, z)$  depends on the pressure (line profile), the temperature (integrated absorption cross section and line profile) and the vertical profile of the species j. It also varies with the wavenumber.
- 3. Generally, for species with a decreasing density profile, the centres of strong lines have W functions that peak higher in the atmosphere than a channel located in the wings of the lines.

These statements can be illustrated with the example of the R(21) line (2218.745 cm<sup>-1</sup>) in the 1–0 band of CO (panel (a) of Figure 2.4.1). For this example, we have calculated the weighting functions (panel (d) of Figure 2.4.1) at three different wavenumbers located at

<sup>&</sup>lt;sup>5</sup>A geometric factor is added in the case of  $\theta \neq 0^{\circ}$ .

the line center (green), in the line wings (blue) and between the two of them (red). In the calculation, we have considered an atmosphere constituted of only CO, whose number of density profile is shown in panel (b) of Figure 2.4.1. The pressure and temperature profiles have been taken from the US Standard model (Anderson et al., 1986). A Lorentz profile has been considered for the line profile. The transmittances  $t(\tilde{\nu}, 0, z, z_{\text{TOA}})$  are also indicated (panel (c)). Figure 2.4.1 shows that, moving from the line center to the wings, the height where the weighting functions peak decreases. This is related to the value of  $\sigma(\tilde{\nu})$ . At the line center, the absorption is the strongest. In the lowest layers, where the density of CO is the largest, the transmittance is close to 0 at the center of the line, implying an opaque atmosphere at this wavenumber. The transmittance is almost constant and the weighting function stays close to 0. At higher altitudes, where the density of CO decreases, the atmosphere is no more opaque and the transmittance starts to change more rapidly. The weighting function reaches a maximum before decreasing due to the decrease of the CO density, which becomes vanishingly small at these high altitudes. When moving away from the center of the line, the strength of the absorption decreases. At these wavenumbers, the atmosphere is never opaque and the weighting functions have their maximum lower in the atmosphere. In the line wings, the absorption is favoured by the pressure broadening. Its strength thus rapidly decreases when the height increases, and the transmittance rapidly changes in the lowest layers compared to the upper layers, where the atmosphere becomes transparent. The weighting functions calculated for the line wings peak therefore at the surface. All the parameters that affect the transmittance (see statement 2 above) will influence the weighting functions. Note as a final remark that, if an interfering species, i.e., species that absorbs radiation in the same spectral range as the targeted one, had been considered in our example (e.g.,  $H_2O$ ), it would have impacted the weighting functions values. For example, the presence of a strong  $H_2O$  line in the line wings would have shifted the maximum of the weighting functions towards higher altitudes.



Figure 2.4.1: (a) Line R(21) of the 1–0 band of CO for which three weighting functions have been calculated for different wavenumbers (indicated in blue, red and green). (b) Vertical profile of the number of density (molecules cm<sup>-3</sup>) of CO used to calculate the weighting functions. (c) Transmittance  $t(\tilde{\nu}, 0, z, z_{\text{TOA}})$  calculated at the three wavenumbers indicated with the same colors as in panel (a). (d) Weighting functions (in cm<sup>-1</sup>) calculated at three wavenumbers, indicated again with the colors referring to panel (a).



Weighting functions

Figure 2.4.2: Ideal weighting functions to measure vertical information with a nadir sounder. (left) Delta-Dirac weighting functions allowing the observation of the atmospheric state at different levels (single altitudes). (right) Weighting functions presenting a finite width and allowing the observation of different layers of the atmosphere. Figure inspired from Petty (2006).

The weighting functions can thus be used to understand the vertical information content of TIR measurements. As explained above, these functions indicate, for each wavenumber, the part of the atmosphere that is sounded. In the ideal case, to be able to independently measure the atmospheric state at different heights (vertical information content larger than 1), the weighting functions calculated at different wavenumbers should present sharp peaks at different altitudes, as shown in Figure 2.4.2 (left). In this first ideal case, the sounder is able to observe the atmosphere at different levels because the vertical information provided by each wavenumber is different. This would allow retrieving information about the state of the atmosphere at single altitudes. A more realistic view is shown in the right panel of Figure 2.4.2, where the weighting functions have a finite width. In this case, the sounder observes different layers of the atmosphere. Because, there is no overlap between these weighting functions, each wavenumber contains information about different atmospheric layers.

Unfortunately, in reality, weighting functions for nadir sounding do not behave like the ideal cases discussed above. They are significantly broader and present a high degree of overlap with the adjacent functions, as shown in panel (d) of Figure 2.4.1. This means that the wavenumbers probe similar large parts of the atmosphere, and the retrieval of independent vertical information about different layers is thus complicated. Moreover, the weighting functions say nothing about which atmospheric parameters can be measured; it gives only the part of the atmosphere that is sounded at each wavenumber. The values of the TOA radiance at each wavenumber depend however on several parameters, such as the temperature, the concentrations of one or more gases, etc. Retrieving independent information about these parameters at different heights is therefore even more complicated. This will require the use of constrained inversion methods (chapter 3). Finally, it is worth noting that the values of the weighting functions are independent of the radiative transfer, and therefore do not take into account some factors, such as the TC, which can have a strong influence on the sensitivity and information content as we shall see next.

#### 2.4.3 Jacobians

The Jacobians, denoted as  $K(\tilde{\nu})$ , are the derivatives of the TOA radiance measured by the sounder with respect to atmospheric/surface parameters at wavenumber  $\tilde{\nu}$ :

$$\mathbf{K}(\tilde{\nu}) = \frac{\partial I(\tilde{\nu}, \theta, z_{\text{sounder}})}{\partial x},$$
(2.4.3)

where x represents the targeted parameter (e.g., surface temperature,...).  $K(\tilde{\nu})$  defines thus the sensitivity of the TIR measurement to the targeted parameter at wavenumber  $\tilde{\nu}$ . Jacobians are generally calculated for different spectral channels (e.g., over a vibrational band) and are in this case represented as vectors **K** (for which each element corresponds to  $K(\tilde{\nu}_m)$  at a different wavenumber  $\tilde{\nu}_m$ ). Contrary to the weighting functions, the values of the Jacobians are dependent on the radiative transfer, and their definition is related to a particular atmospheric parameter.

Using the Jacobians, we can derive the vertical sensitivity of a TIR sounder to a particular atmospheric parameter. Let's take the example of CO to illustrate this. We can now consider that  $x_i$  corresponds to the partial column of CO in layer i. We can therefore calculate Jacobians for each layer i and for a spectral range in the 1–0 band of CO. We obtain in this way an estimation of the variation of the sensitivity to CO with height in this spectral range. Each Jacobian defines the sensitivity of the TOA radiance with respect to CO in a certain layer for the spectral range considered. An example is shown in the left panel of Figure 2.4.3 for the IASI instrument in the 2143–2181.25  $\rm cm^{-1}$  range, for which a weak TC of 5 K has been considered. The values of the Jacobians calculated for CO in layers of 1 km thickness (from 0 to 19 km) are represented as functions of height and of wavenumber. From this figure, we can notice first of all that, independently on the altitude, the sensitivity to CO is maximal at the center of the lines. At these wavenumbers, the Jacobians present their largest absolute values between 2 and 8 km. This means that an identical change in CO concentration in one of these layers would make a similar spectral response in the IASI spectrum. In other words, the sensitivity of IASI to CO is maximal and almost constant in this region of the atmosphere for the atmospheric conditions considered.

The values and shape of the Jacobians (and thus the vertical sensitivity) are impacted by different factors. Those having the largest influences are:

- Effects of saturation (opacity). For channels presenting strong absorption, saturation can occur in a part of the atmosphere if the species is present in large quantities<sup>6</sup>. Such atmospheric regions are opaque in these channels. The Jacobian values calculated for these regions and at these channels are equal to 0 (note that this is not the case in our example).
- Interfering species. The absorption of other species in the same spectral range as the targeted one can strongly influence the values and shape of the Jacobians. Effect of opacity can also be caused by interfering species. As we will see in part II, this is the case of H<sub>2</sub>O, which strongly absorbs the radiation in the spectral range of the  $\nu_3$  band of SO<sub>2</sub>.
- The TC. Because it drives the sensitivity to the near-surface atmosphere (subsection 2.4.4), the TC strongly influences the values of Jacobians close to the ground. This will be shown for SO<sub>2</sub> and CO in parts II and III respectively.

<sup>&</sup>lt;sup>6</sup>Note that this means that Jacobians depend on the density profile of the targeted species



Figure 2.4.3: (Left) Jacobians (in W m<sup>-2</sup> sr<sup>-1</sup> m per scaling factor, color scale) of CO as a function of height, calculated for a TC of 5 K and for the 2143–2181.25 cm<sup>-1</sup> spectral range. The IASI instrument has been considered. (Right) Normalised Jacobians (same as left panel) for the 0–1 km, 6-7 km, 8-9 km and 14–15 km layers. They have been normalised and offset for display purposes.

Finally, in addition to quantify the vertical sensitivity of TIR sounders, Jacobians, and more particularly variations of their spectral shapes with height, can be related to the information content of the measurement. First of all, to be able to retrieve information about the vertical distribution of a trace gas, the TIR instrument has to be sensitive to this targeted gas at different heights. Then, to favour the distinction between the concentrations of this gas in different atmospheric layers, the Jacobians, calculated for each of these layers over the spectral range considered, should present different shapes according to the layer. Taking again the example of CO, the right panel of Figure 2.4.3 presents Jacobians calculated for the spectral range 2143-2181.25 cm<sup>-1</sup> for different layers (they correspond to those shown in the left panel but only for some layers). We can see that the Jacobians for the 6-7 km and 8–9 km layers are almost identical to each other in their spectral shape. This means that a change of CO in one of these two layers produces exactly the same shape for the spectral response in the sounder's measurement. It it therefore very difficult to determine in which layer the change has occurred even if the spectral response is different in intensity, as the latter can indeed be modulated as well with the magnitude of the CO concentration change. The Jacobians calculated for the 0-1 km and 14-15 km layers are on the contrary slightly different compared to those of the mid-tropospheric layers. For example for the 0-1 km layer, we observe a larger difference between the intensities of the line at around  $2162 \text{ cm}^{-1}$  and its neighbours than for the three other layers. This means that a change of CO concentration in the 0-1 km layer does not produce exactly the same spectral response as in the mid-tropospheric layers. This shows that the distinction of CO between these parts of the atmosphere is favoured compared to the one between the 6-7 km and 8-9 km layers. In conclusion, the number of independent information in a measurement can be understood through variations in the spectral shape (taken over the spectral range considered) of the Jacobians with height: the largest the variations, the more decorrelated the layers are, and the larger the information content is. Note that this concept will be better illustrated with the case of  $SO_2$ , for which large differences in the shape of Jacobians will be used to determine the height of  $SO_2$  plumes (chapter 7).

# 2.4.4 Sensitivity of TIR sounders to PBL composition

The sensitivity of TIR sounders to the PBL composition is for a large part driven by the TC. The TC is defined as the difference between the temperature of the ground and the temperature of the air above it<sup>7</sup>. To illustrate the effect of TC on the sensitivity, following equation (2.3.18), we can write the change undergone by the radiation,  $\Delta I$ , after going through the first layer of a discretised atmosphere (i = 1) as

$$\Delta I = I_1 - I_0 = (1 - \bar{t}_1)(B(\bar{T}_1) - B(T_S))$$
(2.4.4)

In this example, we have neglected the contribution of the reflection of the downwelling atmospheric emission (an emissivity of 1 has been considered) and of the solar incoming radiance (see below). Written in this way, equation (2.4.4) reveals the TC in the right term, which is expressed through the difference of the two Planck functions. It allows distinguishing three general behaviours, similar to those highlighted already in section 2.2 with the general case of the Schwarzschild equation:

1.  $T_S = \overline{T}_1$ , TC = 0

 $\Delta I$  is equal to zero and the radiance leaving the first layer is that of a blackbody at temperature  $\overline{T}_1$ . Information on the composition of the first layer can not be retrieved (no spectral feature in  $I_1$ ).

2.  $T_S > \overline{T}_1$ , TC > 0

This is true in general for daytime observations.  $\Delta I$  is negative; spectral lines are in absorption in  $I_1$ .

3.  $T_S < \overline{T}_1$ , TC < 0

This is the thermal inversion scenario.  $\Delta I$  is positive; spectral lines are in emission in  $I_1$ .

The TC directly influences the sensitivity of IASI to the PBL composition. The larger TC (in absolute value) is, the better the sensitivity is, and the larger  $\Delta I$  is. Of course this sensitivity also depends on the abundance of trace gases in the first layer due to the  $1 - \bar{t}_1$  term (see equation (2.3.19)).

# 2.4.5 Final remarks

In the previous subsections, we have seen that both the vertical sensitivity and the information content of TIR measurements are influenced by several different factors, that the weighting functions and the Jacobians have helped to identify. In the rest of the manuscript, because they are dependent on the radiative transfer (and on TC above all), the Jacobians will be used as one diagnostic tool to discuss the sensitivity of TIR sounders to the nearsurface atmosphere. Other functions, which will be presented in chapter 3, will be jointly exploited to fully characterise the sensitivity to near-surface CO (part III).

Finally, from the discussions above, we have highlighted why it is difficult to derive independent information about the vertical distribution of trace gases from nadir TIR measurements, notably because spectral channels contain similar vertical information. Retrieving information about their concentration in the PBL is even more challenging, because of the

<sup>&</sup>lt;sup>7</sup>The definition of the TC is not always strictly the same throughout the manuscript and the altitude above ground considered for the atmospheric temperature can vary. It is specified when needed.

influence of TC. It is however worth noting that the challenge depends on the trace gas and its mixing in the atmosphere. For the species studied in this thesis, the difficulty is larger in the case of CO compared to SO<sub>2</sub>. Due to its relative long lifetime (2 months), CO is relatively well mixed in the whole troposphere. Its concentration in the near-surface atmosphere has thus to be decorrelated from the rest of the troposphere. This is not the case of SO<sub>2</sub>, which has a short lifetime; if emitted at the surface, it mostly remains confined in the PBL<sup>8</sup>. The challenge for SO<sub>2</sub> is then more on the detection of a signal than on the retrieval of a resolved vertical profile.

<sup>&</sup>lt;sup>8</sup>Note however, that in the case of a volcanic eruption, the concentration at the surface has to be distinguished from that in the volcanic plume.

# CHAPTER 3

#### INVERSE METHODS

In chapter 2, we have derived the radiative transfer equation. This equation is solved to calculate the TOA radiance, and thus to simulate nadir TIR observations. However, in atmospheric problems, we generally do not know perfectly the state of the atmosphere, and the measurements are precisely used to retrieve information about this state. This constitutes the inverse problem. Inversion methods are required to retrieve information about the atmospheric parameters from the observations. As we have seen in the previous chapter, retrieving independent vertical information about different parameters is not easy and renders the inverse problem complicated.

In this chapter, we present three different inverse methods that have been used during the PhD to retrieve the near-surface concentrations of  $SO_2$  and CO from IASI observations. We start with the method of the optimal estimation (section 3.1), principally used in the case of CO, and then present an alternative version of this method (section 3.2), which has been developed for  $SO_2$  retrievals in the region of Norilsk. The third method, used for the retrievals of  $SO_2$  at global scale, is based on a look-up-table approach. It is also derived from the optimal estimation method and is discussed in section 3.3.

# 3.1 Optimal estimation method

#### 3.1.1 The under-constrained nature of the inverse problem

The relation between the nadir TIR measurements and the state of the atmosphere can be written in a general way as (Rodgers, 2000)

$$\mathbf{y} = \mathbf{F}(\mathbf{x}, \mathbf{b}) + \boldsymbol{\epsilon}, \tag{3.1.1}$$

where  $\mathbf{x}$  is the state vector, including the atmospheric parameters to be retrieved (e.g., CO profile),  $\mathbf{b}$  represents fixed atmospheric variables that have an impact on the measured radiances,  $\mathbf{y}$  is the measurement vector, including the measured radiances for different spectral channels,  $\boldsymbol{\epsilon}$  is the measurement noise vector, and  $\mathbf{F}$  is the forward model, which is described by the radiative transfer (equation (2.3.11)). The inverse problem consists in finding the state vector  $\mathbf{x}$  based on the measurements  $\mathbf{y}$ . In many cases, the inverse problem is underconstrained, which means that there are more unknowns than independent measurements (Rodgers, 2000). In other words, the instrument does not provide enough information to

derive exactly the state of the atmosphere. Indeed, most of the unknown variables, such as vertical profiles, are continuous functions, that we intend to retrieve with measured radiances in several spectral channels. Therefore, continuous functions are usually discretised at a certain number of levels/layers (vector  $\mathbf{x}$ ), which depends on the targeted functions. Despite this, the inverse problem can still be under-constrained, because the channels provide similar vertical information. In other words, the number of independent measurements is usually lower than the number of measured radiances. It is also worth noting that, because generally several parameters interfere spectrally, the state vector  $\mathbf{x}$  contains several variables that have to be retrieved simultaneously (e.g., surface temperature, CO vertical profile, H<sub>2</sub>O vertical profile,...), and thus the number of unknowns can be large. Finally, the measurements come with certain errors due to the measurement noise, which have to be taken into account and render the determination of  $\mathbf{x}$  more complicated.

For these reasons, there is generally an infinity of solutions to the inverse problem, which can only be solved in a constrained manner. The constraints in the optimal estimation take the form of an *a priori* knowledge<sup>1</sup> of the state of the atmosphere. As we will see in the next subsections, the concept of the optimal estimation method (OEM) is to find the most probable solution  $\hat{\mathbf{x}}$  among the infinity of possibilities, which will be the most consistent with both the measurement and the *a priori* atmospheric state.

## 3.1.2 The Bayesian approach

We have just mentioned above that the measurements always come with some noise, which has to be properly taken into account in the inversion. This is done by using probability density functions (PDF), which allow us to describe any random variable by taking into account its uncertainty. The PDF, P(x), of a variable x is defined such that P(x) dx is the probability that x lies in (x, x + dx). The probability that x lies between values a and b is therefore given by

$$P(a \le x \le b) = \int_{a}^{b} P(x) \,\mathrm{d}x.$$
 (3.1.2)

Many random variables have PDFs that can be represented by a Gaussian function (Rodgers, 2000), and have therefore the form:

$$P(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(x-\overline{x})^2}{2\sigma^2}\right), \qquad (3.1.3)$$

where  $\overline{x}$  is the mean value of x, and  $\sigma$  is the associated standard deviation. This is usually a good approximation for the measurement noise.

The concept of PDF can be extended to vectors.  $P(\mathbf{x})$  is defined so that  $P(\mathbf{x}) d\mathbf{x}$  is the probability that the components of  $\mathbf{x}$  lie in the multidimensional interval  $(\mathbf{x}, \mathbf{x} + d\mathbf{x})$ . The Gaussian distribution of the PDF of a vector is of the form:

$$P(\mathbf{x}) = \frac{1}{(2\pi)^{\frac{n}{2}} |\mathbf{S}|^{\frac{1}{2}}} \exp\left[-\frac{1}{2} (\mathbf{x} - \overline{\mathbf{x}})^T \mathbf{S}^{-1} (\mathbf{x} - \overline{\mathbf{x}})\right], \qquad (3.1.4)$$

where *n* is the dimension of the vector  $\mathbf{x}$ ,  $\overline{\mathbf{x}}$  includes the mean values of the elements of  $\mathbf{x}$ , and  $\mathbf{S}$  is the covariance matrix associated to  $\mathbf{x}$ . The diagonal elements of this matrix are the variances of the individual elements of  $\mathbf{x}$ , and the off-diagonal elements correspond to the covariances between the elements of  $\mathbf{x}$ , describing how much the variations of each element depend on the variations of the others.  $|\mathbf{S}|$  represents the determinant of the matrix  $\mathbf{S}$ .

<sup>&</sup>lt;sup>1</sup>The knowledge of the state of the atmosphere before the measurements are made.

Now that we have introduced the concept of PDF, we turn to the question of relating the PDF of the measurement to the one of the state vector. This is done using the *Bayes* theorem (Rodgers, 2000). Let's first define two probabilities linking the vectors  $\mathbf{x}$  and  $\mathbf{y}$ :

- $P(\mathbf{x}, \mathbf{y})$  is the *joint probability* of  $\mathbf{x}$  and  $\mathbf{y}$ . It is defined so that  $P(\mathbf{x}, \mathbf{y}) d\mathbf{x} d\mathbf{y}$  is the probability that  $\mathbf{x}$  lies in  $(\mathbf{x}, \mathbf{x} + d\mathbf{x})$  and  $\mathbf{y}$  lies in  $(\mathbf{y}, \mathbf{y} + d\mathbf{y})$ .
- $P(\mathbf{x}|\mathbf{y})$  is the *conditional probability*, which is defined so that  $P(\mathbf{x}|\mathbf{y}) d\mathbf{x}$  is the probability that  $\mathbf{x}$  lies in  $(\mathbf{x}, \mathbf{x} + d\mathbf{x})$  when  $\mathbf{y}$  has a given value. Similarly,  $P(\mathbf{y}|\mathbf{x}) d\mathbf{y}$  is the probability that  $\mathbf{y}$  lies in  $(\mathbf{y}, \mathbf{y} + d\mathbf{y})$  when  $\mathbf{x}$  has a given value.

Using the above definitions, we can show that (Rodgers, 2000)

$$P(\mathbf{x}, \mathbf{y}) = P(\mathbf{x}|\mathbf{y}) P(\mathbf{y}). \tag{3.1.5}$$

Because  $P(\mathbf{x}, \mathbf{y}) = P(\mathbf{y}, \mathbf{x})$ , we can write

$$P(\mathbf{x}|\mathbf{y}) P(\mathbf{y}) = P(\mathbf{y}|\mathbf{x}) P(\mathbf{x}), \qquad (3.1.6)$$

and from this equation, we can derive the Bayes theorem:

$$P(\mathbf{x}|\mathbf{y}) = \frac{P(\mathbf{y}|\mathbf{x}) P(\mathbf{x})}{P(\mathbf{y})}.$$
(3.1.7)

In the frame of the inversion of nadir TIR measurements, we can define each term of equation (3.1.7):

- $P(\mathbf{x}|\mathbf{y})$  is the PDF of the atmospheric state when the measurement has been made. It is the unknown variable.
- $P(\mathbf{y}|\mathbf{x})$  is linked to the probability of measuring  $\mathbf{y}$  if the atmospheric state  $\mathbf{x}$  is known. This is described by the radiative transfer equation, including the measurement noise.
- $P(\mathbf{x})$  is the prior knowledge of the atmospheric state (before the measurement is made).
- $P(\mathbf{y})$  is the PDF of the measurement. In practice, it is a normalising factor and is generally not needed.

The Bayes theorem therefore allows us to relate the atmospheric state that is measured to the knowledge we have about this state before the measurement, and to our knowledge of the radiative transfer and measurement noise. It is however important to note that, based on this, the Bayes theorem provides an ensemble of atmospheric states that could be the solution of the inverse problem instead of one unique solution; it gives an intuition of how the measurement improves the knowledge of the atmospheric state. Among the solutions obtained, some are more likely than others. The idea of the OEM is to find the state that maximizes  $P(\mathbf{x}|\mathbf{y})$ . This state is called the maximum a posteriori (MAP) solution.

## 3.1.3 Linear inverse problems

In this section, following the discussion above, we derive the maximum *a posteriori* solution of linear inverse problems based on the Bayes theorem. Linear problems are those for which the forward model (equation (3.1.1)) is linear. For these cases, equation (3.1.1) can be rewritten as

$$\mathbf{y} \approx \frac{\partial \mathbf{F}(\mathbf{x}, \mathbf{b})}{\partial \mathbf{x}} \mathbf{x} + \boldsymbol{\epsilon} = \mathbf{K}\mathbf{x} + \boldsymbol{\epsilon},$$
 (3.1.8)

where **K** is the matrix of Jacobians (see subsection 2.4.3), whose rows contain the derivatives of  $\mathbf{F}(\mathbf{x}, \mathbf{b})$  with respect to each element of  $\mathbf{x}$ . Recalling equation (3.1.4) and assuming that the prior knowledge of  $\mathbf{x}$  can be described by a Gaussian PDF, we can write

$$P(\mathbf{x}) = \frac{1}{(2\pi)^{\frac{n}{2}} |\mathbf{S}_{\mathbf{a}}|^{\frac{1}{2}}} \exp\left[-\frac{1}{2}(\mathbf{x} - \mathbf{x}_{\mathbf{a}})^T \mathbf{S}_{\mathbf{a}}^{-1} (\mathbf{x} - \mathbf{x}_{\mathbf{a}})\right],$$
(3.1.9)

where  $\mathbf{x}_{\mathbf{a}}$  is the *a priori* profile and  $\mathbf{S}_{\mathbf{a}}$  is the associated *a priori* covariance matrix. By taking the natural logarithm of this equation, we obtain

$$-2\ln P(\mathbf{x}) = (\mathbf{x} - \mathbf{x}_{\mathbf{a}})^T \mathbf{S}_{\mathbf{a}}^{-1} (\mathbf{x} - \mathbf{x}_{\mathbf{a}}) + c_1, \qquad (3.1.10)$$

where  $c_1$  is a constant. In a similar way, because measurement noise is generally well described by Gaussian statistics, we can write

$$-2\ln P(\mathbf{y}|\mathbf{x}) = (\mathbf{y} - \mathbf{F}(\mathbf{x}, \mathbf{b}))^T \mathbf{S}_{\epsilon}^{-1} (\mathbf{y} - \mathbf{F}(\mathbf{x}, \mathbf{b})) + c_2$$
  
=  $(\mathbf{y} - \mathbf{K}\mathbf{x})^T \mathbf{S}_{\epsilon}^{-1} (\mathbf{y} - \mathbf{K}\mathbf{x}) + c_2,$  (3.1.11)

where  $\mathbf{S}_{\epsilon}$  is the measurement error covariance matrix (or noise covariance matrix), and  $c_2$  is a constant. Substituting equations (3.1.10) and (3.1.11) in the Bayes theorem (equation (3.1.7)), we obtain

$$-2\ln P(\mathbf{x}|\mathbf{y}) = (\mathbf{x} - \mathbf{x}_{\mathbf{a}})^T \mathbf{S}_{\mathbf{a}}^{-1} (\mathbf{x} - \mathbf{x}_{\mathbf{a}}) + (\mathbf{y} - \mathbf{K}\mathbf{x})^T \mathbf{S}_{\epsilon}^{-1} (\mathbf{y} - \mathbf{K}\mathbf{x}) + c_3, \qquad (3.1.12)$$

with  $c_3$  including  $c_1$ ,  $c_2$  and  $P(\mathbf{y})$ , which hence does not depend on  $\mathbf{x}$ . To find the MAP solution, we have to determine the state  $\hat{\mathbf{x}}$  for which  $P(\mathbf{x}|\mathbf{y})$  is maximum, i.e., the state that makes the right hand side of equation (3.1.12) as small as possible. This function that has to be minimised will be hereafter called *cost function* (and denoted as J). By doing this, we want to find the state  $\hat{\mathbf{x}}$  that is the most consistent with both the *a priori* knowledge of the atmospheric state and the measurement.

The right hand side of equation (3.1.12) is a sum of two quadratic terms<sup>2</sup>. This gives another quadratic term, and  $-2\ln P(\mathbf{x}|\mathbf{y})$  can therefore be expressed as

$$-2\ln P(\mathbf{x}|\mathbf{y}) = (\mathbf{x} - \hat{\mathbf{x}})^T \, \hat{\mathbf{S}}^{-1} \, (\mathbf{x} - \hat{\mathbf{x}}) + c_4.$$
(3.1.13)

This means that the posterior PDF is also described by a Gaussian distribution, whose most probable value (the mean value) is  $\hat{\mathbf{x}}$ , which is associated to the covariance matrix  $\hat{\mathbf{S}}$ . Equation (3.1.13) and the right hand side of equation (3.1.12) can be equated. Then, equating quadratic terms in  $\mathbf{x}$  gives:

$$\mathbf{x}^T \hat{\mathbf{S}}^{-1} \mathbf{x} = \mathbf{x}^T \mathbf{S}_{\mathbf{a}}^{-1} \mathbf{x} + \mathbf{x}^T \mathbf{K}^T \mathbf{S}_{\epsilon}^{-1} \mathbf{K} \mathbf{x}, \qquad (3.1.14)$$

and hence

$$\hat{\mathbf{S}} = (\mathbf{K}^T \mathbf{S}_{\epsilon}^{-1} \mathbf{K} + \mathbf{S}_{\mathbf{a}}^{-1})^{-1}.$$
(3.1.15)

<sup>&</sup>lt;sup>2</sup>A quadratic term is of the form  $\mathbf{z}^T \mathbf{M} \mathbf{z}$ .
Then, similarly, terms linear in  $\mathbf{x}^T$  can be equated, which gives

$$\mathbf{x}^T \hat{\mathbf{S}}^{-1} \hat{\mathbf{x}} = \mathbf{x}^T \mathbf{S}_{\mathbf{a}}^{-1} \mathbf{x}_{\mathbf{a}} + (\mathbf{K} \mathbf{x})^T \mathbf{S}_{\epsilon}^{-1} \mathbf{y}.$$
 (3.1.16)

By cancelling  $\mathbf{x}^T$  and substituting for  $\hat{\mathbf{S}}$ , we obtain

$$\left(\mathbf{K}^{T}\mathbf{S}_{\boldsymbol{\epsilon}}^{-1}\mathbf{K} + \mathbf{S}_{\mathbf{a}}^{-1}\right)\hat{\mathbf{x}} = \mathbf{S}_{\mathbf{a}}^{-1}\mathbf{x}_{\mathbf{a}} + \mathbf{K}^{T}\mathbf{S}_{\boldsymbol{\epsilon}}^{-1}\mathbf{y}, \qquad (3.1.17)$$

which by rearranging terms leads to

$$\hat{\mathbf{x}} = \mathbf{x}_{\mathbf{a}} + (\mathbf{K}^T \mathbf{S}_{\epsilon}^{-1} \mathbf{K} + \mathbf{S}_{\mathbf{a}}^{-1})^{-1} \mathbf{K}^T \mathbf{S}_{\epsilon}^{-1} (\mathbf{y} - \mathbf{K} \mathbf{x}_{\mathbf{a}}).$$
(3.1.18)

#### Characterisation of the retrievals

Equation (3.1.18) thus provides the most probable state of the atmosphere (for linear inverse problems), by taking into account the *a priori* information we have, the measurement and its associated noise. It is now interesting to estimate how good is the derived state  $\hat{\mathbf{x}}$ . The OEM offers for this a very adequate framework and allows characterising the retrieval in terms of errors and vertical sensitivity (Rodgers, 2000). We can discuss these separately:

#### 1. Retrieval errors

An estimation of the retrieval errors can be obtained from the matrix  $\hat{\mathbf{S}}$ . More particularly, the square roots of the diagonal elements of this matrix correspond to the standard deviations associated to each retrieved variable contained in  $\hat{\mathbf{x}}$ . Because the measurement improves the knowledge of the atmospheric state compared to the prior knowledge, the retrieval errors should always be smaller than the prior uncertainties.

Depending on the choice of  $\mathbf{S}_{\epsilon}$  (see notably section 3.2), the matrix  $\hat{\mathbf{S}}$  can include different types of errors:

- The smoothing error: because the instrument does not have an infinite vertical resolution, the retrieved profile is generally smoothed compared to the real one. In other words, the instrument is not able to measure fine vertical structures. This causes an error on the retrieved profile called the smoothing error. It depends on the sensitivity of the retrieved state to the true state (see below).
- The forward model parameter error: in equation (3.1.1), we have seen that **b** corresponds to fixed parameters that have an impact on the measured radiances. The knowledge of these parameters has some uncertainty associated, which propagates to cause errors in the retrieved state.
- The forward model errors: these errors can be seen as modelling errors, and are related to the degree of accuracy of the forward model that is used in the retrieval. Approximations made in the resolution of the radiative transfer equation (e.g., for time efficiency) can lead to errors in the estimation of  $\hat{\mathbf{x}}$ .
- *The measurement error*: this type of error, caused by the measurement noise, leads as well to uncertainty on the retrieved state.

#### 2. Vertical sensitivity and information content

The vertical sensitivity of the retrieval can be characterised by the *averaging kernels* functions (AVK). These are a measure of the sensitivity of the retrieved state to the true state:

$$\mathbf{A} = \frac{\partial \hat{\mathbf{x}}}{\partial \mathbf{x}},\tag{3.1.19}$$

where  $\mathbf{A}$  is the matrix of averaging kernels, whose rows define one dimensionless AVK function per element of  $\hat{\mathbf{x}}$ , i.e., per retrieved variable. We can show that the matrix  $\mathbf{A}$  can also be written as (Rodgers, 2000)

$$\mathbf{A} = (\mathbf{K}^T \mathbf{S}_{\epsilon}^{-1} \mathbf{K} + \mathbf{S}_{\mathbf{a}}^{-1})^{-1} \mathbf{K}^T \mathbf{S}_{\epsilon}^{-1} \mathbf{K}.$$
 (3.1.20)

Let's consider the example of the retrieval of the CO vertical profile on a certain number of layers. One AVK is associated to the retrieved CO amount in each layer, and peaks at the altitude from which most of the information is coming. In other words, the AVK functions provide an estimation of the vertical sensitivity of the retrieval, and peak at the altitude where this sensitivity is maximum. Moreover, the full width at half maximum of the AVK functions can be interpreted as the vertical resolution of the retrieval. In an ideal case represented in Figure 3.1.1, the AVK functions of each retrieved layer peak at a maximum value of 1 in the middle of the layer and are equal to 0 everywhere else. This means that the sensitivity of the retrieved CO concentration in one layer is maximum and should allow retrieving the true concentration in the same layer. In other words, the CO concentration in each layer is retrieved independently of the CO concentrations in the other layers. Unfortunately, this is usually not the case: the retrieved concentrations in different layers can be strongly correlated. As we have seen in section 2.4, this is because spectral channels do not contain independent information about the atmosphere, leading to a limited vertical resolution for nadir TIR sounders.



Figure 3.1.1: Ideal AVK functions for the retrieval of a vertical profile. The dashed black lines delimit the different layers considered in the retrieval.

To complete the characterisation of the information content of the retrieval, we can define the degrees of freedom for signal (DOFS) as the trace of the matrix  $\mathbf{A}$  (Rodgers, 2000). It represents the number of independent pieces of information that is retrieved for the profile. Considering the ideal example of Figure 3.1.1, the DOFS would be equal to the number of layers for which the concentration of CO is retrieved (5 for the example of Figure 3.1.1). Consistent with what we have explained for the AVK functions, the DOFS is usually lower, due to the limited vertical resolution of nadir TIR instruments.

The retrieval errors, the AVK functions and their associated DOFS have been used in this work, in addition to the Jacobians, as diagnostics to investigate the sensitivity of the IASI sounder to the near-surface atmosphere. This has been especially done for the case of near-surface CO (part III).

#### 3.1.4 Moderately non-linear inverse problems

In the previous section, we have assumed that the state  $\mathbf{x}$  is linearly related to the measurement  $\mathbf{y}$ , and that we could write

$$\mathbf{y} = \mathbf{F}(\mathbf{x}, \mathbf{b}) + \boldsymbol{\epsilon} \approx \mathbf{K}\mathbf{x} + \boldsymbol{\epsilon}. \tag{3.1.21}$$

However, the inverse problems that we encountered in this work are mostly moderately nonlinear, and for these the above equation is not a good approximation. In these cases, the solution given by equation (3.1.18) does not minimise the cost function. There is actually no analytical expression for the MAP solution to moderately non-linear problems, and the latter must be found numerically using several iterations.

In case of moderately non-linear problems, we can still applied the Bayes theorem (equation (3.1.7)). Assuming that the prior knowledge and the measurement noise are still described by Gaussian PDFs, we can write

$$-2\ln P(\mathbf{x}|\mathbf{y}) = \left[\mathbf{x} - \mathbf{x}_{\mathbf{a}}\right]^{T} \mathbf{S}_{\mathbf{a}}^{-1} \left[\mathbf{x} - \mathbf{x}_{\mathbf{a}}\right] + \left[\mathbf{y} - \mathbf{F}(\mathbf{x}, \mathbf{b})\right]^{T} \mathbf{S}_{\epsilon}^{-1} \left[\mathbf{y} - \mathbf{F}(\mathbf{x}, \mathbf{b})\right] + c. \quad (3.1.22)$$

The MAP solution that minimises this cost function is found by equating to zero the derivative of the latter with respect to  $\mathbf{x}$ :

$$\nabla_{\mathbf{x}} \left\{ -2\ln P(\mathbf{x}|\mathbf{y}) \right\} = \mathbf{S}_{\mathbf{a}}^{-1} \left[ \mathbf{x} - \mathbf{x}_{\mathbf{a}} \right] - \left[ \nabla_{\mathbf{x}} \mathbf{F}(\mathbf{x}, \mathbf{b}) \right]^{T} \mathbf{S}_{\epsilon}^{-1} \left[ \mathbf{y} - \mathbf{F}(\mathbf{x}, \mathbf{b}) \right] = 0.$$
(3.1.23)

Because we have  $\mathbf{K} = \nabla_{\mathbf{x}} \mathbf{F}(\mathbf{x}, \mathbf{b})$ , we obtain:

$$\mathbf{S}_{\mathbf{a}}^{-1} \left[ \mathbf{x} - \mathbf{x}_{\mathbf{a}} \right] - \mathbf{K}^{T} \mathbf{S}_{\epsilon}^{-1} \left[ \mathbf{y} - \mathbf{F}(\mathbf{x}, \mathbf{b}) \right] = 0.$$
(3.1.24)

To determine the MAP solution, this equation is solved numerically using an iterative method. In this work, a Gauss-Newton method (Rodgers, 2000) is used. At each iteration, the new vector  $\mathbf{x}_i$  is thus calculated as

$$\mathbf{x}_{i+1} = \mathbf{x}_i - \left[\nabla_{\mathbf{x}} \mathbf{g}(\mathbf{x}_i)\right]^{-1} \mathbf{g}(\mathbf{x}_i), \qquad (3.1.25)$$

where *i* refers to the iteration,  $\mathbf{g}(\mathbf{x}_i)$  is the derivative of the cost function, given by the left hand side of equation (3.1.24), and  $\nabla_{\mathbf{x}}\mathbf{g}(\mathbf{x}_i)$  is the second derivative of the cost function equal to

$$\nabla_{\mathbf{x}}\mathbf{g}(\mathbf{x}_i) = \mathbf{S}_{\mathbf{a}}^{-1} + \mathbf{K}_i^T \mathbf{S}_{\epsilon}^{-1} \mathbf{K}_i - \left[\nabla_{\mathbf{x}} \mathbf{K}_i^T\right] \mathbf{S}_{\epsilon}^{-1} \left[\mathbf{y} - \mathbf{F}(\mathbf{x}_i, \mathbf{b})\right], \qquad (3.1.26)$$

where  $\mathbf{K}_i = \nabla_{\mathbf{x}} \mathbf{F}(\mathbf{x}_i, \mathbf{b})$ . In the Gauss-Newton method, the third term in equation (3.1.26) is ignored<sup>3</sup> (Rodgers, 2000), and by substituting equations (3.1.24) and (3.1.26) in equation (3.1.25), we finally obtain

$$\mathbf{x}_{i+1} = \mathbf{x}_{\mathbf{a}} + \left(\mathbf{K}_i^T \mathbf{S}_{\epsilon}^{-1} \mathbf{K}_i + \mathbf{S}_{\mathbf{a}}^{-1}\right)^{-1} \mathbf{K}_i^T \mathbf{S}_{\epsilon}^{-1} \left[\mathbf{y} - \mathbf{F}(\mathbf{x}_i, \mathbf{b}) + \mathbf{K}_i(\mathbf{x}_i - \mathbf{x}_{\mathbf{a}})\right].$$
(3.1.27)

The retrieved state  $\hat{\mathbf{x}}$  is obtained by iteratively evaluating equation (3.1.27) until convergence. This one is reached when the absolute difference between the elements of the forward model of the two last iteration steps is lower than a certain fraction<sup>4</sup> of the noise:

$$|\mathbf{F}_k(\mathbf{x}_{i+1}, \mathbf{b}) - \mathbf{F}_k(\mathbf{x}_i, \mathbf{b})| < \eta \sqrt{S_{\epsilon}(k, k)}, \qquad (3.1.28)$$

<sup>&</sup>lt;sup>3</sup>This method is derived from the more general Newton method, for which this term is not neglected. <sup>4</sup>In this work, we have mostly considered 20%.

where  $F_k(\mathbf{x}_i, \mathbf{b})$  is the value of the forward model in channel k for the state at iteration i,  $\eta$  is the fraction of noise considered, and  $S_{\epsilon}(k, k)$  is the diagonal element of matrix  $\mathbf{S}_{\epsilon}$  for channel k. This relation has to be fulfilled for all the elements of **F** to reach the convergence. Finally, it is worth noting that the retrieval characterisation presented for linear problems can be applied in case of moderately non-linear problems (Rodgers, 2000).

# 3.2 Simplified OEM

In the previous section, we have seen that the OEM allows determining the most probable state of the atmosphere based on a measured TIR spectrum in nadir view (and taking into account its associated noise) and on the *a priori* knowledge we have on this state. Because we are confronted to moderately non-linear problems, the retrieval consists of simultaneous iterative adjustments of the atmospheric parameters of interest and of the spectrally interfering variables. The method presented in this section is a simplified version of the OEM, for which the retrieval is reduced to the adjustment of only the targeted parameters, and is therefore faster. It has been first introduced by Carboni et al. (2012), for the retrieval of SO<sub>2</sub> volcanic plumes. In this work, we have expanded it to the retrieval of near-surface SO<sub>2</sub> and this will be discussed in chapter 6; we limit the present section to the general description of the method.

The idea of the method developed by Carboni et al. (2012) is to interpret the spectrally interfering unknown variables as part of the spectral noise and to account for these in a generalised noise covariance matrix,  $\mathbf{S}_{\epsilon}^{\text{tot}}$ . While complete information on these interfering variables is not available, there is however some *a priori* information that can be exploited to construct  $\mathbf{S}_{\epsilon}^{\text{tot}}$ . The latter is built from the differences between observed spectra, for which there is no detectable spectral signature of the targeted species, and forward simulated spectra. It is calculated according to

$$\mathbf{S}_{\boldsymbol{\epsilon}}^{\mathbf{tot}} = \frac{1}{N_{obs}} \sum_{l=1}^{N_{obs}} \left[ (\mathbf{y}_{\mathbf{obs}} - \mathbf{y}_{\mathbf{sim}})_l - (\overline{\mathbf{y}_{\mathbf{obs}} - \mathbf{y}_{\mathbf{sim}}}) \right]^T \left[ (\mathbf{y}_{\mathbf{obs}} - \mathbf{y}_{\mathbf{sim}})_l - (\overline{\mathbf{y}_{\mathbf{obs}} - \mathbf{y}_{\mathbf{sim}}}) \right], \quad (3.2.1)$$

where  $\mathbf{y}_{obs}$  is the observed spectrum,  $\mathbf{y}_{sim}$  is the forward simulated spectrum,  $\overline{\mathbf{y}_{obs}} - \mathbf{y}_{sim}$  represents the averaged difference between observed and simulated spectra (hereafter written  $\mathbf{w}$ ), and  $N_{obs}$  is the number of spectra considered in the calculation of  $\mathbf{S}_{\epsilon}^{tot}$ . In this way, the matrix  $\mathbf{S}_{\epsilon}^{tot}$  is representative of our missing information on the interfering parameters, and includes: the measurement noise, the forward model errors, the errors in the meteorological fields (e.g., temperature profile), and errors coming from the lack of knowledge on the parameters that affect the measured radiances (included in the vector  $\mathbf{b}$ ).

With this new approach, the cost function (J) to be minimised takes the form

$$J = \left[\mathbf{x} - \mathbf{x}_{\mathbf{a}}\right]^{T} \mathbf{S}_{\mathbf{a}}^{-1} \left[\mathbf{x} - \mathbf{x}_{\mathbf{a}}\right] + \left[\mathbf{y} - \mathbf{F}(\mathbf{x}, \mathbf{b}) - \mathbf{w}\right]^{T} \mathbf{S}_{\epsilon}^{-1} \left[\mathbf{y} - \mathbf{F}(\mathbf{x}, \mathbf{b}) - \mathbf{w}\right], \quad (3.2.2)$$

where the bias  $\mathbf{w}$  associated to the missing information on the interfering unknown variables has to be subtracted. Note that the interfering parameters that were previously adjusted in the OEM (included in  $\mathbf{x}$ ) are now included in  $\mathbf{b}$ . The vector  $\mathbf{x}$  contains only the parameters of interest. The MAP state  $\hat{\mathbf{x}}$  is still obtained using Gauss-Newton iterations<sup>5</sup>. Note that the characterisation that we have introduced in subsection 3.1.3 is still valid in this simplified version of the OEM, but was however not used for the retrievals of near-surface SO<sub>2</sub> (see chapter 6).

 $<sup>^{5}</sup>$ Note that Carboni et al. (2012) used the Levenberg-Marquard iteration method (see Rodgers (2000) for details).

# 3.3 Look-up-table approach

The look-up-table (LUT) approach corresponds to the most simplified version of the OEM that we have used during the PhD. Indeed, this simple method allows retrieving the concentrations of short-lived species in one way (without iterations). It is based on the calculation of radiance indexes and on their conversion into concentrations using pre-built LUTs. This method was first introduced by Walker et al. (2011) and was used later by Van Damme et al. (2014) to retrieve NH<sub>3</sub> concentrations at global scale. Because this method needs low computational resources, it has been used in this work to retrieve SO<sub>2</sub> near-surface concentrations at global scale. This will be discussed in chapter 7, and we focus the present section on the general description of the method.

The idea of the LUT approach follows the one of the simplified version of the OEM presented in the previous section. It consists in considering all the interfering unknown parameters that affect the radiance in the spectral range of interest as part of the noise, and these are accounted for in a generalised noise covariance matrix. This matrix,  $\mathbf{S}_{y}^{\text{tot}}$ , is however built differently in this case, following the equation

$$\mathbf{S}_{\mathbf{y}}^{\text{tot}} = \frac{1}{N-1} \sum_{l=1}^{N} (\mathbf{y}_{l} - \overline{\mathbf{y}})^{T} (\mathbf{y}_{l} - \overline{\mathbf{y}}), \qquad (3.3.1)$$

where N is the number of considered spectra for which there is no detectable spectral signature of the targeted gas, and  $\overline{\mathbf{y}}$  is the mean background spectrum, calculated for the N observations. The matrix  $\mathbf{S}_{\mathbf{y}}^{\text{tot}}$  includes therefore the spectral variability coming from all the interfering parameters affecting the radiance in the spectral range under consideration, except the targeted species. This matrix is then used to calculate a normalised hyperspectral range index (that we will call *HRI*) for each observation  $\mathbf{y}$ , following the relation

$$HRI = \frac{\mathbf{K}^T \mathbf{S}_{\mathbf{y}}^{\text{tot}} \left(\mathbf{y} - \overline{\mathbf{y}}\right)}{\sqrt{\mathbf{K}^T \mathbf{S}_{\mathbf{y}}^{\text{tot}} \mathbf{K}}}.$$
(3.3.2)

The HRI, which is dimensionless, can be seen as an index of detection, whose value represents the strength of the spectral signal of the targeted species in the radiance spectrum. It is related to the amount of the species in the atmosphere: the larger its value is, the more likely the enhancement of the gas is. An ensemble of spectra free of the gas signature has a mean of 0 and a standard deviation of 1. An HRI of 3 (which corresponds to  $3\sigma$ ) can reasonably be considered as the limit of detection. Note that the HRI value is also related to the sensitivity of the instrument.

Because the HRI does not correspond to the actual column of the targeted species, it is therefore needed to convert it in a subsequent step. This can be done using LUTs built from forward model simulations, which link the simulated HRI values to the known columns of the gas. The way the LUTs have been set up for the retrieval of near-surface of  $SO_2$  will be explained in chapter 7. Also, it is important to note that the HRI does not provide any information on the altitude of the gas, as it is a measure of the strength of the spectral signal integrated over the whole atmosphere. As we are interested in retrieving near-surface  $SO_2$ concentrations, an additional step is required to determine the altitude of the  $SO_2$  plumes and to select only those located close to the surface. This will be described in chapter 7 as well.

As a final remark, the use of the HRI values for the detection of short-lived species is by far more efficient than the usual detection method of brightness temperature differences (BTD) (Walker et al., 2011). This one consists in calculating the difference between the BT of some chosen channels (one or few) that are sensitive to the targeted species, and the BT of some others that are insensitive to the species and represent a reference (see also subsection 5.1.1 for the example of SO<sub>2</sub>). These channels can be chosen to give a BTD close to the noise of the instrument in the absence of the targeted gas; in this case, BTD values larger than the noise indicate the presence of the spectral signature in the spectrum. This method has the disadvantage of taking into account only a limited number of channels instead of exploiting a wide spectral range (e.g., a whole vibrational band), and is therefore less sensitive than the method using the HRI values. BTDs have been used in this work to preselect SO<sub>2</sub>-free IASI spectra to build the total noise covariance matrices ( $\mathbf{S}_{\epsilon}^{\text{tot}}$  and  $\mathbf{S}_{y}^{\text{tot}}$ ), and this will be described in chapters 6 and 7.

# CHAPTER 4

# THE IASI INSTRUMENT AND ALGORITHMS

In chapters 2 and 3, we have explained how nadir TIR satellite observations are analysed. We have shown that this requires a forward model, which describes the transfer of the TIR radiation emitted/reflected by the Earth surface, and an inverse model, which allows retrieving the most likely state of the atmosphere based on the satellite measurement and *a priori* knowledge. In this work, the TIR observations that have been used are those of the IASI instrument. This chapter focuses on the description of IASI and of the associated algorithms used to analyse its observations.

# 4.1 The IASI instrument onboard MetOp

IASI is a hyperspectral sounder<sup>1</sup> circling the Earth on the MetOp platforms on a polar orbit. It has been developed jointly by the CNES (Centre National d'Études spatiales, french agency) and by EUMETSAT (European Organisation for the Exploitation of Meteorological Satellites) (Clerbaux et al., 2009; Hilton et al., 2012). The MetOp mission includes three satellites (MetOp-A, -B, and -C) onboard which three similar IASI (IASI-A, -B, and -C) instruments are carried. MetOp-A has been launched on 19<sup>th</sup> October 2006, and was followed by MetOp-B on 17<sup>th</sup> September 2012. MetOp-C is foreseen for launch in 2018. The main objective of the MetOp mission is to provide continuous and long-term datasets to support meteorology, and the monitoring of both environment and global climate. Thanks to the launch of three successive platforms, the MetOp mission will provide continuous and global observations for a period of more than 15 years. In addition to IASI, the MetOp platforms carry several other instruments (see Figure 4.1.1), which are

- The Global Ozone Monitoring Experiment-2 (GOME-2); a UV-visible spectrometer developed to measure the O<sub>3</sub> content and other trace gases in the atmosphere.
- The Advanced Very High Resolution Radiometer (AVHRR); a visible-IR imaging radiometer used for the global measurement of cloud cover, sea surface temperature, ice, snow and vegetation cover.

 $<sup>^{1}</sup>$ A hyperspectral sounder is an instrument capable of measuring the radiation in hundreds or in thousands of spectral channels simultaneously. In the TIR, these sounders have typically a spectral resolution better than 1 cm<sup>-1</sup>.

- The Advanced Scatterometer (ASCAT); a radar whose main objective is to measure the wind speed and direction over oceans.
- The Global Navigation Satellite System Receiver for Atmospheric Sounding (GRAS); a radio occulation receiver that sounds the temperature and humidity profiles of the atmosphere.
- The High Resolution Infrared Radiation Sounder (HIRS); an IR radiometer that measures the temperature and humidity profiles, the surface temperature, the cloud parameters and the total column of  $O_3$ .
- The Advanced Microwave Sounding Unit-A (AMSU-A); a microwave sounder designed for the sounding of the temperature profile of the atmosphere at global scale.
- The Microwave Humidity Sounder (MHS); a microwave radiometer which provides information on atmospheric  $H_2O$ .
- The Argos Advanced Data Collection System (A-DCS), which has the objective to collect and disseminate ocean data.
- The Search and Rescue Satellite (SARSAT) Aided Tracking system, which collects and relays emergency signals.
- The Space Environmental Monitor (SEM), which provides information on the solar activity and space weather, which can affect the satellites and instruments.

The IASI instrument is described further in the next subsection.





# 4.1.1 Characteristics of IASI

The IASI instruments have been designed by CNES in collaboration with EUMETSAT first to improve the meteorological forecasts by providing measurements of temperature and humidity tropospheric profiles with high vertical resolution and precision. Its second objective is to contribute to the measurement of the atmospheric composition. Therefore, its design and characteristics result from a compromise between the requirements associated to these two objectives: IASI combines a large spatial coverage and a moderate spectral resolution. Its characteristics are described in more details in the next subsections (see also Clerbaux et al. (2009) and Hilton et al. (2012)).

#### 4.1.1.1 Design, orbit and horizontal coverage

IASI is a Fourier Transform Spectrometer associated with an imaging instrument. Using the nadir geometry, it measures at TOA the upwelling TIR radiation emitted by the Earth and the atmosphere. On MetOp platforms, it circles the Earth on a polar orbit at 817 km of height on average. The orbit of the platform is Sun-synchronous: it crosses the Equator two times per day at 9:30 local time (morning and evening). MetOp completes one orbit in about 101 minutes, and thus circles the Earth around 14 times per day.

The IASI effective field of view is composed of  $2 \times 2$  circular footprints (pixels), each of 12 km diameter on the ground at nadir, and providing one independent spectrum (Figure 4.1.2). The effective field of view has dimensions of  $3.3^{\circ} \times 3.3^{\circ}$  or  $50 \times 50$  km<sup>2</sup> at nadir. To achieve a maximal spatial coverage, IASI observes the Earth up to an angle of 48.3° (satellite viewing angle) on both sides of the satellite track (Figure 4.1.2). This corresponds to the measurement of 15 fields of view on both sides of the nadir position, and thus to a swath of  $2 \times 1100$  km. The combination of this large swath and of the two Equator crossing times allows IASI to acquire a global coverage of the Earth twice a day.



Figure 4.1.2: Field of view of the IASI instrument. Figure taken from Hilton et al. (2012).

#### 4.1.1.2 Spectral range, spectral resolution and radiometric noise

IASI covers a spectral range in the TIR, extending from 645 cm<sup>-1</sup> (15.5  $\mu$ m) to 2760 cm<sup>-1</sup> (3.62  $\mu$ m) with no gap. This is allowed by three detectors, each measuring the spectrum in three distinct spectral ranges: 645–1210 cm<sup>-1</sup> (8.26–15.5  $\mu$ m), 1210–2000 cm<sup>-1</sup> (5.0–8.26  $\mu$ m), and 2000–2760 cm<sup>-1</sup> (3.62–5.0  $\mu$ m). Figure 4.1.3 presents a typical IASI spectrum, in both radiance and brightness temperature units. In this figure, we can distinguish the strong absorption  $\nu_2$  band of CO<sub>2</sub> at 667 cm<sup>-1</sup> (15  $\mu$ m), which contributes to the retrieval of temperature profiles, the  $\nu_3$  band of O<sub>3</sub> at 1042 cm<sup>-1</sup> (9.6  $\mu$ m), and the strong  $\nu_2$  band

of H<sub>2</sub>O at around 1595 cm<sup>-1</sup> (6.25  $\mu$ m). The IASI spectral range includes three vibrational bands of SO<sub>2</sub> (represented in grey in Figure 4.1.5), namely the intense  $\nu_3$  band centered at 1362 cm<sup>-1</sup>, the  $\nu_1$  band centered at 1152 cm<sup>-1</sup>, and the weaker  $\nu_1 + \nu_3$  combination band at 2500 cm<sup>-1</sup>, and the 1–0 vibrational band of CO at 2143 cm<sup>-1</sup> (in red in Figure 4.1.5). Other atmospheric trace species have absorption bands in the spectral range covered by IASI and have contributed to the success of the instrument for composition measurements, as we will discuss in subsection 4.1.2. Most of these species are identified in Figure 4.1.5. Note that we can see in Figure 4.1.3 the contribution of the reflected solar radiation to the measured radiance above 2400 cm<sup>-1</sup>.



Figure 4.1.3: IASI spectrum measured in the region of Mexico City (19.71°N, 100.26°W) on 01/06/2013 in radiance units (top) and brightness temperature units (bottom). The  $\nu_2$  band of CO<sub>2</sub>, the  $\nu_3$  band of O<sub>3</sub> and the  $\nu_2$  band of H<sub>2</sub>O are indicated. The red dashed line in the top panel represents the Planck function of the Earth, considering a surface temperature of 300 K.

The spectral resolution of IASI varies from  $0.35 \text{ cm}^{-1}$  to  $0.5 \text{ cm}^{-1}$  in the spectral range covered by the instrument due to self-apodisation effects. For convenience, spectra are post-apodised by a Gaussian function of full width at half maximum (FWHM) of  $0.5 \text{ cm}^{-1}$ , which can be considered as the apodised spectral resolution. Note that each spectrum is sampled in  $0.25 \text{ cm}^{-1}$  channels, and thus includes 8461 spectral channels.

The IASI spectra have low noise over most of the spectral range, as illustrated in Figure 4.1.4 (black), showing the radiometric noise of the instrument. Below 1200 cm<sup>-1</sup>, the noise is indeed of the order of  $2 \times 10^{-6}$  W m<sup>-2</sup> sr<sup>-1</sup> m. It then drops to around  $4 \times 10^{-7}$  W m<sup>-2</sup> sr<sup>-1</sup> m between 1200 cm<sup>-1</sup> and 1900 cm<sup>-1</sup>, and to  $1-2 \times 10^{-7}$  W m<sup>-2</sup> sr<sup>-1</sup> m above 1900 cm<sup>-1</sup>. Expressed in noise equivalent temperature difference (blue curve of Figure 4.1.4), the noise of IASI is around 0.2 K below 2200 cm<sup>-1</sup>, except for the 1800–2000 cm<sup>-1</sup> spectral range, for which it reaches 0.3 K. Note that in the 1150–1500 cm<sup>-1</sup> range, the noise is smaller than 0.1 K. From 2200 cm<sup>-1</sup>, the noise increases more drastically towards the near-IR spectral range.



Figure 4.1.4: IASI radiometric noise expressed in radiance (black) and in brightness temperature difference (blue). For the conversion, a reference temperature of 280 K has been considered. Figure taken from Clerbaux et al. (2009).

#### 4.1.1.3 Data levels and distribution

The raw measurements of IASI are interferograms, which correspond to data of level 0. Onboard MetOp, they are converted into spectra by an inverse Fourier transform, leading to data of level 1A. Then, three kind of calibrations are performed: a spectral calibration, a radiometric calibration, which transforms the measured signal in absolute radiance, and a geometric calibration, which geographically localise each measured pixel. The calibrated and geolocalised spectra correspond to level 1B data. Finally, spectra are apodised (Gaussian function of FWHM of  $0.5 \text{ cm}^{-1}$ ). They correspond to level 1C data, which are distributed to users and which are the measurements that are analysed in this work.

The acquisition of one complete across track scan of IASI ( $2 \times 15$  fields of view) takes 8 seconds, including the onboard calibrations. This measurement sequence corresponds to 120 ( $30 \times 4$ ) interferograms, converted to 120 spectra onboard the platform. These spectra are then transferred on Earth. In this way, IASI delivers about 1 300 000 spectra per day.

The stability of the instrument is regularly monitored by the CNES and EUMETSAT, and the IASI products are operationally distributed by the EUMETSAT Data Distribution System, called EumetCast. Since June 2007, EumetCast has been distributing the level

1C data, and from September 2007, it started to distribute the meteorological level 2 data (hereafter abbreviated L2). These data consist of temperature and humidity profiles, surface and cloud properties, which are retrieved by the EUMETSAT L2 Product Processing Facility (PPF) (Schlüssel et al., 2005; August et al., 2012). Note that the EumetCast system also distributes information on the atmospheric composition (total and partial columns of some trace gases), but these were not used in this work.

# 4.1.2 Measuring the atmospheric composition with IASI

Since the first launch in 2007, the IASI instrument has provided a huge amount of observations, which have led to important developments in operational meteorology and in the monitoring of the atmospheric composition. In this last area, in which we are particularly interested in this work, IASI measurements have allowed the detection of volatile species that have never been observed before using the nadir geometry. They have also led to the development of operational applications, such as the identification and monitoring of volcanic plumes. The combination of the excellent calibration and stability, and the expected long period of observation (more than 15 years) is such that IASI observations largely contribute to current climate studies. In this section, we briefly review the achievements made with the IASI instrument for the study of the atmospheric composition.

Since the beginning of the mission, a large number of different atmospheric species have been detected in IASI spectra (e.g., Clarisse et al., 2011b). These species can be separated in two different classes (see also Figure 4.1.5):

- 1. The species that contribute to each single IASI spectrum and have clear spectral signatures. Among these species, CO, O<sub>3</sub>, CH<sub>4</sub>, CO<sub>2</sub> and HNO<sub>3</sub> have been the most extensively studied up to now. CO, O<sub>3</sub> and HNO<sub>3</sub> are for instance retrieved in near-real time by the operational FORLI (Fast Optimal Retrievals on Layers for IASI) software (Hurtmans et al., 2012), which will be described in subsection 4.2.2. FORLI data has among other allowed acquiring their daily global distributions (e.g., George et al., 2009; Wespes et al., 2009) and studying their temporal evolutions, vertical distributions and transport (e.g., Turquety et al., 2009; Safieddine et al., 2013). The three FORLI products (CO, O<sub>3</sub>, HNO<sub>3</sub>) have been also validated (Kerzenmacher et al., 2012; Boynard et al., 2016; Ronsmans et al., 2016). Details on the sounding of near-surface CO with IASI will be given in chapter 9. More in relation to climate studies, tropospheric CH<sub>4</sub> has been retrieved in the tropical regions from IASI observations, and its temporal variation over the period 2007–2011 has been evaluated (Crevoisier et al., 2013). Similarly, retrievals of CO<sub>2</sub> have allowed acquiring the spatial and temporal evolution of the gas (e.g., in the upper troposphere (Crevoisier et al., 2009)).
- 2. The species that are detected only locally and have weak spectral signature in IASI L1C spectra (Clarisse et al., 2011b). Among these species, we find SO<sub>2</sub>, NH<sub>3</sub> and a series of VOCs (e.g., HCOOH, CH<sub>3</sub>OH,...). Due to their weak spectral signal, the detection of such species generally requires large concentrations in plumes released after extreme events (volcanic eruption (Karagulian et al., 2010; Clarisse et al., 2011c), large biomass burning (Coheur et al., 2009),...) or strong natural/anthropogenic emissions (e.g., Van Damme et al., 2014; Bauduin et al., 2014). In addition to their detection, the global distributions of NH<sub>3</sub> (Van Damme et al., 2014; Whitburn et al., 2016), CH<sub>3</sub>OH (Razavi et al., 2011), HCOOH (Razavi et al., 2011) and of anthropogenic SO<sub>2</sub> (Bauduin et al., 2016a) have been acquired successfully by averaging IASI observations over longer period than one day. Note also that specific retrieval method have been introduced to detect and measure these trace gases (e.g., Walker et al., 2011;



Carboni et al., 2012; Whitburn et al., 2016). The details on the retrieval of  $SO_2$  and the acquisition of distributions and time series are the subject of part II.

Figure 4.1.5: Normalised IASI spectrum (top panel, black) and spectral bands of most of the atmospheric species observed by the instrument. Figure taken from Clerbaux et al. (2009).

Finally, IASI is capable of detecting different types of aerosols, and more particularly to classify these according to their composition. This has been demonstrated by Clarisse et al. (2013), who have developed a unified detection method and have applied it to five different types of aerosols, namely volcanic ash, sand, sulphuric acid droplets, ammonium sulphate  $((NH_4)_2SO_4)$  and smoke particles. Note that the detection of the last three species was unprecedented in the nadir TIR satellite remote sensing.

# 4.2 Retrieval algorithms used for IASI

The analysis of the IASI radiances and the retrieval of trace gases concentrations from these radiances have started in various research groups early after the distribution of level 1C data in 2007. In the next subsections, we briefly present the two algorithms developed at the ULB for the retrieval of trace species that have been used in this work. They include a forward model and rely both on the OEM to solve the inverse problem.

## 4.2.1 Atmosphit

The Atmosphit software (Barret et al., 2005; Coheur et al., 2005) is based on a line-by-line radiative transfer model: the radiative transfer is calculated for each line, according to the description given in chapter 2 and using the line parameters of a spectroscopic database (in this work, *HITRAN* 2008). It proposes different inverse methods, notably the OEM presented in section 3.1.

Atmosphit is a versatile software. It has been developed to be applicable to different instruments (it accommodates different ILS functions and observing modes). It is of course

suitable for the nadir geometry, but can simulate and inverse as well limb or occultation spectra. In this way, in addition to its application to IASI measurements, Atmosphit was used for example for the retrieval of vertical profiles of  $O_3$  from IMG<sup>2</sup> observations (Coheur et al., 2005), of vertical profiles of hydrogen fluoride (HF) and chloride (HCl) from ground-based FTIR measurements (Barret et al., 2005), and of the vertical profiles of different organic compounds from the occultation observations of the ACE-FTS<sup>3</sup> instrument (Coheur et al., 2007). Finally, the retrieval parameters (*a priori* profile, *a priori* covariance matrix,...) are not fixed and are fully determined by the user.

As a final remark, Atmosphit does not retrieve the partial columns of atmospheric constituents directly, but dimensionless scaling factors that are related to the *a priori*. Equation (2.3.19) for the transmittance is then rewritten as

$$\bar{t}_{i} = \exp\left[-\sum_{j=retrieved} M_{i,j} P C_{i,j} \sum_{j,k} \sigma_{j,k}(\tilde{\nu}, \overline{T}_{i}, \overline{P}_{i}) - \sum_{j=fixed} P C_{i,j} \sum_{j,k} \sigma_{j,k}(\tilde{\nu}, \overline{T}_{i}, \overline{P}_{i})\right],\tag{4.2.1}$$

where  $M_{i,j}$  represents the retrieved scaling factor of species j for layer i. The retrieved partial columns in each layer are obtained after convergence by multiplying the *a priori* partial columns by the retrieved scaling factors.

#### 4.2.2 FORLI

FORLI is a fast operational algorithm that has been developed to retrieve the total columns and vertical profiles of some trace species in near-real time from IASI observations (Hurtmans et al., 2012). This algorithm is implemented in the processing chain at the ULB and provides the global distributions of CO,  $O_3$ , HNO<sub>3</sub> and NH<sub>3</sub>. Recently, the FORLI-CO software package has been implemented in the EUMETSAT PPF; the total column and vertical profiles of CO are now distributed by the EumetCast system. FORLI-O<sub>3</sub> and FORLI-HNO<sub>3</sub> are to be included in the PPF soon.

FORLI includes a radiative transfer model (similar to that described in chapter 2) and performs the inversion of IASI spectra using the OEM (section 3.1). Contrary to Atmosphit, FORLI is specific to IASI observations only. Moreover, FORLI does not resolve the radiative transfer line-by-line, but uses precalculated absorption cross sections tables, at various couples of pressure and temperature, to speed up the forward calculations. Finally, the inversion parameters are fixed.

For the FORLI-CO product (Hurtmans et al., 2012) that will be used later in the thesis, the retrieval is performed on the 2143–2181.25 cm<sup>-1</sup> spectral range, considering a noise varying around  $2 \times 10^{-7}$  W m<sup>-2</sup> sr<sup>-1</sup> m, but following the expected wavenumber dependency (Table 4.1 presents the main retrieval settings that are used). Temperature and pressure profiles distributed by EumetCast are used in the retrieval and are kept fixed. Surface temperature and H<sub>2</sub>O profiles are also taken from the EUMETSAT L2 PPF but are adjusted. A constant CO<sub>2</sub> profile of 380 ppm is considered, and static but spectrally resolved emissivities from the atlas derived by Zhou et al. (2011) are used. The *a priori* profile  $\mathbf{x}_a$  of CO and its associated *a priori* covariance matrix  $\mathbf{S}_a$  used in FORLI are shown in Figure 4.2.1. They have been built using modelled and measured profiles to represent the global averaged CO concentrations and variability. The *a priori* profile is around 100 ppb at the surface and then stays close to 90 ppb up to the middle troposphere, before smoothly decreasing. The  $\mathbf{S}_a$  matrix introduces the largest variability in the lowest layers, where it reaches 63%. In the free troposphere, it is never higher than 30%. Finally, in FORLI, CO is retrieved in

 $<sup>^{2} \</sup>mathrm{Interferometric}$  Monitor for Greenhouse gases.

<sup>&</sup>lt;sup>3</sup>Atmospheric Chemistry Experiment-Fourier Transform Spectrometer.

 $1~{\rm km}{-}{\rm thick}$  layers, from 0 km to 18 km, and in an additional layer extending from 18 km to TOA.

Table 4.1: Summary of the retrieval settings used in the FORLI software to retrieve CO profiles.

Parameter	Values/a priori
Spectral range	$2143-2181.25 \text{ cm}^{-1}$
Instrumental noise	$\approx 2{\times}10^{-7}~{\rm W}~{\rm m}^{-2}~{\rm sr}^{-1}$ m, diagonal ${\bf S}_{\epsilon}$
CO profile	Figure 4.2.1
Surface temperature	L2 EUMETSAT PPF
Temperature profile	L2 EUMETSAT PPF
$\mathbf{CO}_2$	380 ppm constant
$H_2O$	L2 EUMETSAT PPF
Emissivity	Zhou et al. (2011)



Figure 4.2.1: (Left) *a priori* vertical profile of CO ( $\mathbf{x}_{\mathbf{a}}$ , blue) used in the FORLI software. The red dashed lines represents the  $1\sigma$  associated variability (square root of the diagonal elements of  $\mathbf{S}_{\mathbf{a}}$ ). (Right) *a priori* covariance matrix ( $\mathbf{S}_{\mathbf{a}}$ ) used in the FORLI software. The color scale represent the square of the *a priori* variability ( $\%^2/100$ ).

# Part II

Measuring near-surface  $SO_2$  with IASI -From local to global scales

# CHAPTER 5

#### INTRODUCTION

In the first part of the thesis, we have exposed the theoretical background required for the understanding and analysis of IASI TIR observations. In this second part, we focus on the sounding of near-surface  $SO_2$  using the IASI instrument. The present chapter introduces part II, by reviewing briefly the main achievements in the satellite sounding of  $SO_2$  (section 5.1), and by defining the main objective of our work (section 5.2).

# 5.1 Sounding SO<sub>2</sub> from space

As mentioned in subsection 1.2.1.1,  $SO_2$  has both anthropogenic and natural sources. Volcanic degassing is the largest natural source (Halmer et al., 2002), whereas combustion of sulfur-rich fuels and smelting of heavy metals are the major contributions to anthropogenic emissions (Smith et al., 2011). In the next subsections, satellite remote sensing of  $SO_2$  is separately presented for volcanic and anthropogenic  $SO_2$ .

#### 5.1.1 Volcanic $SO_2$

Monitoring  $SO_2$  emitted by volcanic eruptions is of particular importance because they are known to affect air quality (e.g., Boichu et al., 2016) and climate, through the formation of sulfate aerosols (Robock, 2000). Satellite remote sensing is particularly attractive for tracking volcanic plumes as it allows following their temporal evolution and transport, and estimating the  $SO_2$  burdens emitted in the atmosphere. Moreover, monitoring the evolution of volcanic plumes is crucial to aviation hazard mitigation (Rix et al., 2009).

Nowadays, SO<sub>2</sub> emissions of most volcanoes are well monitored from space, especially eruptive degassing. Significant amounts of SO<sub>2</sub> are in this case mainly injected in the high troposphere or stratosphere and cover large areas. In the UV, retrievals of volcanic SO<sub>2</sub> have started in 1978 with the TOMS (Total Ozone Mapping Spectrometer) instrument (Krueger, 1983; Carn et al., 2003) and have continued since then with GOME (Eisinger and Burrows, 1998), SCIAMACHY (SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY) (Lee et al., 2008), GOME-2 (Rix et al., 2009) and OMI (Ozone Monitoring Instrument) (Krotkov et al., 2006). In the TIR, volcanic SO<sub>2</sub> has been measured first from multi-channel instruments with coarse spectral resolution (e.g., Realmuto and Watson, 2001; Watson et al., 2004) and later with high-spectral resolution instruments such as TES (Tropospheric Emission Spectrometer) (Clerbaux et al., 2008a), AIRS (Atmospheric Infrared Sounder) (Carn, 2005) and IASI (Clarisse et al., 2008).

Regarding what has been achieved with IASI at the ULB, different volcanic eruptions and their time evolution have been studied (e.g., the Jebel at Tair in September 2007, Clarisse et al. (2008), the Kasatochi in 2008, Karagulian et al. (2010)). A robust algorithm has been developed to measure  $SO_2$  emitted by volcanoes at altitude higher than 5 km (Clarisse et al., 2012). Consistent with what we have explained in subsection 2.4.4, monitoring periodic near-surface  $SO_2$  degassing by some volcanoes, such as the Etna (Tamburello et al., 2013; Ganci et al., 2012), is more difficult because the IASI sensitivity to the lowest part of the atmosphere is limited by the generally low TC. We will see in chapter 7, however, that it is possible to measure volcanic degassing in cases of high TC. Note finally that, in November 2008, a near-real time system for the detection of volcanic eruptions has been implemented at the ULB and assists, via the SACS<sup>1</sup> operational system (Brenot et al., 2014), the Volcanic Ash Advisory Centres (VAACS) in alerting airlines and air traffic control organisations in case of a positive detection. This system relies on the identification of the SO<sub>2</sub>  $\nu_3$  band in IASI spectra, using BTDs as already mentioned in section 3.3. In the case of  $SO_2$ , the average of the BTs of channels 1407.25  $\rm cm^{-1}$  and 1408.75  $\rm cm^{-1}$  constitutes the reference, and the average of the BTs of channels  $1371.50 \text{ cm}^{-1}$  and  $1371.75 \text{ cm}^{-1}$  gives an estimation of the strength of the  $\nu_3$  band (see Figure 5.1.1). The channels have been chosen to have a BTD (reference  $BT - \nu_3 BT$ ) of the order of the IASI noise in case of the absence of SO<sub>2</sub> in the atmosphere. This BTD is also at the heart of the method described by Clarisse et al. (2012).



Figure 5.1.1: Spectral channels used in the calculation of BTD for the detection of SO<sub>2</sub> from IASI. The SO<sub>2</sub>  $\nu_3$  band is shown in red for reference.

## 5.1.2 Anthropogenic SO<sub>2</sub>

Measuring near-surface  $SO_2$  emitted by anthropogenic activities is also important in regards to its impact on the environment (acid rain,...) and health (subsection 1.2.1). In contrast to volcanoes,  $SO_2$  pollution from these sources is difficult to monitor from space because it

<sup>&</sup>lt;sup>1</sup>Support to Aviation Control Service.

is often confined horizontally and vertically. In the UV, different methods have successfully been developed to retrieve surface  $SO_2$  and provide different global products. These methods include the operational PBL OMI  $SO_2$  (Krotkov et al., 2006, 2008) and the recent OMI algorithm based on a multi-windows DOAS (Differential Optical Absorption Spectroscopy) scheme developed by Theys et al. (2015). The latter will be used for comparison purposes in the next chapters of this part of the thesis. The availability of the satellite-derived columns from the UV nadir sounders have allowed quantifying  $SO_2$  anthropogenic emissions (e.g., Carn et al., 2007; Fioletov et al., 2011, 2013, 2015; McLinden et al., 2012, 2014).

For TIR sounders, measuring near-surface anthropogenic SO<sub>2</sub> is even more challenging because their sensitivity is limited by and heavily depending on the values of TC. Before the beginning of this PhD, clear demonstrations that TIR instruments could sound the near-surface atmospheric composition in case of large TC, was provided for CO (it will be discussed in part III) and for NH<sub>3</sub> (e.g., Clarisse et al., 2009, 2010). In the particular case of SO<sub>2</sub>, the evidence has been brought first by the results from the Master thesis<sup>2</sup> (some of which are briefly presented in Appendix B), obtained for the industrial area of Norilsk (Bauduin, 2012). By exploiting the large temperature inversions (and thus the large associated negative TC) that develop in this region during the winter, we were indeed able of retrieving the 0–1 km partial column of SO<sub>2</sub> from IASI observations, using the  $\nu_3$  band. This has allowed us to map the gas in the region and to record the time evolution of the columns for the period 2009–2011 (limited to the winter). The impact of atmospheric H<sub>2</sub>O, linked to the strong interfering absorption in the  $\nu_2$  band (Figure 4.1.5), was evidenced (Appendix B) during the Master thesis, and will be reminded in next chapters.

# 5.2 Objectives

The main goal of this second part of the thesis is to extend the results obtained in the Master thesis, both temporally and spatially. In a first step, this will be achieved by reanalysing the IASI measurements in the Norilsk region, but using the simplified version of the OEM presented in section 3.2 (chapter 6). By exploiting the gain in computation time brought by this method, we have the specific objective to measure  $SO_2$  in a larger region around Norilsk, and also on a longer period (2008–2013). Moreover, the inclusion in the analysis of mid-season and summer (for 2008–2011), which encounter different geophysical conditions of TC and humidity, allows us to complete the analyses in regard to the seasonal variation of the IASI sensitivity to near-surface  $SO_2$  in this region.

In addition to Norilsk, other local anthropogenic sources emit significant  $SO_2$  quantities in the atmosphere. This has led us to develop in a second step a fast retrieval scheme to measure near-surface  $SO_2$  at global scale (chapter 7). It is based on the LUT approach described in section 3.3. By correlating the global distributions of  $SO_2$  with those of TC and H<sub>2</sub>O, we revisit the capability of IASI to measure the different sources of  $SO_2$  in terms of the TC and humidity values worldwide (chapter 8).

Said in other words, the main objective of this part of the thesis is to establish the geophysical conditions (TC,  $H_2O$  content,...) in which IASI is sensitive to near-surface  $SO_2$ . The study performed above Norilsk provides observations for the case of large negative TC, whereas the global distributions include more situations, and especially those associated with high positive TC conditions.

<sup>&</sup>lt;sup>2</sup>Note that anthropogenic SO<sub>2</sub> brought at high altitude (mid-high troposphere) had been previously observed by Clarisse et al. (2011a).

# CHAPTER 6

# LOCAL SCALE - THE INDUSTRIAL AREA OF NORILSK

In this chapter, we analyse the IASI observations taken above the area of Norilsk. After presenting the region and briefly discussing the sensitivity of the instrument to  $SO_2$  in this region (section 6.1), we present the retrieval method (section 6.2) used for the retrieval of a 0–2 km layer, which is based on the simplified version of the OEM. The spatial distribution of the gas and the time series are then discussed separately in sections 6.3 and 6.4 respectively. The retrieved  $SO_2$  near-surface columns are evaluated against other existing measurements in section 6.5. Finally, the  $SO_2$  emissions of the city along with the retrieval errors are estimated and discussed respectively in sections 6.6 and 6.7. The main part of this chapter comes from the publication of Bauduin et al. (2014). The cross-validation with OMI presented in subsection 6.5.2 is reported in Theys et al. (2015).

# 6.1 Sounding SO<sub>2</sub> in the Norilsk region with IASI

Norilsk (69.3°N-88.2°E) is the largest industrial area beyond the Arctic Circle. It belongs to the Krasnoyarsk Krai of Russia (northwestern Siberia) and is located on one of the largest nickel deposits of the Earth. The main industrial activity of the region is without surprise the extraction of heavy metals (nickel, copper, platinum,...) from the sulfide ores of the deposit, and is led by the company MMC Norilsk Nickel. Because of its extraction activities, Norilsk is also well-known for its extremely high levels of pollution (e.g., Fukasawa et al., 2000). According to the Blacksmith Institute<sup>1</sup>, Norilsk is one of the ten most polluted cities of the world (Blacksmith Institutes, 2007). Each year, Norilsk's smelters emit significant quantities of heavy metals in the atmosphere (Boyd et al., 2009; Fukasawa et al., 2000), but also of acidifying gases, especially SO<sub>2</sub> (AMAP, 1998, 2006; Fukasawa et al., 2000). This is well illustrated by Figure 6.1.1, which shows the  $SO_2$  emissions (top panel) and concentrations (bottom panel) of Norilsk and other Russian cities for the 90's. Around 2 Mt of  $SO_2$  were emitted per year by Norilsk's facilities during 1992–2003, and yearly concentrations exceeding 100  $\mu g m^{-3}$  were recorded for this same period. Note that these concentrations are about five times larger than those measured in close polluted regions, and are almost always above the limit values for human health defined by European directives

<sup>&</sup>lt;sup>1</sup>The Blacksmith Institute is an international non-profit organisation dedicated to solving pollution problems in low and middle income countries, where human health is at risk (http://www. blacksmithinstitute.org/).

(subsection 1.2.1.1). The high levels of pollution emitted by Norilsk are directly responsible for the degradation and contamination of the surrounding environment (Vlasova et al., 1991; Blais et al., 1999; Tutubalina and Rees, 2001; Allen-Gil et al., 2003; Zubareva et al., 2003), and contribute to the Arctic air pollution (Law and Stohl, 2007; Hirdman et al., 2010) and acidification (AMAP, 1998, 2006).



Figure 6.1.1: (Top) SO<sub>2</sub> emissions (kt) from metallurgical industry sources and major coal-fired power plants in Russia. The four histograms represent the SO<sub>2</sub> emissions for the period 1992–2003 for different regions extracting heavy metals. The orange columns indicate the emissions for the year 2002. The total emissions for this same year are also indicated for five regions located in North Russia. (Bottom) SO<sub>2</sub> concentrations ( $\mu$ g m<sup>-3</sup>) in the air of different cities of Northern Russia between 1990 and 2003. The concentration scale associated to Norilsk is on the right y-axis of the graph. Figures are taken from AMAP (2006).

Recalling subsection 4.1.1, IASI can probe SO<sub>2</sub> in two spectral ranges<sup>2</sup>, in the  $\nu_1$  band (around 1100–1200 cm<sup>-1</sup>) and in the  $\nu_3$  band (around, 1300–1400 cm<sup>-1</sup>, see also Figure 4.1.5). However, the  $\nu_1$  band is weaker than the  $\nu_3$  band by a factor of 7.8 if the intensities of the strongest lines are compared (from HITRAN database 2008, (Rothman et al., 2009)). The weakness of the  $\nu_1$  band is such that it is detected only for very high levels of SO<sub>2</sub> and very large TC. This was notably shown in the Master thesis, and is reminded in Appendix B.1. For this reason, we consider only the  $\nu_3$  band in the retrieval. The  $\nu_3$ band is unfortunately located in the spectral range that includes the strong  $\nu_2$  band of H<sub>2</sub>O (Figure 4.1.5) and this causes an additional difficulty. Indeed, for a very humid near-surface atmosphere, the strong absorption of H<sub>2</sub>O renders this region of the atmosphere completely opaque. This means that IASI measures the radiation emitted from the top of the opaque layers (where the H<sub>2</sub>O content is lower) and absorbed by the layers above; spectral features of the  $\nu_3$  band are in this case not seen and precludes deriving information on the SO<sub>2</sub> near-surface pollution. In conclusion, when using the  $\nu_3$  band in the retrieval, there are two conditions that are simultaneously required for IASI to be sensitive to PBL SO<sub>2</sub>:

- 1. Large values of TC,
- 2. Low  $H_2O$  concentrations close to the surface.

These two conditions are found in the Norilsk region during the winter, as it is illustrated in panel (b) of Figure 6.1.2 for an example scene (see also the two bottom panels of Figure 6.4.1): in the lowest layers the H<sub>2</sub>O mixing ratio in winter is indeed generally well below 0.2 g/kg, while the thermal inversion can be as high as -15 K. To demonstrate the effect of these conditions on the measurements, two spectra have been compared in panel (a) of Figure 6.1.2 (for the scene characterised by the temperature and humidity as shown in panel (b) of the same figure). The IASI spectrum is shown in blue and a corresponding simulated spectrum, for which we have assumed an atmosphere free of SO<sub>2</sub>, is represented in red. The difference between the two spectra (green curve in Figure 6.1.2) shows spectral features in emission between 1320 and 1390 cm<sup>-1</sup> well above the noise (of about  $4 \times 10^{-7}$  W m<sup>-2</sup> sr<sup>-1</sup> m in this spectral range, see section 4.1.1), which are unambiguously associated to SO<sub>2</sub> (see orange curve in panel (a) of Figure 6.1.2). The fact that SO<sub>2</sub> is observed in emission is consistent with the presence of a thermal inversion. Note in addition that the temperature inversion prevents vertical transport and therefore traps SO<sub>2</sub> close to the surface and allows pollution to build up (subsection 1.2.2).

# 6.2 Retrieval method and parameters

To retrieve the near-surface SO<sub>2</sub> concentrations in the Norilsk region, we have used the simplified version of the OEM presented in section 3.2 of chapter 3. As a reminder, the idea of the method is to interpret the spectrally interfering variables as part of the spectral noise and to account for these in a generalised noise covariance matrix  $\mathbf{S}_{\epsilon}^{\text{tot}}$ . Using this method, the retrieval is reduced to the adjustment of only the targeted parameters, which is here the 0–2 km and 2–5 km SO<sub>2</sub> columns. In next subsections, we describe first of all, how the matrix  $\mathbf{S}_{\epsilon}^{\text{tot}}$  has been built (subsection 6.2.1). We then define the settings used in the retrieval itself (subsection 6.2.2).

<sup>&</sup>lt;sup>2</sup>We neglect here the region of the  $\nu_1 + \nu_3$  band, which is by far weaker than the other two bands (from *HITRAN* 2008 database (Rothman et al., 2009)).



Figure 6.1.2: (a) IASI spectrum (W m<sup>-2</sup> sr<sup>-1</sup> m) recorded on 9<sup>th</sup> of February 2010 in the area of Norilsk (blue). Surface temperature, H<sub>2</sub>O and CH<sub>4</sub> profiles have been retrieved from it and then used in the simulation of a corresponding spectrum for an atmosphere containing no SO<sub>2</sub> (red). The residual of the two is the green curve and shows only SO<sub>2</sub> spectral features in emission. The spectral contribution of SO<sub>2</sub> to the spectrum is shown in orange. (b) Associated temperature (K, blue), H<sub>2</sub>O (g/kg, red) profiles and ground temperature (K, blue triangle) retrieved by the EUMETSAT L2 PPF. These data have been used in the retrieval leading the adjusted spectrum shown in red in panel (a). The TC (defined as the difference between the surface temperature and the first available atmospheric temperature) for this particular case is -16.3 K.

## 6.2.1 The total error covariance matrix $\mathbf{S}_{\epsilon}^{\text{tot}}$

Three  $\mathbf{S}_{\epsilon}^{\text{tot}}$  matrices have been built to represent three different periods for the Norilsk region, defined according to values of TC and humidity. These periods correspond to the winter (here taken from November to March), characterised by high negative TC and low H<sub>2</sub>O content in the PBL, the summer (June to August) with low positive TC and the highest humidities, and the mid-season (April-May, September-October) representing intermediate TC and humidity values. Note that it would have been possible to use only one  $\mathbf{S}_{\epsilon}^{\text{tot}}$  for these three periods but it would have then included larger variability, with as a consequence higher errors on the SO<sub>2</sub> retrieved columns (Carboni et al., 2012).

The  $\mathbf{S}_{\epsilon}^{\text{tot}}$  have been calculated using equation (3.2.1) and, for each period, about 20 000 IASI spectra from 2010 and 2011. Only those with less than 25% of cloud coverage (information taken from EUMETSAT L2 products) and with no detectable SO<sub>2</sub> were selected. For this, observed spectra relatively far from the source region were used (60–62°N/75–100°E and 74–75°N/75–100°E). This area usually does not have observable quantities of SO<sub>2</sub> (as can be seen from Figure 6.3.1). In addition, to avoid possible contaminated spectra associated with transported SO<sub>2</sub> plumes (from volcanic origin for example), data were filtered using the BTD method presented in subsection 5.1.1: only spectra with a BTD lower than the noise of the instrument have been selected to generate  $\mathbf{S}_{\epsilon}^{\text{tot}}$ . Then, for each observed spectrum, one is simulated. These simulated spectra were calculated for the spectral

range 1330–1390  $\rm cm^{-1}$  with the Atmosphit software. Temperature and humidity profiles used in the simulations were taken from EUMETSAT L2 products. This was also the case for the surface temperature, if available. When surface temperature was not included in the L2 distributed by EumetCast, it was evaluated by averaging the BT of six window channels (857.50, 866.25, 868.50, 879.00, 892.75, 1231.75 cm<sup>-1</sup>). Vertical profiles of other atmospheric constituents have been taken from the standard subarctic models (winter and summer) (Anderson et al., 1986). These define average VMRs for  $CH_4$  and  $N_2O$ , that absorb/emit radiation in the spectral range along with H<sub>2</sub>O. The CH<sub>4</sub> model profile was scaled by a factor of 1.06, to adjust the surface VMR to 1800 ppm, in closer agreement with surface measurements (see, e.g., http://www.esrl.noaa.gov/gmd/aggi/). Figure 6.2.1 presents as an example the  $\mathbf{S}_{\epsilon}^{\text{tot}}$  (left panel) and the associated bias  $\mathbf{w}$  (right panel) built for the winter period. The contribution of the spectral channels to the retrieval of  $SO_2$  (minimisation of the cost function J) is determined by their associated values in the  $\mathbf{S}_{\epsilon}^{\text{tot}}$ : the largest it is, the lowest their contribution is. From Figure 6.2.1, we can conclude that channels located below 1360  $\rm cm^{-1}$  contribute the most to the retrieval. Note that the features observed in the bias (right panel) below 1360  $\rm cm^{-1}$  correspond to  $\rm CH_4$  lines. They are probably caused by a misrepresentation of the  $CH_4$  profile chosen in the forward simulations.



Figure 6.2.1:  $\mathbf{S}_{\epsilon}^{\text{tot}}$  matrix (W<sup>2</sup> m<sup>-4</sup> sr<sup>-2</sup> m<sup>2</sup>, color scale) built for the winter season according to equation (3.2.1) (left) and its associated bias **w** (right).

## 6.2.2 Retrieval parameters

Just as for the forward simulations, retrievals have been performed with the Atmosphit software in the spectral range 1330–1390 cm<sup>-1</sup> and on spectra with less than 25% of cloud coverage. The chosen reduced state vector  $\mathbf{x}$  contains two SO<sub>2</sub> columns, the first one extending from 0 to 2 km and the second one from 2 to 5 km. We expect indeed negligible amounts of SO<sub>2</sub> above 5 km, given the short lifetime of this gas in general. Furthermore, more specifically for the winter cases, the presence of strong temperature inversions frequently confines the pollution at near-surface level. The standard subarctic SO<sub>2</sub> profile (Anderson et al., 1986) has been used for the *a priori* profile. A large variability of 150% has been considered (diagonal elements of the *a priori* covariance matrix  $\mathbf{S}_{\mathbf{a}}$ ), to allow retrievals of high concentrations which occur frequently (Figure 6.1.1). The off-diagonal elements in  $\mathbf{S}_{\mathbf{a}}$  have been calculated using an exponential decay from the diagonal as follows:

$$S_a(i,k) = \sqrt{S_a(i,i) S_a(k,k)} \exp\left(-\frac{|z_i - z_k|}{H}\right),$$
 (6.2.1)

where  $z_i$  and  $z_k$  are the correlated altitudes, and H is the correlation length (scale height) which was chosen equal to 7 km. The fixed parameters (temperature and humidity profiles,...) have been chosen the same way as for the forward simulations. The complete retrieval scheme has been applied on IASI spectra recorded for four years, between 1<sup>st</sup> January 2008 and 31<sup>st</sup> December 2011 in a large area around Norilsk (61–75°N/75–96°E and 67–75°N/96–100°E).

# 6.3 Spatial distribution

Figure 6.3.1 presents the spatial distribution of the average retrieved 0–2 km column of  $SO_2$  for February 2009. The highest mean retrieved columns are above 2 Dobson Units  $(1 \text{ DU}=2.69\times10^{16} \text{ molecules/cm}^2)$  and located above the city. The plume then spreads away from the source, as seen by a gradual decrease of the retrieved concentrations. Averaged over one month, it seems that the pollution plume follows two distinctive transport pathways, one eastward and the other westward, surrounding the mountains. The entire SO<sub>2</sub> plume observed by IASI covers a large region of about 165 000 km<sup>2</sup> around Norilsk, suggesting a significant influence on its surrounding environment, as discussed in Vlasova et al. (1991), Tutubalina and Rees (2001), and Zubareva et al. (2003). It is noting that we can distinctly observe the plume following the Plutorana Plateau (the concentrations above 300 m never being higher than 0.5 DU). This clearly demonstrates that the detected SO<sub>2</sub> is located close to the surface, where the temperature inversions develop. Actually, the mean altitude of these inversion layers, calculated over the whole retrieved area for February 2009, and based on the temperature profiles provided by the EUMETSAT L2 PPF, is 410 m above the ground. Most of the SO<sub>2</sub> pollution is thus probably being transported below this altitude.

Similar SO<sub>2</sub> distributions can be drawn for other winter months. However, during summer and mid-season, higher humidity and lower TC hamper measurement of near-surface SO<sub>2</sub>. The detection is only possible for some days, with particular favourable conditions (see later Figure 6.4.1). In contrast, during the winter and as shown in Figure 6.4.1 (discussed in next sections), TC and humidity are favourable almost permanently.

# 6.4 Time series

Time series of the retrieved 0–2 km SO<sub>2</sub> column are presented in Figure 6.4.1 (first panel) for the period 01/01/2008-31/12/2011. For each day, the 0–2 km column is an average of all columns in a circle of 50 km radius centered on Norilsk. However, in summer and mid-season notably, average columns can be strongly underestimated due to changes in PBL sensitivity, and thus do not correspond to the real pollution above the area. Moreover, the average is made over a quite large area around Norilsk and is thus not very representative of the high concentrations of SO<sub>2</sub> just above the city. Therefore, daily maximum SO<sub>2</sub> columns are also presented in Figure 6.4.1 (second panel). The third panel shows the mean TC values, calculated as the difference between the temperature of the surface and of the air at 350 m altitude (surface temperature is the one distributed by the EUMETSAT L2 PPF; the temperature at 350 m has been interpolated from the distributed profile) above the ground. The last panel finally presents the mean humidity (at 350 m), calculated over the same area as the SO<sub>2</sub> columns and for the same period. The altitude of 350 m above the ground was



Figure 6.3.1: Distribution of the average retrieved 0–2 km SO<sub>2</sub> columns over the Norilsk's region for February 2009, expressed in Dobson Units (color scale). The average have been performed on a  $0.25^{\circ} \times 0.25^{\circ}$  grid and then interpolated. The contours show the terrain height in meters.

chosen to be equal to the average altitude of the temperature inversion (calculated here for the area of interest and only for winter months), below which most of the gas is probably located and which is also the altitude where the peak sensitivity is expected.

In Figure 6.4.1, the  $SO_2$  measurements from morning and evening overpasses have been averaged together. In wintertime, solar radiation at the latitude of Norilsk is low (or even absent during the Polar Night) and surface, atmospheric temperatures, and humidity are similar during day and night (see green and red curves in the two last panels of Figure 6.4.1). Therefore, the IASI sensitivity to PBL  $SO_2$  is very similar in the two cases. This is no more the case in summer, when the diurnal variability of temperatures and humidity is high: differences between day and night can reach 10 K for TC and 5 g/kg for  $H_2O$ . This variability is such that the sensitivity can be very different between the two successive IASI overpasses, leading to differences in  $SO_2$  measurements. For the same reasons as those explained above, calculating an average column for the mid-season and summer periods, for which it is already difficult to retrieve near-surface  $SO_2$  due to the weak sensitivity, produces large underestimation. This is well seen in Figure 6.4.1, with the average concentrations from May to October being below 5 DU and essentially close to 0, while daily maximum values can be significantly larger, typically up to 10 DU, and in few cases even 50 DU. In fact, it can be seen from Figure 6.4.1 that retrievals during the summer and the mid-season have been possible only for days (morning and/or evening) combining exceptionnally low humidity and high TC (in absolute value). Both conditions coexist for example in April 2008, August 2008, September 2008, July 2009, April 2010, May 2010, July 2010 and May 2011. Note that in August 2008, most of the detected  $SO_2$  was probably emitted by the Kasatochi eruption and transported over the Norilsk region (Karagulian et al., 2010). Because of these limitations, mid-season and summer retrieved  $\mathrm{SO}_2$  columns are only qualitatively discussed in the following.

Although the number of successful retrievals is much larger in winter owing to the more favourable conditions for detecting PBL pollution, we observe also a large variability of  $SO_2$  columns. Daily means range from 0.04 DU (the *a priori* column) to about 20 DU in February 2011. Most average columns however vary between 1 and 5 DU. The maximum columns reach 50 DU on several days. It clearly appears that most days for which  $SO_2$  columns stay close to the *a priori* correspond to situations where IASI is not sensitive to the PBL, when TC values are close to zero (humidity stays low for the entire winter and therefore does not contribute to the loss of sensitivity). This kind of unfavourable situations occurs for instance in January 2008, end of March 2008, November 2008, January 2009, beginning of November 2009, November 2010, end of January 2011, end of March 2011, December 2011.



Figure 6.4.1: From top to bottom: daily average retrieved SO<sub>2</sub> columns (0–2 km), expressed in DU; daily maximum SO<sub>2</sub> columns (0–2 km, DU); daily average TC, calculated as the difference between the surface temperature and the temperature at 350 m above the ground; daily average H<sub>2</sub>O amount at 350 m, expressed in g/kg. All averages have been calculated for data in a circle of 50 km radius centered on Norilsk, for the period 01/01/2008-31/12/2011. Data from morning and evening IASI overpasses have been simultaneously averaged for SO<sub>2</sub> columns and the distinction is made for the TC and H<sub>2</sub>O. Note that some measurements are missing for some days. They correspond to gaps in the data or cloudy scenes, which have been filtered out.

# 6.5 Evaluation against other measurements or methods

In this section, retrieved 0-2 km columns of SO<sub>2</sub> are compared with other surface SO<sub>2</sub> measurements. In a first step, they are confronted with the columns retrieved during the Master thesis using the OEM (subsection 6.5.1). They are then compared to observations made by other instruments (subsection 6.5.2).

## 6.5.1 Comparison with the results of the Master thesis (OEM)

Figure 6.5.1 shows a comparison between the retrieved 0–2 km columns of SO<sub>2</sub> using the simplified OEM and those obtained during the Master thesis using the full OEM (reminded in Appendix B.2). Only measurements of 2009 and 2010 have been used, because there were very low amount of convergent retrieval obtained with the full OEM for the year 2011. The comparison is presented in the left panel as a function of the root mean square<sup>3</sup> (RMS) of the spectral fit made with the full OEM, and in the right panel as a function of the HRI, calculated using equation (3.3.2) (the matrix  $S_y^{tot}$  that was used to calculate the HRI is described later in subsection 7.1.1). From Figure 6.5.1, we see a clear correlation between both sets of retrieved SO<sub>2</sub> columns. However, we can see that a part of the data have retrieved columns using the full OEM close to 0 DU (the *a priori*) with corresponding columns from the simplified OEM well above 2 DU. Around 60% of these data are associated to HRIs larger than 4 in absolute value (right panel), which confirm the presence of the SO<sub>2</sub> signature in IASI spectra. The failure of the OEM for these cases is also supported by the large values of the RMS (up to 3 times the radiometric noise in this spectral range, see section 6.1), which suggest that there are remaining SO<sub>2</sub> spectral features in the residual.



Figure 6.5.1: Comparison between the retrieved 0–2 km columns of SO<sub>2</sub> using the simplified OEM (PhD thesis) and the OEM (Master thesis). The comparison is presented as a function of the RMS (W m<sup>-2</sup> sr<sup>-1</sup> m, color scale) associated to the residual from the full OEM retrievals (left panel) and of the HRI (colorscale, right panel). A linear regression (reduced major axis) is also shown between the two coincident datasets (black line), and the corresponding equation and Pearson's correlation coefficient (r) are indicated.

<sup>&</sup>lt;sup>3</sup>The root mean square is calculated as  $\sqrt{\frac{\sum_{k}(I_{k}^{obs}-I_{k}^{fit})^{2}}{N_{k}}}$ , where  $I_{k}^{obs}$  and  $I_{k}^{fit}$  are respectively the observed and adjusted radiances for the spectral channel k, and  $N_{k}$  is the total number of spectral channels considered in the retrieval.

An example of such problematic fit with the OEM (RMS= $2.0751 \times 10^{-6}$  W m<sup>-2</sup> sr<sup>-1</sup> m) is shown in the top panel of Figure 6.5.2. Both observed IASI (blue) and adjusted (red) spectra are plotted (see Appendix B.2 for the inversion parameters, third step). As expected, the residual, calculated as the difference between the observed and adjusted spectra (green curve), contains spectral features well above the noise level (shown by the back dashed lines) which match those of SO<sub>2</sub>. For this example, the retrieved 0–2 km columns of SO<sub>2</sub> are 0.1 DU and 19.5 DU respectively for retrievals performed with the OEM and the simplified OEM. One possible explanation for the bad fit could be the choice of a non optimal set of retrieval settings during the Master thesis. To verify this, we have performed a new retrieval for this spectrum with the *a priori* profile multiplied by 20, to start the retrieval. The new adjusted spectrum is shown in the bottom panel of Figure 6.5.2 (red curve) along with the residual (green curve). The RMS is now in the range of the noise level (RMS=7.5411 ×  $10^{-7}$  W m<sup>-2</sup> sr<sup>-1</sup> m), and the retrieved 0–2 km column of SO<sub>2</sub> is 25.9 DU, in better agreement with the one retrieved with the simplified OEM.



Figure 6.5.2: IASI spectrum (blue) recorded on the 01/01/2010 in the area of Norilsk (69.0630°N-88.0563°E), for which the 0–2 km SO<sub>2</sub> columns retrieved with the simplified OEM is 19.5 DU and the HRI is -26.5. (Top) Adjusted spectrum (red) and residual (observed-adjusted, green) obtained with the OEM using the inversion settings of the Master thesis (Appendix B.2, third step). The retrieved 0–2 km column of SO<sub>2</sub> is here equal to 0.08 DU. (Bottom) Adjusted spectrum (red) and residual (observed-adjusted, green) obtained with the OEM using a more polluted *a priori* profile (see text). The retrieved 0–2 km column of SO<sub>2</sub> is 25.9 DU. The RMS of both spectral residuals is indicated in each panel.

Following the discussion above, a linear regression between the two datasets generated (full OEM and simplfied OEM) has also been calculated using only the full OEM retrievals associated to a RMS lower than  $1 \times 10^{-6}$  W m<sup>-2</sup> sr<sup>-1</sup> m. It is shown in both panels of

Figure 6.5.1 as black line. It has been calculated using the reduced major axis method (Smith, 2009) to account for the fact that both datasets come with errors. The agreement between the two datasets is very good, characterised by a Pearson's correlation coefficient of 0.94. The slope of 0.74 and an intercept close to 0 indicate that the retrieved SO<sub>2</sub> columns using the simplified OEM are 26% smaller on average than those retrieved with the full OEM. This underestimation could be explained in part by the training set used in the generation of the  $\mathbf{S}_{\epsilon}^{\text{tot}}$  matrix, which could still contain spectra with very weak SO<sub>2</sub>.

# 6.5.2 Comparison with other measurements

There are several previous reports of  $SO_2$  measurements in Norilsk, which were made either by surface instruments (Fukasawa et al., 2000), airplanes (Walter et al., 2012) or satellites, but in the latter cases using reflected solar radiation in the UV-Vis (Khokhar et al., 2005; Walter et al., 2012; Fioletov et al., 2013). Table 6.1 summarises the different available  $SO_2$ measurements and compares them to the daily winter average<sup>4</sup> 0-2 km columns of SO<sub>2</sub> retrieved from IASI observations. Although the direct comparison is difficult because they are not colocated in time and space and refer to different quantities (surface concentrations or VMRs, integrated columns), we find that the values obtained in this thesis are in good agreement with the others, especially with the vertical columns reported by Walter et al. (2012), which were retrieved from OMI. The retrieved SO<sub>2</sub> concentrations from our work are in contrast smaller than those measured by Fukasawa et al. (2000) and those reported by the AMAP (2006) during the 90's. This is likely due to the fact that these concentrations were measured at the surface while our averaged concentrations were calculated over a 0-2 km thick layer. As we have demonstrated above, the main part of the  $SO_2$  is likely confined at lower altitude, and therefore our reported  $SO_2$  concentrations are biased low. Part of the difference could also be related to a reduction of Norilsk's SO<sub>2</sub> emissions. For instance, Walter et al. (2012) referring to a report of the Norwegian Council on Ethics (Council on Ethics for the Government Pension Fund Global, 2009), mention that the company MMC Norilsk Nickel planned to reduce its  $SO_2$  emissions by 70% by 2010, even though the same report states that "[...] no significant decrease in  $SO_2$  emissions have so far been observed". Although the comparison provided here may be evidence of the impact of emission regulations, a definitive conclusion would require more investigation and validation of the IASI measurements.

#### Comparison with OMI measurements

A dedicated comparison has been performed at the end of the thesis between the  $SO_2$  columns retrieved from IASI (simplified OEM) and those from OMI. The cross-comparison is reported by Theys et al. (2015) in their paper describing a new algorithm dedicated to the retrieval of  $SO_2$  from OMI observations, using a multi-windows DOAS scheme. Figure 6.5.3 shows the comparison in terms of (top panel) spatial distributions and of (bottom panel) a time series of monthly averaged columns of IASI (blue circles) and of OMI (red circles) for the period 2005–2013. These are discussed separately in the following.

## 1. Distributions

The distributions shown in Figure 6.5.3 have been built using IASI and OMI retrievals of SO<sub>2</sub> for the year 2009. For IASI, only retrieved 0-2 km columns of SO<sub>2</sub> for the winter months (January, February, March, November and December), for which the sensitivity to PBL SO<sub>2</sub> is maximal, have been used. For OMI, only measurements

 $<sup>^4\</sup>mathrm{They}$  have been calculated for a 50 km radius area around Norilsk.

Table 6.1: Comparion between different available  $SO_2$  measurements made in the Norilsk region. The slant column density (SCD) corresponds to the  $SO_2$  column integrated along the light path. For this work, we give a range of averaged 0–2 km columns, concentrations or VMR of  $SO_2$  (of the 50 km radius area around Norilsk) in which most of the daily winter fluctuate. The maximum recorded average is also indicated. VMRs and concentrations given for this work have been calculated from the IASI retrieved 0–2 km columns, and respectively represent the mean VMR and the mean concentration of  $SO_2$  in the 0–2 km atmospheric layer.

	$SO_2$ measurements	Period	Comments
This work	Range/Maximum 10–30 ppb/105 ppb 20–75 $\mu$ g m <sup>-3</sup> /280 $\mu$ g m <sup>-3</sup> 1.5–5.6 DU/18.6 DU	2008–2011	Satellite (IASI)
Fukasawa et al. (2000)	Half month averages fluctuating between 30 and 60 ppb	04/1995-12/1995	Surface
Khokhar et al. (2005)	Slant column density of about 0.74 DU	Average over 1996–2002	Satellite (GOME)
AMAP (2006)	Annual averages fluctuate between 70 and 210 $\mu g m^{-3}$	1990–2003	-
Walter et al. (2012)	Slant column density of about 29.7 DU at about 5 km of Norilsk	22 October 2010	Aircraft
	Vertical column density in the range of 1.9–7.4 DU		Satellite (OMI)
Fioletov et al. (2013)	Averaged values of 2.0–2.5 DU	2005–2010 (depends on instrument)	Satellite (OMI, SCIAMACHY, GOME-2)

(vertical column density, VCD) with solar zenith angle lower than 70° have been considered, restricting the data mainly to spring-summer at these latitudes. Although the two datasets do not cover the same months, they provide similar distributions of PBL SO<sub>2</sub>. OMI sees a more spatially extended pollution plume than IASI, possibly in part due to the different periods covered, but more likely to a lower detection limit of PBL SO<sub>2</sub> with OMI. If we consider a small area around the city center of Norilsk, the agreement between the two sounders is very good, with measured averaged columns of around 2 DU for both instruments.

#### 2. Timeseries

The time series presented in the bottom panel of Figure 6.5.3 has been built using only the IASI and OMI observations in a circle of 50 km radius centered on Norilsk. To cover a longer time period, new IASI retrievals have been extended to the winters of 2012 and 2013. Only IASI measurements associated to a TC larger than 7 K (in absolute value) have been considered for the monthly averages to ensure sufficient

near-surface sensitivity to  $SO_2$  (derived from the times series shown in Figure 6.4.1). For the same reason, due to a limited sensitivity during most of the summer and the mid-season (that could lead to underestimation of averaged 0–2 km columns of  $SO_2$ ), only measurements from the winter have been used. For OMI, the distinction is made between data associated to an averaged solar zenith angle lower (filled red circles) and larger (empty red circles) than 65°. For both instruments, averaged columns for month with less than 5 days of successful retrievals are not shown.



Figure 6.5.3: (Top) Spatial distribution of  $SO_2$  in the region of Norilsk measured by OMI (left) and IASI (right) for 2009. (Bottom) 2005–2013 time series of monthly averaged columns of  $SO_2$  measured by IASI (blue circles) and OMI (red circles). Empty red circles represent OMI data for which the averaged solar zenith angle is larger than 65°. Averaged columns for month with less than 5 days of successful retrievals are not shown. Only IASI observations associated to TC larger than 7 K (absolute value) have been considered. Figure taken from Theys et al. (2015).

From the time series, we see that IASI and OMI values are overall in good agreement. The averaged column over the 8 years is respectively 1.9 DU and 2.2 DU for OMI and IASI. Both sounders seem to catch a decrease in  $SO_2$  columns from the end of 2010 to mid 2011. This time series also shows well the complementary between the TIR and UV sounders for the monitoring of near-surface  $SO_2$  at high latitudes. Indeed, measurements of TIR instruments are mainly limited to the winter months, when their PBL sensitivity is maximal thanks to large negative TC and low humidity, whereas UV sounders, for which the measurements depend on the availability of the solar radiation, are limited to the summer.

# 6.6 SO<sub>2</sub> emissions of Norilsk

From the IASI SO<sub>2</sub> measurements, we have estimated the winter emissions of Norilsk. For this, we have first calculated daily SO<sub>2</sub> total masses M according to the relation:

$$M = \frac{M_{\rm SO_2} \, C_{\rm SO_2} \, S}{N_a},\tag{6.6.1}$$

where  $M_{SO_2}$  is the molar mass of SO<sub>2</sub> (64.0638 g mol<sup>-1</sup>),  $C_{SO_2}$  is the mean SO<sub>2</sub> total column (here calculated as the sum of the 0–2 km and 2–5 km retrieved columns) in molecules cm<sup>-2</sup> for the chosen box of surface area S, and  $N_a$  is the Avogadro number. SO<sub>2</sub> masses have been calculated for each  $0.25^{\circ} \times 0.25^{\circ}$  box of a grid covering the entire retrieved area (60– 75°N/75–100°E), and then summed to obtain the SO<sub>2</sub> total mass for the region. To avoid underestimation of the total masses because of lack of sensitivity on some days in winter (obvious in Figure 6.4.1 from the low column averages), only measurements with TC higher or equal to 10 K in absolute value were taken into account. Moreover, instead of calculating a daily total mass based on daily retrieved SO<sub>2</sub> columns, we have estimated a mean daily total mass for the entire region, using one month of retrieved SO<sub>2</sub> columns for each box of the grid.

The emissions (E) for the winter months have then been calculated using a simple box model and first order loss terms (Jacob, 1999):

$$E_{i+1}(\mathrm{SO}_2) = \frac{M_{i+1} - M_i \exp\left(-\frac{t}{\tau}\right)}{\tau \left[1 - \exp\left(-\frac{t}{\tau}\right)\right]},\tag{6.6.2}$$

where  $E_i$  and  $M_i$  are respectively the emission and total mass of SO<sub>2</sub> for the day  $i, \tau$  is the effective lifetime of SO<sub>2</sub>, and t is the time between two observations (here one day). Because we have estimated a mean daily total mass for each month, the previous equation simplifies in  $E = \frac{M}{\tau}$  and leads to constant daily emissions for each month. The calculation has only been done for winter months (November to March). Only emissions calculated for 2009 are discussed hereafter, because this year presents the largest and the most constant amount of available data.

As seen from equation (6.6.2), the choice of the lifetime is crucial in estimating the emission. Lee et al. (2011) have calculated the seasonal zonal mean lifetime of  $SO_2$  in the PBL using the GEOS-Chem model. They show that it is very variable with season and latitude, mainly because of changes in dry deposition velocities and in supply of oxidants (as we mentioned in section 1.3). In wintertime and particularly during the polar night,  $SO_2$  lifetime is longer than for the summer, because of smaller concentrations of oxidants and reduced velocities of dry deposition due to snow coverage (Chin and Jacob, 1996; Wesely, 2007). Here, we have used a  $SO_2$  lifetime of three days representative of winter conditions at high latitude.

Table 6.2 compares  $SO_2$  emissions derived in this work and in other studies. Emissions for 2009 from IASI add up to 0.46 Mt in the winter and 1.10 Mt for the whole year. Yearly totals were calculated from the winter months, assuming constant monthly emissions. This is a reasonable assumption as smelting facilities usually run continuously (24 hours per day, 7 days per week). This value is in good agreement with Khokhar et al. (2008) and Walter et al. (2012). Total emissions reported in Blacksmith Institutes (2007) and Fioletov et al. (2013) are about a factor two larger. However the latter study uses a rather short  $SO_2$  lifetime of five hours, which could explain the observed difference. Note that it is
also possible that the winter  $SO_2$  lifetime is larger than the three days we have used. In conclusion,  $SO_2$  lifetime has to be better constrained to make more accurate estimation of emissions from the satellite measurements only.

Table 6.2: Norilsk's winter emissions derived from IASI  $SO_2$  measurements. Emissions obtained in other studies are also presented. For all, the period and the chosen lifetime (if required in the study) are given. Winter includes five cold months: January, February, March, November, and December.

	Period	Lifetime	Emissions	Comments
This work	2009	3 days	Winter/Yearly 0.46 Mt/1.10 Mt	Satellite (IASI)
Fioletov et al. (2013)	2005-2007	5 hours	$2.65 \pm 0.61 \text{ Mt}$ per year	Satellite (OMI, SCIAMACHY,
	2008-2010	5 hours	$2.27 \pm 0.96 \text{ Mt}$ per year	GOME-2)
Walter et al. (2012)	2010	-	0.92 Mt per year (0.41–1.46 Mt depending on chosen parameters)	Aircraft (CARIBIC)
	2010	1 day	0.7 Mt per year (0.6–0.9 Mt depending on the area of calculation)	Satellite (OMI)
Khokhar et al. (2008)	1996-2002	1 day	$1.685 \pm 0.3 \text{ Mt}$ per year	Satellite (GOME)
Blacksmith (2007)	-	-	2 Mt per year	

# 6.7 Estimation of the retrieval errors

In this section, we estimate the error on the IASI retrieved SO<sub>2</sub> columns independently of the diagnostic of the OEM, which is highly dependent on the *a priori* constraints. As there are also no suitable independent measurements available for validation, an alternative approach has been developed based on retrievals of a set of synthetic IASI spectra with known SO<sub>2</sub> columns. This allows a rigorous estimate of the errors, characterised by the global error spectral covariance matrix  $\mathbf{S}_{\epsilon}^{\text{tot}}$ , which includes the IASI noise, uncertainties in relevant meteorological parameters, in the spectroscopy of interfering trace gases and radiative transfer.

The synthetic IASI spectra have been generated with 340 randomly chosen SO<sub>2</sub> columns and representative surface temperatures, temperature and humidity profiles for the winter months in Norilsk. Then a synthetic noise was added, generated from the multivariate normal distribution corresponding to the  $\mathbf{S}_{\epsilon}^{\text{tot}}$  matrix. From these spectra, SO<sub>2</sub> was retrieved in exactly the same way as for the observed IASI spectra. The relative difference between the input and the retrieved columns then gives the error term described above. A histogram of the errors as a function of TC (in absolute value) and the 0-2 km SO<sub>2</sub> column is shown in Figure 6.7.1. All the calculated errors are positive and indicate that the retrieved SO<sub>2</sub> columns are underestimated. A clear dependence of the errors on the TC values is observed: for TC above 12 K the errors range from 10% to 40%; they are between 20% to 85% for TC values between 6 and 12 K and finally above 80% for TC below 6 K. When TC is small, the sensitivity of IASI to PBL SO<sub>2</sub> is small, and hence the retrieval depends heavily on the choice of the *a priori*. As TC increases, the sensitivity to the PBL increases and the retrieved values are in better agreement with the real ones.

The magnitude of the  $SO_2$  columns has also an effect on the sensitivity, as larger columns yield larger spectral signatures, and hence larger signal to noise ratio. This can be seen in Figure 6.7.1, where the distinction was made for columns below (blue) and above (orange) 5 DU.

Ultimately, it has to be recognised that, even for very large TC and large columns, there is a remaining low bias of about 15%. This is in agreement with the comparison discussed in subsection 6.5.1, which concluded that the retrieved SO<sub>2</sub> columns using the simplified OEM are 26% lower than those retrieved with the full OEM. As we already mentioned, this difference could be explained by an imperfect training set used in the generation of the  $\mathbf{S}_{\epsilon}^{\text{tot}}$  matrix (e.g. including residual SO<sub>2</sub> signatures).



Figure 6.7.1: Histogram of the relative error on the 0–2 km SO<sub>2</sub> column as a function of TC (absolute value). The relative error is calculated according to the relation:  $\frac{[PC(SO_2)_{true} - PC(SO_2)_{retrieved}] \times 100\%}{PC(SO_2)_{true}}$ Bars represent the mean error calculated for fields of 2 K range of TC. The blue bars are the mean errors for columns smaller than 5 DU and the orange are the mean errors for columns larger than 5 DU.

The influence of humidity on the retrieval was also investigated, as larger  $H_2O$  columns are expected to adversely affect the retrieval. However, wintertime conditions in Norilsk are dry (less than 1 g/kg of  $H_2O$  at 350 m) and constant, so that no dependence was found.

Because the calculation of the  $\mathbf{S}_{\epsilon}^{\text{tot}}$  included only spectra free of SO<sub>2</sub> spectral features, one category of errors is not accounted for in the analysis presented above and relates to the strength of the SO<sub>2</sub> spectral signature (for a given column). These include errors in the spectroscopic parameters, uncertainties on the SO<sub>2</sub> profile and the impact of the TC on the SO<sub>2</sub> lines in the forward model. For instance, an underestimation of the TC values leads to an overestimation of the SO<sub>2</sub> near-surface columns and inversely. Independent validation/calculation would be required to properly estimate such errors.

# 6.8 Final remarks

The present chapter has demonstrated the capability of IASI to measure near-surface  $SO_2$  pollution in the  $\nu_3$  band in case of large negative TC and low humidity, and this has been shown using a simplified scheme based on the OEM. It is important to note that this method has also been applied during the PhD to two particular events, which are not documented in details here. They correspond to:

- 1. A strong pollution episode in the North China Plain in January 2013 (Boynard et al., 2014). During this event, the development of large thermal inversions combined with large anthropogenic emissions led to the build up of pollutants. Large negative TC enhanced the sensitivity of IASI to the near-surface pollution and allowed the simultaneous retrieval of four pollutants: CO, SO<sub>2</sub>, NH<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.
- 2. The 2014–2015 Holuhraun eruption of the Bárðarbunga volcano in Iceland. As shown in Figure 6.8.1, this eruption emitted SO<sub>2</sub> at relatively low altitude; close to the source, the plume is mainly located below 4 km of height, before being transported at higher altitudes. The retrieval of SO<sub>2</sub> concentrations using the simplified OEM has allowed studying the impact of the Bárðarbunga eruption on air quality in Western Europe in September 2014 (Boichu et al., 2016), and have contributed to the validation of climate models (here HadGEM3) predictions of the interactions between aerosols and cloud droplets (Haywood et al., 2016). The latter study is still under review.

These studies, to which we have contributed, confirm the potential of using IASI to quantify  $SO_2$  near-surface atmospheric concentrations (and emissions when combined with a model).



Figure 6.8.1: (Top) SO<sub>2</sub> distribution (DU, color scale) inferred from IASI measurements on the 28/10/2014, following the Bárðarbunga eruption. Morning and evening measurements have been averaged together. (Bottom) Altitudes distribution (km, color scale) for the plume shown in the top panel. Close to the source, SO<sub>2</sub> mainly remains below 4 km of height. Altitudes have been calculated using the method presented in section 7.1.1 and developed by Clarisse et al. (2014).

# CHAPTER 7

# GLOBAL SCALE

In the previous chapter, we have shown that large negative TC, associated to thermal inversions, combined to low H<sub>2</sub>O amount in the lowest part of the atmosphere enhance the sensitivity of IASI to near-surface SO<sub>2</sub> pollution in the  $\nu_3$  band. This has been demonstrated in the particular case of the industrial area of Norilsk using the simplified version of the OEM. However, as we have shown in chapter 2, IASI can in theory detect PBL SO<sub>2</sub> in other situations, particularly in the case of large positive TC, and therefore could be able to measure SO<sub>2</sub> pollution above other strong anthropogenic sources, such as in China. The aim of the present chapter is to extend the local study performed above Norilsk to global scale. It relies on the development of a retrieval method, based on the LUT approach and the calculation of HRIs (see section 3.3 of chapter 3). First of all, we describe how the LUTs have been built and how the altitude of SO<sub>2</sub> is retrieved (section 7.1). The global distribution of SO<sub>2</sub> and examples of time series are then showed (sections 7.2 and 7.3). Differences between morning and evening overpasses are briefly discussed (section 7.4). A first assessment of the retrievals is finally presented (section 7.5). Note that the main part of this chapter comes from the publication of (Bauduin et al., 2016a).

# 7.1 Near-surface $SO_2$ retrievals at global scale

Given the large number of observations provided by IASI every day, a fast retrieval method has to be used to retrieve near-surface  $SO_2$  concentrations at global scale. A LUT-based approach using HRI is an excellent candidate for this purpose and already demonstrated its strength with the acquisition of improved  $NH_3$  global distributions (Van Damme et al., 2014). However, as we mentioned in section 3.3, the HRI value does not provide information on the altitude of  $SO_2$ . Because we are interested in retrieving near-surface pollution, the retrieval method developed in this thesis consists of two successive steps:

- 1. The retrieval of the altitude of the plumes and the selection of those located at low altitudes.
- 2. The retrieval of the near-surface  $SO_2$  column for the selected observations.

These two retrieval steps are described separately in the next subsections. Note that this approach exploits only the information contained in the  $\nu_3$  band of SO<sub>2</sub>.

# 7.1.1 Retrieval of the altitude of the plume

The altitude of  $SO_2$  is retrieved using the algorithm developed by Clarisse et al. (2014). The method relies on the fact that depending on the altitude at which  $SO_2$  is located, the calculated Jacobians present different spectral shapes. Indeed, we have shown in subsection 2.4.3 that variations in the shapes of Jacobians with altitude are an indication of possible decorrelation between the concentrations of the targeted gas at different altitude levels. In the case of  $SO_2$ , which is generally not distributed in the whole troposphere but located in thin layers (surface, high troposphere,...), the variations in the shapes of Jacobians can be used to determine the height of  $SO_2$  plumes. The left panel of Figure 7.1.1 shows normalised Jacobians calculated with respect to a  $SO_2$  layer located at different altitudes for the range  $1300-1410 \text{ cm}^{-1}$ . Large differences in the shape of the Jacobians are observed up to 15 km. These come mostly from the interference of the  $SO_2$  absorption lines with those of  $H_2O$ . As mentioned before, in the low troposphere, the absorption of  $H_2O$  opacifies the atmosphere in such a way that the  $SO_2$  spectral features disappear. As seen from Figure 7.1.1 (left), this is especially the case above  $1360 \text{ cm}^{-1}$  for a plume located at 2 km of height, where  $SO_2$  lines are absent in the Jacobians. As one moves higher in the atmosphere, the  $H_2O$ content decreases (along with the strength of the absorption): the atmosphere is no more opaque and the  $SO_2$  lines above 1360 cm<sup>-1</sup> start to appear in the Jacobians.

The idea of the method is thus to compute a HRI for different altitudes following

$$HRI(h) = \frac{\mathbf{K}_{h}^{T} \mathbf{S}_{\mathbf{y}}^{\text{tot}} (\mathbf{y} - \overline{\mathbf{y}})}{\sqrt{\mathbf{K}_{h}^{T} \mathbf{S}_{\mathbf{y}}^{\text{tot}} \mathbf{K}_{h}}},$$
(7.1.1)

where  $\mathbf{K}_h$  are the Jacobians for SO<sub>2</sub> located at altitude h. Based on the discussion above, it is obvious that the Jacobians  $\mathbf{K}_h$  contain the SO<sub>2</sub> signature expected at altitude h. If there is detectable amount of SO<sub>2</sub>, the function HRI(h) will peak at the altitude of the plume, because the overlap between the IASI spectrum and the SO<sub>2</sub> spectral signature will be maximal at this altitude. The height determination therefore consists in calculating the function HRI(h) at predefined altitudes and finding the altitude of its maximum. Examples of functions HRI(h) for different observed spectra are presented in the right panel of Figure 7.1.1. At low altitudes, these functions peak sharply and then become broader at higher altitudes. This is related to the fact that the larger differences in the shape of Jacobians are observed at lower altitudes (left panel).

To determine the height of  $SO_2$ , Jacobians  $K_h$  have been pre-calculated with the finite difference method for the spectral range 1300–1410  $\rm cm^{-1}$  using monthly averaged H<sub>2</sub>O and temperature profiles in 10°x20° boxes. These averages were calculated from the EUMETSAT L2 data using the 15<sup>th</sup> of each month of 2009, 2011 and 2013. One set of 30 vectors  $\mathbf{K}_h$  has been generated for each box and for each month, considering 1 km-thick layer of 5 DU of SO<sub>2</sub>, located every 1 km from 1 km to 30 km. For each IASI observation, local Jacobians are then calculated using a bilinear interpolation of the four closest grid boxes, to better take into account the variation of the atmospheric conditions when observations move away from the center of the boxes. The mean background spectrum  $\overline{\mathbf{y}}$  and the associated covariance matrix  $\mathbf{S}_{\mathbf{v}}^{\text{tot}}$  needed to calculate the HRI (equation (7.1.1)) have been built using a sample of one million randomly chosen IASI spectra. Those with detectable  $SO_2$  have been filtered out using an iterative approach: first, spectra with observable SO<sub>2</sub> signatures were rejected using the BTD method presented in subsection 5.1.1 and a first estimate of the matrix  $\mathbf{S}_{u}^{\text{tot}}$ is made. The second step uses this initial matrix to exclude spectra with measurable HRI from the remaining set of measurements (a similar method is used in Van Damme et al. (2014)). Similarly to the Jacobians,  $\overline{\mathbf{y}}$  and  $\mathbf{S}_{\mathbf{v}}^{\text{tot}}$  are calculated over the spectral range 1300– 1410  $\rm cm^{-1}$ . Note that an altitude was retrieved when a HRI larger than 2 was found, even



Figure 7.1.1: (Left) Jacobians calculated with respect to a layer of SO<sub>2</sub> located at different altitudes. They have been normalised and offset for display purposes. (Right) Examples of HRI(h)functions calculated for IASI spectra recorded during the Nabro eruption. Their values have been normalized for the comparison. Figure taken from Clarisse et al. (2014).

though in practice we expect the altitude retrieval to be accurate only for HRI values above 4 or 5.

As explained in Clarisse et al. (2014), because of the use of averaged Jacobians, the retrieved altitude can be biased, especially close to the surface. The best accuracy is achieved between 5 and 15 km, and the altitude estimate is provided within 1–2 km. Below 5 km, the retrieved altitude is more uncertain. However, this is not an important issue here as the altitude is used only to filter out SO<sub>2</sub> plumes emitted by volcanoes directly in the free troposphere. In the following, only spectra for which the plume was estimated to be between the surface and 4 km above ground are kept and analysed. The retrieved SO<sub>2</sub> corresponds therefore to a 4 km-thick column (hereafter called 0–4 km column).

From the calculated  $\mathbf{K}_h$ , we can estimate where in the retrieved 0–4 km layer IASI is the most sensitive to SO<sub>2</sub>. We found that, for favourable conditions of TC and humidity, IASI is sensitive down to the surface but has its maximum sensitivity in the upper part of the 0–4 km layer. In case of low TC and/or large column of H<sub>2</sub>O, IASI becomes insensitive to the lower part of the 0–4 km layer. This is illustrated in Figure 7.1.2, presenting Jacobians (from 1 km to 4 km) calculated for three different conditions of TC and H<sub>2</sub>O content. We find that in the three cases, the Jacobians are indeed maximal at 4 km. With increasing TC, the Jacobians calculated for SO<sub>2</sub> at 1 km increase (black curve in the left and middle panel): for 10 K of TC, the ratio between Jacobians at 4 km and at 1 km is around 3; it becomes 10 for 3 K of TC. Moreover, for a large H<sub>2</sub>O column (left panel), Jacobians at 1 km is almost vanishing, due to extreme opacity.

## 7.1.2 Retrieval of near-surface SO<sub>2</sub> concentrations

For the selected spectra associated to low SO<sub>2</sub> plumes, the next step consists in computing an HRI (according to equation (3.3.2)) for each IASI measurement and converting it to a SO<sub>2</sub> column. Different Jacobians,  $\overline{\mathbf{y}}$  and  $\mathbf{S}_{\mathbf{y}}^{\text{tot}}$  have been built for this second step (see



Figure 7.1.2: Jacobians (W m<sup>-2</sup> sr<sup>-1</sup> m DU<sup>-1</sup>) calculated for SO<sub>2</sub> (5 DU) located at 1 km, 2 km, 3 km and 4 km, for different conditions of TC and H<sub>2</sub>O total columns identified on top.

subsection below). Because a constant Jacobian is used in the calculation of the HRI, there are several parameters that impact its value in addition to the  $SO_2$  abundance itself and they need to be accounted for. We have considered the impact of viewing angle (by building angle-dependent matrices for the HRI calculation, see subsection 7.1.2.1), of humidity and TC, which become separate entries in the LUTs (subsection 7.1.2.2).

#### 7.1.2.1 Angular dependency

The dependence of the signal strength on the viewing angle has to be taken into account in the conversion of HRI values. As reported by Van Damme et al. (2014), the application of a cosine factor to account for the increased path length tends to overcorrect the HRI and leads to a bias for larger angles. As they suggested, angular dependent  $\mathbf{K}, \, \overline{\mathbf{y}}, \, \mathbf{S}_{\mathbf{y}}^{\text{tot}}$  have been used. Specifically, between  $0^{\circ}$  and  $55^{\circ}$ ,  $5^{\circ}$  angle bins have been defined and a last one of  $4^{\circ}$  is considered for  $55^{\circ}$ - $59^{\circ}$  (IASI zenith angle ranges between  $0^{\circ}$  and  $58.8^{\circ}$ ). For the median angle of each bin, a Jacobian has been generated for a standard atmosphere (Anderson et al., 1986), with a scaling factor applied to the methane profile as described in subsection 6.2.1. A TC of 10 K has been considered. All K have been calculated with the finite difference method for 200 ppb  $SO_2$  well-mixed between 4 and 5 km, and over the 1300–1410 cm<sup>-1</sup> range. For  $\overline{\mathbf{y}}$  and  $\mathbf{S}_{\mathbf{y}}^{\mathbf{tot}}$  almost the totality of cloud-free (i.e., cloud fraction below 20% and available EUMETSAT L2 surface temperature, atmospheric temperature and  $H_2O$  profiles) observations of the 15<sup>th</sup> of each month of 2009 and 2011 have been used, sorted by angle bins. Measurements with detectable  $SO_2$  have been filtered as described in subsection 7.1.1. In this way, for each angle bin,  $\overline{y}$  and  $S_v^{tot}$  have been calculated from about 750 000 spectra.

For the sake of illustration, an example of  $\mathbf{S}_{\mathbf{y}}^{\mathbf{tot}}$  (left) and  $\overline{\mathbf{y}}$  (right) is given in Figure 7.1.3 for the angle bin 20–25°. The contribution of each spectral channel in the calculation of the HRI depends on its respective value in  $\mathbf{S}_{\mathbf{y}}^{\mathbf{tot}}$ : the larger it is, the larger the spectral variability in this channel is, and the lower its contribution to the HRI. From the left panel of Figure 7.1.3, we can see that channels located above 1350 cm<sup>-1</sup> contribute the most to the calculation of the HRI. The mean background spectrum presented in the right panel shows mainly CH<sub>4</sub> and H<sub>2</sub>O lines.



Figure 7.1.3: (Left) Matrix  $\mathbf{S}_{\mathbf{y}}^{\mathbf{tot}}$  (W<sup>2</sup> m<sup>-4</sup> sr<sup>-2</sup> m<sup>2</sup>, color scale) calculated using equation (3.3.1) for the angle bin 20–25° and spectral range 1300–1410 cm<sup>-1</sup>. (Right) Associated background spectrum  $\overline{\mathbf{y}}$ .

# 7.1.2.2 Look-up-tables

The conversion of the HRI into  $SO_2$  column is done using LUTs, which, as for  $\overline{\mathbf{y}}$  and  $\mathbf{S}_{\mathbf{y}}^{\text{tot}}$ , have been separated per angle bin. The LUTs include 4 dimensions linking TC, total column of H<sub>2</sub>O, HRI and SO<sub>2</sub> column. To build the LUTs, forward simulations of IASI spectra have been performed for a series of situations, summarised in Table 7.1, using the Atmosphit software. More specifically the following parameters were varied to provide a representative set of atmospheric conditions:

## 1. $SO_2$ columns

To obtain a reference  $SO_2$  vertical profile for anthropogenic emissions, we relied on the global chemistry transport MOZART model (Emmons et al., 2010) outputs of January, April, July and October 2009 and 2010. An average profile was calculated from all modelled profiles above Eastern United States, Europe and Eastern China, with the SO<sub>2</sub> concentration above 4 km set to zero. The resulting reference profile is shown in Figure 7.1.4 (blue). The set of atmospheric SO<sub>2</sub> columns included in the LUTs was then obtained by scaling this reference profile by the 16 factors listed in Table 7.1, leading to a range of 0–4 km SO<sub>2</sub> columns (ground to 4 km above it) going from 0 to 415 DU.

## 2. $H_2O$

In a similar way, the H<sub>2</sub>O profile from the US Standard model (Figure 7.1.4 in red) has also been varied using 16 scaling factors (Table 7.1), covering a range of H<sub>2</sub>O total columns from  $9.5 \times 10^{19}$  to  $2.3 \times 10^{23}$  molecules cm<sup>-2</sup>.

## 3. Temperature

A single temperature profile has been used (US standard, Figure 7.1.4 right). To include a range of TC values, which are here defined as the difference between the temperature of the ground and the temperature of the air at 500 m (see Figure 7.1.4),

we have varied the surface temperature to provide 25 different situations, listed in Table 7.1. These include extreme cases of TC, from -30 K to +40 K, but also a range of low and moderate values.

Note finally that a constant emissivity of 0.98 has been used in the forward simulations; for most of cases, differences between using a spectrally varying emissivity and a constant emissivity are the order of the noise of the instrument.

	${f Reference} \ {f profile}^1$	Range of values <sup>2</sup>
$\mathbf{SO}_2$	MOZART average for polluted conditions up to 4 km; 0 above	Multiplicative factor applied on the entire reference profile: 0, 1, 5, 10, 15, 20, 30, 40, 50, 80, 100, 160, 240, 320, 640 and 1000
$H_2O$	US Standard model	Multiplicative factor applied on the entire reference profile: 0.002, 0.005, 0.01, 0.05, 0.1, 0.2, 0.5, 1, 1.5, 1.8, 2, 2.5, 3, 3.5, 4 and 5
$\mathrm{T}\mathrm{C}^3$	Temperature profile from US Standard model	-30, -25, -20, -17, -15, -12, -10, -7, -5, -3, 0, 3, 5, 7, 10, 12, 15, 17, 20, 22, 25, 27, 30, 35, 40

Table 7.1: Range of atmospheric situations considered for the forward model runs used as reference for the LUTs.

<sup>1</sup> The reference profiles of SO<sub>2</sub>, H<sub>2</sub>O and temperature are shown in Figure 7.1.4. <sup>2</sup> In degrees for the TC, unit less for SO<sub>2</sub> and H<sub>2</sub>O scaling factors. <sup>3</sup> TC is defined as the difference between the surface temperature (variable) and the temperature of the air at 500 m (from the reference profile shown in Figure 7.1.4).

The LUTs constructed this way have been interpolated on a finer grid in the TC,  $H_2O$  and  $SO_2$  dimensions. An example of resulting LUTs is shown in Figure 7.1.5, which presents the  $SO_2$  columns (color scale) as a function of the HRI and TC (constant  $H_2O$  total column of  $2 \times 10^{20}$  molecules cm<sup>-2</sup>) in panel (a), and as a function of the HRI and  $H_2O$  total column (constant TC of 15 K) in panel (b). The retrieval scheme consists in determining for each IASI measurement the satellite zenith angle, the HRI, the TC, the total column of  $H_2O$  and, using the LUTs, the 0–4 km column of SO<sub>2</sub>.

From Figure 7.1.5, it can be seen that the HRI has the same sign as the TC. In case of positive TC, this is explained by the fact that SO<sub>2</sub> spectral lines are in absorption in IASI measurements (subsection 2.4.4), resulting in a negative difference  $(\mathbf{y} - \overline{\mathbf{y}})$ . Given the fact that the Jacobians are also negative (see definition in subsection 7.1.2.1), the calculated HRI is positive. As a rule, for constant zenith angle, columns of H<sub>2</sub>O and SO<sub>2</sub>, the value of the HRI increases with the TC. This increase in spectral signal corresponds to an increase of IASI sensitivity to near-surface SO<sub>2</sub>. However (see panel (b) of Figure 7.1.5), for increasing H<sub>2</sub>O content, which renders the atmosphere opaque in the low layers, the IASI sensitivity decreases along with the HRI for constant SO<sub>2</sub> columns, TC and viewing angle.

In case of negative TC, SO<sub>2</sub> lines are in emission and the calculated HRI is negative too. For increasing negative TC (more and more negative), the HRI value usually decreases (also more and more negative). However, from panel (a) of Figure 7.1.5, it can be seen that some HRI values are positive for negative TC. We can explained this seemingly odd behaviour with the help of left panel of Figure 7.1.6, which shows HRI as a function of SO<sub>2</sub> for a TC of -10 K and a total column of H<sub>2</sub>O of  $2.4 \times 10^{20}$  molecules cm<sup>-2</sup>. From 0 to 66.33 DU, we find that



Figure 7.1.4: 2-year average SO<sub>2</sub> vertical profile (ppb, blue) calculated from MOZART simulations over polluted regions (2009–2010), US Standard H<sub>2</sub>O profile (ppm, red) and temperature (K, right). The SO<sub>2</sub> profile shown here corresponds to a 0–4 km column of SO<sub>2</sub> of 0.4 DU. The TC is defined as the difference between the surface temperature and the temperature of the air at 500 m (red dots).



Figure 7.1.5: Example of interpolated LUTs to convert HRI in SO<sub>2</sub> column depending on TC and H<sub>2</sub>O total column for the angle bin  $15^{\circ}-20^{\circ}$ . The color scale represents the 0–4 km column of SO<sub>2</sub> in DU. Panel (a) shows the dependency of HRI on TC (constant total column of H<sub>2</sub>O of  $2\times10^{20}$  molecules cm<sup>-2</sup>); Panel (b) shows the dependency on the total column of H<sub>2</sub>O (constant TC of 15 K).

the HRI decreases (implying higher signal) logically for increasing  $SO_2$ . Above 66.33 DU, the HRI starts to increase with increasing  $SO_2$ . From about 250 DU, the HRI becomes positive. This evolution of the HRI is due to the competition between emission in the lowest layer (mainly in the 0–1 km layer where the temperature inversion occurs) and absorption above. The right panel of Figure 7.1.6 presents the contributions (in absolute value) of the emission

in the 0–1 km layer and the absorption in the 1–4 km layer to the total spectral signal, as function of the 0–4 km SO<sub>2</sub> column. They have been evaluated at 1355 cm<sup>-1</sup> using similar techniques as in Clarisse et al. (2010). These consist in simulating the upwelling radiance after the 0–1 km and 0–4 km layers, and in calculating their difference<sup>1</sup>. In Figure 7.1.6, for concentrations ranging from 0 to 66.33 DU, emission in the 0–1 km layer increases more rapidly than absorption in the 1–4 km layer. This results in decreasing HRI (more and more negative). From 66.33 DU, emission comes closer to saturation; its increase is slower than the one of absorption, whose saturation occurs for larger SO<sub>2</sub> columns, and the HRI starts to increase. From around 250 DU, absorption totally counterbalances emission and HRI values become positive. This competition between emission in the lowest layers and absorption higher up depends on the value of the temperature inversion, as the latter determines the strength of the emission. Note that in reality this would also depend on the altitude of the thermal inversion, but which is here constant (just above the ground).

When looking at the example LUT in Figure 7.1.5 or from left panel of Figure 7.1.6, the consequence of this balancing effect is that, for negative TC, a negative HRI can be converted into two SO<sub>2</sub> columns: a small one (emission combined with weak absorption above 1 km) and a large one (larger emission partly counterbalanced by a more rapid increase of absorption above 1 km). The extremely high-column solution is not expected to occur above anthropogenic sources: for this reason, in case a choice has to be made, only the smallest column is considered. Note that the large columns for which the HRI is positive for negative TC have been kept.



Figure 7.1.6: (Left) Evolution of the HRI as function of the 0–4 km column of SO<sub>2</sub>, in case of negative TC (-10 K). In this simulation, the total column of H<sub>2</sub>O is of  $2.4 \times 10^{20}$  molecules cm<sup>-2</sup> and the angle bin is 15°–20°. (Right) Contributions of the emission in the 0–1 km layer (blue) and of absorption in the 1–4 km layer (red) to the IASI spectrum at 1355 cm<sup>-1</sup>, expressed in brightness temperature difference (absolute value). Details are given in the text.

#### 7.1.2.3 Detection limit

From the LUTs, we can estimate the detection limit of IASI to near-surface  $SO_2$ . In Figure 7.1.7, the lowest detectable 0–4 km column of  $SO_2$  is presented as function of TC and the total column of  $H_2O$ . These columns have been calculated using the LUTs assuming a detection threshold of 3 on the value of HRI (see section 3.3). As expected, this limit

<sup>&</sup>lt;sup>1</sup>Note that the contribution of the interfering species is removed by subtracting upwelling radiances calculated for an atmosphere free of  $SO_2$ .

of detection largely depends on TC and humidity. Indeed, when the former is close to 0, IASI stays insensitive even to large SO<sub>2</sub> columns. For large TC, 0–4 km columns lower than 1 DU can be measured. The detection limit similarly depends on the humidity. Below  $2 \times 10^{22}$  molecules cm<sup>-2</sup>, the limit of detection stays below 2 DU for both high positive and high negative TC. For larger H<sub>2</sub>O amount, this limit rapidly increases for negative TC but stays relatively low for large positive TC. From above  $4 \times 10^{22}$  molecules cm<sup>-2</sup> of H<sub>2</sub>O, the detection threshold starts to increase (less sensitivity) for positive TC with increasing H<sub>2</sub>O.



Figure 7.1.7: Lowest detectable 0-4 km SO<sub>2</sub> column (colorbar, in DU) as a function of TC and the total column of H<sub>2</sub>O for the angle bin  $15^{\circ}-20^{\circ}$ . These columns are those that correspond to a HRI of 3 (3 $\sigma$ ), which can be considered as the detection threshold.

#### 7.1.3 Error characterisation

To each LUT, an associated table of errors has been generated by propagating the uncertainties of the different LUT parameters:

$$\sigma_{\rm SO_2} = \sqrt{\left(\frac{\partial SO_2}{\partial TC}\right)^2 \sigma_{\rm TC}^2 + \left(\frac{\partial SO_2}{\partial H_2O}\right)^2 \sigma_{\rm H_2O}^2 + \left(\frac{\partial SO_2}{\partial HRI}\right)^2 \sigma_{\rm HRI}^2},\tag{7.1.2}$$

where  $\sigma_{SO_2}$  is the absolute error of the SO<sub>2</sub> column,  $\sigma_{TC}$  and  $\sigma_{H_{2O}}$  are the errors on TC and the total column of H<sub>2</sub>O, which are respectively taken equal to  $\sqrt{2}$  K and 10% relying on early validation of the IASI L2 data retrieved from the PPF (Pougatchev et al., 2009);  $\sigma_{HRI}$ is the standard deviation of the HRI and is equal to 1.

An example of error tables is given in Figure 7.1.8 (panel (a) corresponds to relative errors and panel (b) to absolute errors) for the angle bin  $0^{\circ}-5^{\circ}$  and for a total column of H<sub>2</sub>O of  $2\times10^{20}$  molecules cm<sup>-2</sup>. As expected, the errors are directly linked to the IASI sensitivity to near-surface SO<sub>2</sub>, with large errors (above 100% and 10 DU respectively for relative and absolute errors) occurring in case of small TC. The errors decrease with increasing TC and drop to 20% (2 DU) or less in the most favourable situations. As discussed above, for large total columns of  $H_2O$ , IASI is also less sensitive to near-surface  $SO_2$  and errors increase accordingly.

Another source of errors, which is not taken into account in the error calculation, is the assumed SO<sub>2</sub> vertical profile. A given column amount of SO<sub>2</sub> located at different altitudes corresponds to different HRI values. For instance, we have estimated the error on the SO<sub>2</sub> column to be of the order of 30% when SO<sub>2</sub> is confined to the 0–1 km layer only (for a TC of 10 K and a total column of H<sub>2</sub>O of  $9.5 \times 10^{21}$  molecules cm<sup>-2</sup>). Note also that the assumed temperature profile can be a source of error (see section 7.4).



Figure 7.1.8: (a) Relative errors (%, color scale) and (b) absolute errors (DU, color scale) as a function of HRI and TC for a total column of  $H_2O$  of  $2 \times 10^{20}$  molecules cm<sup>-2</sup> and for angle bin  $0-5^{\circ}$ .

One last important remark is that the errors have been used to filter the data used in the following. Only the retrieved  $SO_2$  columns with less than 25% relative error and less than 10 DU in absolute error have been used. The second criterion was found necessary to remove spurious data (unrealistic high columns) over the cold Antarctic region. The first criterion was adopted to reject measurements for which IASI sensitivity to near-surface  $SO_2$ is limited, and thus for which the associated retrieved  $SO_2$  columns have large uncertainties. The drawback of this filtering procedure is that it tends to favour large  $SO_2$  columns. As a consequence, the averages (distributions, time series,...) presented next are expected to be biased high. It is important to stress though that individual measurements that pass the filter are not a priori biased but have random uncertainties related to errors on the different input parameters (errors on TC, choice of temperature and  $SO_2$  profile, as explained above). It is also important to note that, by using the HRI> 2 criterion early in the retrieval procedure (see subsection 7.1.1), we have made the choice not to treat observations with small or undetectable amounts of  $SO_2$ . This potentially removes one category of useful observations: those where a low HRI is found together with favourable atmospheric conditions. In this case, a low HRI can be an indication of the absence of large  $SO_2$  concentrations at the surface. Future versions of the retrieval algorithm could be expanded to include those, and this would potentially decrease the high bias when making averages.

# 7.2 Global distribution of near-surface $SO_2$

Using the LUT approach, SO<sub>2</sub> retrievals have been performed on almost 7 years of IASI observations (01/01/2008-30/09/2014). In Figure 7.2.1, an average global distribution of the

near-surface column of SO<sub>2</sub> for this period is presented, separately for day (top) and night (bottom) observations. Only measurements with less than 20% cloud fraction in the IASI field-of-view and with available surface temperature, profiles of temperature and H<sub>2</sub>O from the EUMETSAT IASI L2 PPF have been used. A selection based on the error, described in subsection 7.1.3, has also been applied. The columns that pass these posterior filters have been averaged on a  $0.5^{\circ} \times 0.5^{\circ}$  grid for cells including more than 5 IASI measurements. The bottom-right inset in the daytime map presents the total number of successful measurements (those which pass the error filtering) in each grid boxes. The bottom-right inset in the nighttime map presents the global anthropogenic emissions (in kg s<sup>-1</sup> m<sup>-2</sup>) of SO<sub>2</sub> provided by the EDGAR v4.2 inventory (downloaded from the ETHER/ECCAD database) (EDGAR, 2011).

Figure 7.2.1 reveals several anthropogenic and volcanic hotspots, numbered from 1 to 13. Most of them are observed during the morning overpass, when the TC is large. They are:

1. China

China is one of the world's largest emission sources of  $SO_2$ , mainly due to energy supply through coal combustion (Lu et al., 2010; Smith et al., 2011; Lin et al., 2012). A large region of enhanced  $SO_2$  columns, from 1 to 8 DU on the 7-year average, is seen over the industrial area surrounding Beijing. The largest columns are found close to Beijing, where emissions are the largest according to the EDGAR database, and then decrease westwards.

2. Norilsk

As we already demonstrated in chapter 6, the pollution from the Norilsk smelters is well observed with IASI. In Figure 7.2.1, averaged  $SO_2$  columns varying between 1 and 9 DU are observed above this region. A comparison between measurements obtained with the LUT approach and those retrieved using the simplified OEM (previous chapter) will be given in subsection 7.5.1.

3. South Africa

In Figure 7.2.1, large SO<sub>2</sub> columns are observed close to Johannesburg in South Africa. The averaged columns are around 3 DU for daytime measurements. Emissions of about  $5 \times 10^{-11}$  kg s<sup>-1</sup> m<sup>-2</sup> are reported in the EDGAR database in this area, which correspond to power plants of the Mpumalanga Highveld industrial region (Josipovic et al., 2009).

4. Iran

Several  $SO_2$  sources are observed above Iran. Columns of 1 to 4 DU are measured above the smelters of Sar Cheshmeh copper complex (Rastmanesh et al., 2010, 2011). Emissions of oil industries located on the Khark Island (Ardestani and Shafie-Pour, 2009; Fioletov et al., 2013) are also observed, with columns around 1 to 2 DU.

5. Balkhash

In Figure 7.2.1, we can see that IASI is able to measure  $SO_2$  above the region of copper smelters located in Balkhash, Kazakhstan (Nadirov et al., 2013; Fioletov et al., 2013). Columns around 1 to 2 DU are retrieved.

6. Mexico and Popocatepetl

Columns reaching more than 10 DU are measured in the region of Mexico City and are regularly detected. These can be attributed to low altitude plume released by the



Figure 7.2.1: Averaged global distribution of near-surface SO<sub>2</sub> columns for the period 01/01/2008-30/09/2014. The top panel corresponds to daytime measurements and the bottom panel corresponds to nighttime measurements. The bottom-right inset in the daytime map represents the total number of successful measurements (those which pass the error filtering) in each grid boxes. Bottom-right inset in the nighttime map gives the global anthropogenic emissions (kg s<sup>-1</sup> m<sup>-2</sup>) of SO<sub>2</sub> provided by the EDGARv4.2 inventory. Different sources are numbered and discussed in the text. Note that because of the error filtering, the global averaged columns are biased high (see text for details). They can be seen as an average of measurements which are sensitive to near-surface SO<sub>2</sub>.

Popocatepetl volcano (Varley and Taran, 2003; Grutter et al., 2008) and/or to  $SO_2$  emissions of the Tula industrial complex, located northward of Mexico City (De Foy

et al., 2009). The proximity of these two sources is such that they cannot be separated by using IASI observations only.

7. Kamchatka volcanoes

SO<sub>2</sub> columns of about 2–3 DU are observed above the Kamchatka region. These are likely due to the activity of different volcanoes located in this region (e.g., Kearney et al. (2008); see also the archive of the Global Volcanism Program: http://volcano.si.edu/).

8. Nyiragongo

Above the Democratic republic of the Congo, a plume with columns larger than 10 DU is detected. It corresponds to the  $SO_2$  degassed from Nyiragongo volcano (Carn et al., 2013) and also probably to emissions of its neighbour, the Nyamuragira (Campion, 2014).

#### 9. Etna

In Figure 7.2.1, SO<sub>2</sub> 0-4 km columns around 6 DU are found right above the Mount Etna. As we already mentioned in subsection 5.1.1, this volcano is known for its periodic degassing activity and lava fountaining events (Tamburello et al., 2013; Ganci et al., 2012).

#### 10. Andes

A large SO<sub>2</sub> plume, with columns around 2–3 DU, is observed in the region of the Andes and can have several origins, which are difficult to distinguish. In the South of Peru, some volcanoes showed activity in the last years (e.g., Ubinas or Sabancaya, see the archive of the Global Volcanism Program: http://volcano.si.edu/). Copper smelters are also located in Ilo (Carn et al., 2007), close to the coast, but are further southern compared to the observed plume. SO<sub>2</sub> measured above Bolivia and Chile can originate from active volcanoes of the central Andean volcanic zone (Tassi et al. (2011); e.g., the Putana volcano, Stebel et al. (2015)). Smelters are also located in this area (Huneeus et al., 2006) and anthropogenic emissions are reported by the EDGAR database. Finally, the SO<sub>2</sub> measured above Argentina, Ecuador and Colombia is mainly emitted by local volcanoes (Global volcanism Program, http://volcano.si.edu/).

#### 11. Bulgaria

A narrow plume, with  $SO_2$  columns of about 2 DU, is observed in Bulgaria. This corresponds to the Maritsa-Iztok complex of thermal power plants located close to Galabovo and Radnevo (Eisinger and Burrows, 1998; Prodanova et al., 2008).

12. Turkey

In Turkey, lignite-fired power plants are located in different regions and are known to cause air pollution in the vicinity of the complexes (Say, 2006; Vardar and Yumurtaci, 2010). The emissions of these power plants is likely the cause of the observed  $SO_2$  columns around 2–3 DU.

One unexpected pattern in the daytime distribution is the  $SO_2$  plume at the extreme Western part of China, corresponding to the Taklamakan desert (number 13). In this region, the EDGAR inventory only documents few small sources but no strong ones are known. While this could be an artefact of the calculated HRI due to sand emissivity, which

strongly affects the TIR measurements, it is noteworthy that the issue is not observed similarly above other deserts. For instance, in Figure 7.2.2 we compare the distribution of measured HRI and the total column of  $H_2O$  for three desert regions: the Sahara, the center of Australia and the Taklamakan. We observe that the HRI values are for almost 90% of the cases below the detection limit of 3 above the Sahara and Australian deserts, whereas 30% of the measurements over the Taklamakan are associated to a HRI between 3 and 5, in a few cases even above. It is therefore likely that the measured columns are real, with  $SO_2$  being transported from the source regions in East China over the desert or being emitted there by developing gas and oil industries ((Lin et al., 2013), http://www. cnpc.com.cn/en/Taklamakan/Taklamakan.shtml). The very high TC (up to 20 K) and very low humidity conditions found jointly in that region make it indeed possible to measure such weak columns. However, further investigations are still required to properly assess the source of this plume and to exclude possible false attribution due to surface emissivity effects. Finally, the low-altitude parts of the plume released by the Nabro eruption, which followed complex transport patterns (Clarisse et al., 2014), are also seen during several days above Ethiopia. Note that  $SO_2$  is observed above Iceland and corresponds to the Bárðarbunga eruption that started in September 2014 (Schmidt et al., 2015). The different conditions and filters applied on IASI measurements (notably on the altitude) are responsible for the small area covered by  $SO_2$ .



Figure 7.2.2: Distributions of IASI measurements (expressed in % of the total amount of data considered) as function of HRI values (top panels) and the total column of H<sub>2</sub>O (bottom panels) over Sahara (left panels), center of Australia (middle panels) and Taklamakan (right panels). IASI observations for the period 2011–2014 and located in the areas  $18^{\circ}-27^{\circ}N/6^{\circ}O-28^{\circ}E$ ,  $29^{\circ}-21^{\circ}S/121^{\circ}-140^{\circ}E$  and  $36^{\circ}-40^{\circ}N/78^{\circ}-86^{\circ}E$  have been respectively considered for Sahara, the center of Australia and Taklamakan. Only the IASI measurements with less than 20% of cloud coverage and with available L2 temperature and H<sub>2</sub>O profiles and surface temperature have been selected. No filter using the error on the retrieved SO<sub>2</sub> column has been applied. The red lines in the top panels indicate the detection limit (*HRI* = 3, see section 3.3).

It is worth emphasizing that some of the measured points in the 7-year average are only representative of one year. For continuous/permanent sources, this indeed depends on the inter-annual variations of TC and  $H_2O$  total column that limit IASI sensitivity. Moreover, some particular events are typical of some years, like volcanic eruptions. Finally, as mentioned in subsection 7.1.3, because of the error filtering, the presented global averages are biased high. It is therefore an average of measurements which are sensitive to nearsurface  $SO_2$ . The number of such measurements is presented in the bottom-right inset of the daytime map, and is very variable from a source to another.

The comparison with the EDGAR emission inventory has allowed attributing several observed high  $SO_2$  regions to known sources. It also points the sources missed by IASI. Almost year-round low TC (January-March and September-December) combined with high humidity in summer (May to September) lead to the absence of Eastern United-States and Eastern Europe  $SO_2$  columns in Figure 7.2.1. Sources in India and in South Eastern Asia are also not observed by IASI. This is likely because of the very humid atmosphere in the tropical region. Note that the joint use of the  $\nu_1$  band, less impacted by H<sub>2</sub>O absorption, could allow detecting some of these sources. The problem of these missing sources is not limited to IASI. OMI SO<sub>2</sub> distributions (Figures 6, 7 in Theys et al. (2015), and Figures 1, 6 in Krotkov et al. (2016)) shows the ability of the sounder to measure small sources above India, USA and Europe which are not detected by IASI. These distributions also reveal the absence of some of them, compared to those reported by the EDGAR database: South Eastern Asia (e.g., Thailand), Northern Europe and part of India. These absences in OMI measurements are possibly caused by unfavorable geophysical conditions (presence of clouds,...), but this has to be investigated deeper. However, qualitatively, OMI and IASI global distributions are in good agreement. Both instruments are able to measure large sources such as Northeast China as well as smaller ones, like power plants in Turkey or Bulgaria. The two sounders are also complementary: regions characterised by high humidity and/or low TC, undetectable by IASI, can be measured by OMI whereas IASI better monitors  $SO_2$  at high latitudes, especially during the winter, and is not limited to daytime.

When examining Figure 7.2.1 the differences between the  $SO_2$  distributions retrieved from IASI measurements during morning (top) and evening (bottom) overpasses are also striking. In the evening distribution the plumes are more confined spatially and the columns at the center of the plumes generally larger by about a factor 3. These differences will be discussed in more details in section 7.4. after the description of the time series below, which brings additional clues on this difference.

# 7.3 Time series: examples of China and Iran

In Figure 7.3.1, the 7-year time series (01/01/2008-30/09/2014) above Beijing and the smelters region of Sar Cheshmeh (Iran) are presented as examples. For both areas, daily averages of near-surface SO<sub>2</sub> columns, TC and H<sub>2</sub>O total column are shown, separately for the morning (blue) and evening (red) overpasses of IASI. The averages have been calculated in a circle of 125 km and 75 km radius around respectively Beijing and Sar Cheshmeh. As before, only observations with less than 20% cloud fraction and with available EUMETSAT L2 have been taken into account and only those satisfying the error filtering are considered.

For Beijing and Sar Cheshmeh, the daily-averaged SO<sub>2</sub> columns from the morning overpass vary around 3 DU, with maxima that can reach 15 DU and 25 DU respectively. The time series is incomplete for Beijing, with successful SO<sub>2</sub> retrievals from December to May associated with fairly high TC (10 K on average but up to 20 K -Figure 7.3.1 middle-) and low humidity (below  $5 \times 10^{22}$  molecules cm<sup>-2</sup> -Figure 7.3.1 bottom-). The favourable TC conditions persist mostly year-round in Beijing but the humidity is too high during the other months to allow probing the surface using the LUT approach. For Sar Cheshmeh, the



Figure 7.3.1: Daily averages of near-surface  $SO_2$  (DU), TC (K) and  $H_2O$  total column (molecules cm<sup>-2</sup>) above Beijing (top) and Sar Cheshmeh (bottom). Averages have been calculated in a circle of 125 km and 75 km radius respectively for Beijing and Sar Cheshmeh. Daytime measurements are plotted in blue and nighttime measurements in red.

time series of  $SO_2$  columns from the IASI morning overpass is more extensive and this is due to the dryness of the site as compared to Beijing (a factor 2), combined with also persisting high TC conditions, from 10 K in the colder months to more than 30 K in summer.

It appears clearly in Figure 7.3.1 that IASI is mostly not sensitive to surface  $SO_2$  above the two sites in the evening due to the drop of TC close to 0. Where available, the retrieved  $SO_2$  columns in the evening are larger at the two sites by at least a factor 3 compared to the morning (red vs blue symbols). This is further investigated in next section.

# 7.4 Morning-evening differences

To examine the differences in the SO<sub>2</sub> distributions from morning and evening overpasses, we focus hereafter on a large area  $(30^{\circ} - 40^{\circ}\text{N}/105^{\circ} - 117^{\circ}\text{E})$  above China. For this region and for each month in the period 01/01/2008-30/09/2014, we first calculate for morning and evening the fraction of successful SO<sub>2</sub> retrievals, i.e., those that pass the prior and posterior filters described in the previous sections and for which the HRI has a correspondence in the LUTs, relative to all the retrievals performed in the considered area. Regarding the last condition, it is important to point out that we found that a number of IASI measurements, mainly associated with negative TC, were not covered by the LUTs (i.e., their HRI values have no correspondence in the LUTs). The fraction of these measurements is shown in Figure 7.4.1 (left, second panel from top), along with the fraction of successful SO<sub>2</sub> retrievals (top panel), as time series. They are compared (as in Figure 7.3.1) to the time evolution of TC (third panel from top) and H<sub>2</sub>O content (bottom panel).

From the top panel we see that the amount of successful retrievals during the evening orbit is significantly smaller than during the morning orbit of IASI. In the morning the seasonality is marked, with successful retrievals varying from close to zero in the humid summer months to 20–60% from January to May. For the evening measurements, the number of successful retrievals stays low year-round and is above 5% only for one or two months in spring. The prime rejection criterion for the evening measurements is surprisingly the absence of correspondence, for given angles, TC and humidity, between measured and simulated HRI in the LUTs, as obvious from the second panel. This is especially the case in winter (60–80% of rejected measurements), when TC is negative and humidity low.

The fact that such situations are not included in the LUTs comes very likely from a misrepresentation of nighttime atmospheric temperature profiles and in particular temperature inversions with the conditions used to build the LUTs (Table 7.1). To illustrate this, Figure 7.4.1 (right) shows a comparison between the standard temperature profile used for building the LUTs and a typical profile retrieved above China (35.81°N–117.81°E) on 29<sup>th</sup> of December 2013. This is a situation for which the TC is -5 K and the H<sub>2</sub>O column  $2.42 \times 10^{22}$  molecules cm<sup>-2</sup>, and for which the measured HRI value of -3.9 has no correspondence in the LUTs. The simulation of a IASI spectrum with these two temperature profiles, assuming a  $SO_2$  column of 4.35 DU, results in totally different values of the HRI, +1.2 for the US Standard temperature profile and -4.1 for the retrieved temperature profile. These results pinpoint a limitation of the current LUTs for slightly negative TC (it is not observed for large temperature inversions), which is a range where the competition between absorption and emission contributions to the HRI vary drastically. More work will be needed to avoid this shortcoming of the method in future developments, either by including more temperature profiles in the calculation of the LUTs or by using alternative approaches to better account for the variety of real situations encountered. Note that errors on the TC and on the assumed  $SO_2$  vertical profile also affect the HRI and, as a consequence, the retrieved  $SO_2$  column. They could be partly responsible for the observed non correspondence between measured HRI and the LUTs.

The small number of successful retrievals in the evening measurements combined with the generally lower sensitivity of IASI in this period of the day, is likely responsible in part for the factor 2–3 difference observed in the SO<sub>2</sub> columns between morning and evening measurements. Indeed, as only the retrieved SO<sub>2</sub> columns with small errors are kept and as these are in the evening mainly those with large columns, the averages are biased high. The effect also exists for the morning measurements but is less pronounced because of the better sensitivity to smaller columns with the atmospheric conditions -particularly TCencountered. One should point out that another possible cause for the larger concentrations is photochemistry. During the day, the photochemistry is more active and the concentrations of oxidants such as OH, H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub> are high, creating an important sink for SO<sub>2</sub>, which disappears at night, favouring higher concentrations. Such a diurnal cycle of SO<sub>2</sub> has been observed previously in China (Wang, 2002; Wang et al., 2014) and in other regions of the world (Khemani et al., 1987; Psiloglou et al., 2013) but in others, noontime SO<sub>2</sub> peaks have also been observed (e.g., Lin et al., 2012; Xu et al., 2014), possibly as a result of other meteorogical/dynamical effects (Xu et al., 2014).



Figure 7.4.1: (Left) From top to bottom: 1) Monthly percentage of successful retrievals (see text), 2) Monthly percentage of measurements outside the LUTs, 3) Monthly averages of TC (K) with associated standard deviations, 4) Monthly averages of the total column of  $H_2O$  (molecules cm<sup>-2</sup>) with associated standard deviations. Daytime measurements correspond to blue and nighttime measurements to red. (Right) Vertical temperature profiles of the US Standard 1976 model (blue) and given by the EUMETSAT L2 PPF (red) for one IASI spectrum recorded above China at  $35.81^{\circ}N-117.81^{\circ}E$  on the  $29^{th}$  of December 2013.

# 7.5 Product evaluation

In the two next subsections, we perform a first assessment of the  $SO_2$  retrieved columns obtained using the LUT approach. A first comparison is made between the LUT retrievals and the retrievals performed with the simplified OEM presented in previous chapter above the industrial area of Norilsk (subsection 7.5.1). A second evaluation is realised by comparing the retrieved columns with the OMI-derived ones (subsection 7.5.2).

# 7.5.1 Comparison with OEM retrievals

The 0–4 km SO<sub>2</sub> columns derived with the LUT approach are compared above Norilsk with the 0–5 km columns retrieved using the simplified OEM. For the comparison, we consider observations located in a circle of 150 km radius around the city of Norilsk. Only measurements with less than 25% cloud fraction, with a TC larger than 5 K in absolute value and with a humidity below 4 g/kg at 350 m above ground have been selected (reminder: this altitude corresponds to the average height of the temperature inversions). As we have seen in the previous chapter, these last conditions ensure that near-surface SO<sub>2</sub> is well probed (see Figure 6.4.1). Finally, we only consider the SO<sub>2</sub> columns retrieved with the LUT approach satisfying the error criteria exposed in subsection 7.1.3. The entire period 2008–2013 is analysed, resulting in a total of 1233 pairs of columns to compare. The comparison between the two sets of SO<sub>2</sub> columns is shown in Figure 7.5.1. A linear regression is also shown between the two coincident sets of data using the reduced major axis method (Smith, 2009) to account for the fact that both datasets come with errors.



Figure 7.5.1: Comparison between SO<sub>2</sub> columns retrieved above the industrial area of Norilsk using the LUT approach and the 0–5 km SO<sub>2</sub> columns retrieved using the simplified OEM (chapter 6). Measurements located in a circle of 150 km radius centered in Norilsk with less than 25% of cloud coverage and retrieved with relative errors smaller than 25% and absolute errors smaller than 10 DU have been taken into account. Furthermore, only measurements with H<sub>2</sub>O VMRs at 350 m lower than 4 g/kg and with TC larger than 5 K in absolute value have been considered (see detailed explanations in the text). The pink line corresponds to the linear regression (reduced major axis) calculated between the two sets of data. The color scale represents the humidity at 350 m expressed in g/kg.

The agreement between the two column datasets is very good, characterised by a correlation coefficient of 0.94. The intercept, which is close to zero, and the slope of 0.80 indicate that the SO<sub>2</sub> columns retrieved using the LUTs tend to be 20% smaller than those retrieved with the simplified OEM. This difference is partly due to the difference in columns (0–4 km with the LUT approach against 0–5 km for the simplified OEM) and to the difference in the profile used to build the LUTs compared to the *a priori* profile used in the simplified OEM. The use of the constant temperature profile for the LUTs can also cause this difference.

Finally, it is worth to emphasise in Figure 7.5.1 the measurements for which the LUTs provide a column above 2.5–3 DU and the simplified OEM a column close to 0 corresponding to the *a priori* column. As obvious from the color scale these retrievals are all associated with a relatively high humidity of 3 g/kg. These measurements have an HRI around 5, indicating small signal strength; this probably explains the difference observed between the two methods.

# 7.5.2 Comparison with OMI-derived $SO_2$ columns

We have also compared the 0-4 km SO<sub>2</sub> columns retrieved from IASI using the LUT approach with those retrieved from OMI using the algorithm of Theys et al. (2015) for anthropogenic SO<sub>2</sub>. For the IASI columns, the same filters on cloud fraction and errors as described in previous sections are applied. For the OMI columns, only those retrieved in the spectral range 312–326 nm from measurements not too much affected by the row anomaly, with solar zenith angles smaller than  $65^{\circ}$  and less than 30% cloud fraction are used (see Theys et al. (2015) for details). The comparison is performed on monthly averages for the period 2010–2013 and for an area corresponding to a circle of 125 km around Beijing. Figure 7.5.2 shows the comparison in terms of (top) a time series of the monthly averaged columns of IASI and OMI, and in terms of regional maps (2010–2013) above China (bottom). For the time series, IASI columns are shown in blue, and OMI VCDs in red for the standard retrieval and in green for the retrieval using an updated air mass factor of 0.4(AMF). From Figure 7.5.2, it can be seen that the IASI columns are on average a factor 2.5 larger than the standard OMI retrieved columns. The mean relative difference between the monthly averages of the two instruments is -135% (OMI-IASI/OMI), and has several possible origins. First, monthly means calculated from IASI are probably overestimated by the fact that only the columns with low errors are kept, which favours the higher values of the columns. Secondly, it is likely that OMI  $SO_2$  columns are at the same time underestimated. This has already been observed by Theys et al. (2015) above Xianghe (China), in the comparison with MAX-DOAS measurements (Wang et al., 2014) and explained by the inappropriate AMF used to convert the OMI derived  $SO_2$  SCDs in VCDs. In their study, Theys et al. showed that the use of better AMF significantly improves the agreement between MAX-DOAS and OMI observations. For the sake of illustration, we also show in Figure 7.5.2 the  $SO_2$  vertical column densities from OMI retrieved using the method of Theys et al., but with a constant AMF of 0.4, which is the one used in the operational OMI PBL  $SO_2$  product (Krotkov et al., 2008). With this correction, the agreement between the two instruments is improved; the mean relative difference becomes - 65%. Discrepancies are within the range of what we can expect given the difference in the overpass times of the two satellites and given the high bias introduced by averaging only the IASI observations with a low relative uncertainty. Note also that the difference between the vertical sensitivity profiles of the two instruments is likely to contribute to observed differences.

Finally, we have calculated the correlation coefficient between IASI and OMI monthly averaged measurements. It is very low for both OMI data sets, respectively -0.03 and 0.15 for the OMI standard retrieval with the varying AMF and for the retrieval with the constant

AMF = 0.4. These low correlations are mainly caused by one outlier on 05/2012, where IASI has a large SO<sub>2</sub> column of 5.7 DU, which corresponds however to very few measurements (3). When this outlier is removed, the coefficients improve to 0.23 and 0.54.



Figure 7.5.2: (Top) Monthly mean SO<sub>2</sub> columns (DU) retrieved for the period 2010–2013 in a circle of 125 km radius around Beijing from IASI (blue) and OMI (red) observations. Green triangles correspond to OMI measurements for which an AMF of 0.4 has been used to calculate vertical SO<sub>2</sub> columns. Details are given in the text. (Bottom) Spatial distributions of SO<sub>2</sub> (DU, different color scales) above China for the period 2010–2013 from IASI observations (left) and from OMI observations (right, without AMF changes). SO<sub>2</sub> columns have been averaged on a  $0.5^{\circ} \times 0.5^{\circ}$  grid.

# SENSITIVITY OF IASI TO NEAR-SURFACE $SO_2$ - Conclusion

In this second part of the thesis, we have developed two retrieval approaches to measure nearsurface SO<sub>2</sub> based on the information contained in the  $\nu_3$  band. The first one relies on the simplified OEM and has been applied to the industrial area of Norilsk. The second method relies on the LUT approach and, thanks to its low need for computation resources, it has been used to retrieve near-surface SO<sub>2</sub> at global scale. Both methods clearly assessed the impact of the TC values and humidity on the sensitivity of IASI in the  $\nu_3$  band to PBL SO<sub>2</sub> pollution. In this last chapter of part II, we propose to review the TC and humidity conditions under which IASI is capable of measuring near-surface SO<sub>2</sub> concentrations. First, in section 8.1, we use the LUT approach to determine the periods when near-surface SO<sub>2</sub> is measurable by IASI above the anthropogenic sources identified in the previous chapter. Based on this analysis, but also on the work performed above Norilsk with the simplified OEM, we then establish the TC and H<sub>2</sub>O conditions favouring the monitoring of SO<sub>2</sub> pollution with IASI in the  $\nu_3$  band (section 8.2).

# 8.1 When and where is near-surface $SO_2$ measurable by IASI?

In this section, we determine for each anthropogenic<sup>1</sup> source identified in the previous chapter the periods when they are detectable by the IASI instrument. For this, we compare monthly averaged distributions of SO<sub>2</sub>, TC and total column of H<sub>2</sub>O, calculated over the period 2008–2013. For the sake of illustration, examples of these monthly averaged distributions are presented in Figure 8.1.1 for February and in Figure 8.1.2 for August. For both figures, the distribution of SO<sub>2</sub>, TC and H<sub>2</sub>O total column are represented respectively in the top, middle and bottom panel. In February, IASI measures near-surface SO<sub>2</sub> above China, Norilsk, Iran, Turkey and Bulgaria, where the TC (in absolute value) is equal or even larger than 5 K, and the total column of H<sub>2</sub>O is of the order of  $2 \times 10^{22}$  molecules cm<sup>-2</sup> or lower. On the contrary, the smelters of Balkhash and the power plants in South Africa are not seen for two different reasons: in South Africa, the total column of H<sub>2</sub>O reaches more than  $4 \times 10^{22}$  molecules cm<sup>-2</sup> and probably causes opacity in the PBL, whereas in the region of Balkhash, the humidity is low but the TC is lower than 5 K (absolute value) and limits the sensitivity of IASI.

 $<sup>^{1}</sup>$ We do not consider volcanic sources here, because their emissions are not always continuous.



Figure 8.1.1: February averaged distribution of SO<sub>2</sub> (DU, top panel), of TC (K, middle panel), and of H<sub>2</sub>O total column ( $\times 10^{23}$  molecules cm<sup>-2</sup>, bottom panel). These averages have been calculated over the period 2008–2013. The TC is calculated as the difference between the temperature of the surface and that of air at 500 m above ground. Temperatures and H<sub>2</sub>O are from the EUMETSAT L2 PPF.



Figure 8.1.2: Same as Figure 8.1.1 but for August.

In August (Figure 8.1.2), near-surface SO<sub>2</sub> is measured in South Africa, in Iran, in Turkey, which all experience a dry atmosphere (H<sub>2</sub>O total column  $< 4 \times 10^{22}$  molecules cm<sup>-2</sup>) and high TC values (10 K in absolute value). In this summer month, the SO<sub>2</sub> emitted by the sources in China, Bulgaria and Balkhash are not seen, mainly due to high humidity. A SO<sub>2</sub> plume is observed in the region of Norilsk but is more confined spatially than the plume detected in winter (see also Figure 6.3.1).

By extending the analyses for the other months<sup>2</sup>, we come up with Table 8.1, which summarises the ability of IASI to measure near-surface  $SO_2$  for the various source regions under different conditions. The average TC and total columns of  $H_2O$  for each seasons are also indicated. From this table, we make the following conclusions:

1. North China

In the Northern part of China, IASI is sensitive to near-surface SO<sub>2</sub> almost year-round. The maximum sensitivity is reached during the winter (DJF), which combines average TC of 5 K and a dry atmosphere (total column of H<sub>2</sub>O below  $3 \times 10^{22}$  molecules cm<sup>-2</sup>). The sensitivity then gradually decreases during the spring (MAM) and, in summer (JJA), IASI is no more capable of measuring SO<sub>2</sub> in the region. The loss of sensitivity is mainly driven by an increase of the total column of H<sub>2</sub>O, which reaches  $1 \times 10^{23}$  molecules cm<sup>-2</sup> in summer and causes opacity in the lowest atmospheric layers. The TC remains indeed very high, with values included in the range 10–20 K. Finally, from the end of summer to the beginning of winter, the sensitivity of IASI to near-surface SO<sub>2</sub> increases again as humidity drops.

2. Norilsk

As observed for China and consistent with what we showed in chapter 6, the maximum sensitivity of IASI to near-surface SO<sub>2</sub> in the Norilsk region is found during the winter, when large thermal inversions develop, associated to TC of -10 K on average, and when the humidity is very low (below  $1 \times 10^{22}$  molecules cm<sup>-2</sup>). During the other seasons, the sensitivity of IASI is quite variable, with sporadic SO<sub>2</sub> detections for some months. In spring (MAM) and fall (SON), the atmosphere stays dry but the values of TC, generally between 0 and 5 K (absolute value), limit the capability of IASI to measure SO<sub>2</sub>. During the summer, the sensitivity is mainly driven by the total column of H<sub>2</sub>O, which fluctuates around  $5 \times 10^{22}$  molecules cm<sup>-2</sup>, while the TC can reach 10 K.

3. Sar Cheshmeh (Iran)

Near-surface SO<sub>2</sub> above the smelters complex of Sar Cheshmeh is measured by IASI year-round. This region is indeed characterised by high TC values (almost never below 10 K) and low humidity (never higher than  $3 \times 10^{22}$  molecules cm<sup>-2</sup>) during the whole year. A small decrease of the sensitivity (narrower plumes detected) is observed during the summer (JJA), when the humidity is the highest.

4. South Africa

The same observations made in the case of China are applicable to South Africa. The maximum sensitivity of IASI is reached in winter (here JJA), which combines high TC values (5–10 K) and low humidity (1–2 ×10<sup>22</sup> molecules cm<sup>-2</sup>). The minimum sensitivity is observed during the summer, due to large total columns of H<sub>2</sub>O (5–6 ×10<sup>22</sup> molecules cm<sup>-2</sup>). Decrease and increase in the sensitivity occur then respectively in spring (SON) and fall (MAM) and are driven again by changes in the total column of H<sub>2</sub>O (the TC stays quite high year-round in this region).

<sup>&</sup>lt;sup>2</sup>For Norilsk, we use also the time series of Figure 6.4.1.

Table 8.1: Summary of the IASI sensitivity to near-surface  $SO_2$  for the anthropogenic sources listed in chapter 7. A year has been divided in four periods: 1) December, January, February (DJF), 2) March, April, May (MAM), 3) June, July, August (JJA), and 4) September, October, November (SON). For each period, the associated average TC and total column of H<sub>2</sub>O are given. Check and cross marks indicate respectively periods for which IASI is sensitive and insensitive to near-surface SO<sub>2</sub>. Down arrows mean that a decrease of sensitivity is observed during the period (generally seen by a reduction of the area subtended by the plume), and up arrows mean inversely that there is an increase of sensitivity for the period. Details are given in the text.

Region	Period	Sensitivity	TC  (K)	$C_{ m H_2O}~( m molec./cm^2)$
North China	DJF	$\checkmark$	5	$1 - 3 \times 10^{22}$
	MAM	$\downarrow$	10 - 20	$2-4 \times 10^{22}$
	JJA	×	10 - 20	$1 \times 10^{23}$
	SON	$\uparrow$	10	$4 \times 10^{22}$
Norilsk	DJF	$\checkmark$	10	$0.6 – 0.8 \times 10^{22}$
	MAM	$\downarrow$	5	$1 - 1.5 \times 10^{22}$
	JJA	variable	5 - 10	$5 \times 10^{22}$
	SON	$\uparrow$	0 - 5	$1 \times 10^{22}$
Sar Cheshmeh (Iran)	DJF	1	10	$1 \times 10^{22}$
	MAM	$\checkmark$	15 - 20	$1 - 2 \times 10^{22}$
	JJA	$\downarrow$	20 - 25	$3 \times 10^{22}$
	SON	$\checkmark$	20	$2 \times 10^{22}$
South Africa	DJF	×	10 - 15	$5 - 6 \times 10^{22}$
	MAM	$\uparrow$	5 - 10	$2 - 4 \times 10^{22}$
	JJA	$\checkmark$	5 - 10	$1 - 2 \times 10^{22}$
	SON	$\downarrow$	15 - 20	$2 - 4 \times 10^{22}$
Turkey	DJF	$\checkmark$	5	$1 - 2 \times 10^{22}$
	MAM	$\checkmark$	15	$2 \times 10^{22}$
	JJA	$\downarrow$	20	$3 - 4 \times 10^{22}$
	SON	$\checkmark$	10 - 15	$2 - 3 \times 10^{22}$
Bulgaria	DJF	✓for F	5	$2 - 3 \times 10^{22}$
	MAM	$\checkmark {\rm for}~{\rm MA}$	10	$4 \times 10^{22}$
	JJA	×	10 - 15	$8 \times 10^{22}$
	SON	×	5 - 10	$5 \times 10^{22}$
Balkhash	DJF	×	2	$1.5 \times 10^{22}$
	MAM	$\checkmark {\rm for}~{\rm AM}$	10 - 15	$2 \times 10^{22}$
	JJA	×	15 - 20	$6 \times 10^{22}$
	SON	$\checkmark$ for S	10	$3 \times 10^{22}$

## 5. Turkey

As for Sar Cheshmeh, IASI is capable of measuring near-surface SO<sub>2</sub> year-round above power plants in Turkey, thanks to high TC values (5–20 K) and low H<sub>2</sub>O total columns (never larger than  $4 \times 10^{22}$  molecules cm<sup>-2</sup>). Note that only the power plants located in the center of the country (province of Kahramanmaraş, see Say (2006) and Figure 7.2.1) are observed during the whole year. The observations of power plants located in North-western part of the country are on the contrary more variable.

#### 6. Bulgaria

The observation of near-surface SO<sub>2</sub> plumes above the thermal power plants located in Bulgaria is very variable and has been possible only in February, March and April (for the average calculated for 2008–2013). During the winter, the limitation of the sensitivity to February is explained by low TC, which is generally below 5 K. After April, the sensitivity to near-surface SO<sub>2</sub> is limited by the increase of humidity, with H<sub>2</sub>O total columns reaching  $8 \times 10^{22}$  molecules cm<sup>-2</sup>.

7. Balkhash

As for the power plants in Bulgaria, near-surface  $SO_2$  emitted by Balkhash smelters are observed only occasionally in April, May and September, which encounter favourable conditions of TC and humidity. During the winter (DJF), IASI is indeed insensitive to near-surface  $SO_2$  mostly because of very low TC values (around -2 K). In summer, the sensitivity is limited by the large H<sub>2</sub>O total columns (6 × 10<sup>22</sup> molecules cm<sup>-2</sup>).

# 8.2 What are the geophysical conditions that favour the sounding of PBL SO<sub>2</sub> with IASI?

From the analysis presented in previous section and based on the study realised in chapter 6 for the particular case of the industrial area of Norilsk, we can reasonably well assess the geophysical conditions in which IASI is capable of measuring near-surface  $SO_2$ :

- 1. TC larger than 5 K in absolute value
- 2. H<sub>2</sub>O total column below  $4 \times 10^{22}$  molecules cm<sup>-2</sup>
- 3. Close to the surface,  $H_2O$  VMR below 4 g/kg.

It is worth having in mind that because these conditions have been established using especially the LUT approach, they depend on the chosen filters we have applied on the measurements. Indeed, the choice of less stringent filters on the error could relax the conditions proposed above. However, we are convinced that these give a fair assessment of the capabilities of IASI to measure near-surface  $SO_2$  pollution.

Finally, it is also important to notice that for most of the anthropogenic sources considered, the main limiting factor of the sensitivity is the humidity. Most of these sources are indeed located in regions that encounter year-round TC values equal or larger than 5 K. This limitation is specific to the use of the  $\nu_3$  band of SO<sub>2</sub>. To reduce the impact of H<sub>2</sub>O absorption in the future, it would be a good idea to include in the retrieval the information contained in the  $\nu_1$  band. For example, LUTs built for the  $\nu_1$  band spectral range could be used in case of opacity in the  $\nu_3$  band. This could possibly allow observing the anthropogenic sources considered in previous section on a more regular basis, but also other SO<sub>2</sub> sources located in more humid regions, such as in India.

# Part III

Measuring near-surface CO with IASI - A history of decorrelation

# CHAPTER 9

#### INTRODUCTION

After discussing the capabilities of IASI to measure near-surface SO<sub>2</sub>, we come in this third part of the thesis to the case of CO. Compared to SO<sub>2</sub>, CO has a marked spectral signature in IASI spectra (1–0 band, 2000–2250 cm<sup>-1</sup>), which is significantly less impacted by H<sub>2</sub>O absorption. Nevertheless, deriving near-surface CO concentrations from IASI observations is not necessarily easier than for SO<sub>2</sub>, mainly because CO is distributed in the whole troposphere. This means that, for probing CO down to the surface, we have to decorrelate at least its concentration in the low troposphere from that in the high troposphere.

Following the structure adopted for  $SO_2$ , the present chapter introduces this third part of the thesis. We review the literature in section 9.1, and then describe the main objectives of this part of the work in section 9.2.

# 9.1 Sounding near-surface CO with TIR sounders

In last years, nadir TIR satellite sounders have shown their ability to monitor the variability and trends of tropospheric CO at global scale (e.g., Worden et al., 2013; George et al., 2015). A series of different works have also demonstrated the possibility to observe CO close to the ground in case of high TC, and this was done especially for the MOPITT and IASI instruments. One of the first studies focusing on the influence of TC on the sensitivity of TIR sounders to surface CO was performed by Deeter et al. (2007) for MOPITT. Using Jacobians and averaging kernels calculated for both theoretical and real MOPITT measurements in three different TC conditions (positive, null and negative), the authors showed that the sensitivity of the instrument to surface CO increases in case of large positive TC, whereas they observe a degradation of the retrieval in case of negative TC. Almost simultaneously, following the work of Deeter et al. (2007) and using MOPITT, Clerbaux et al. (2008c) and Kar et al. (2008) measured surface CO pollution above respectively different megacities and the Indian subcontinent, by exploiting large positive TC encountered in those regions. More recently, Deeter et al. (2015) analysed the geographical and temporal variabilities of MOPITT DOFS and discussed among other the impact of TC on the information content of MOPITT retrievals.

Regarding IASI, George et al. (2009) examined briefly the influence of TC on the DOFS at global scale using the FORLI-CO product, and more particularly discussed the difference observed between day and night. They showed that daytime measurements, associated to larger TC values, generally present larger DOFS. Finally, during a severe pollution episode in January 2013 in the North China Plain, Boynard et al. (2014) showed that IASI was able measuring CO close to the surface in case of large negative TC and high levels of pollution.

# 9.2 Objectives

Although there is clear evidence that in case of large TC, TIR sounders can measure CO close to the surface, the influence of TC on the capabilities of such instruments has been up to now mostly qualitatively investigated, with no systematic assessment of the value of the TC needed to allow sensitivity near the ground. Moreover, only restricted ranges of TC values are generally considered, mostly in the range of positive values. The gain in sensitivity to surface CO, brought by large negative TC, has not been firmly assessed, as exemplified by the contradictory results of Deeter et al. (2007) and Boynard et al. (2014).

In this third part of the thesis, we intend to investigate in a more systematic way the influence of TC on the capabilities of IASI to retrieve near-surface CO concentrations. For this, we will rely on different analyses, both with simulations (chapter 10) and with real IASI measurements (chapter 11)<sup>1</sup>. For the theoretical part, we first explore the capability of IASI to detect a spectral signal coming from an enhancement of CO in the PBL. Then, using the OEM formalism, we evaluate theoretically the influence of TC on the error budget and information content of the CO retrievals from IASI observations. In chapter 11, we will analyse IASI observations recorded above different regions (Mexico City, airports) and assess the quality of the retrieved surface CO concentrations through comparisons with co-located measurements (in-situ and aircraft). A small side-study experiment investigates the potential improvement in measuring lower tropospheric CO using a synergy between co-located nadir and limb observations.

As for  $SO_2$ , the final objective of this part of the thesis is to revisit and assess firmly the capabilities of IASI to measure near-surface CO concentrations. More specifically, we establish the geophysical conditions favouring the sounding of near-surface CO with IASI, with a particular attention given to the conditions allowing the decorrelation between the CO concentrations in the low and the high troposphere.

<sup>&</sup>lt;sup>1</sup>Note that most of the results presented in this part of the thesis come from the publication of Bauduin et al. (2016b), which is still in review.
# CHAPTER 10

#### THEORETICAL ANALYSES

In this chapter, we investigate theoretically the impact of TC on the IASI sensitivity to near-surface CO. By calculating differences between simulated spectra for different CO enhancement in the near-surface atmosphere, we first assess how TC influences the spectral signal coming from such enhancement, and the capability of IASI to detect it (section 10.1). We then use the formalism of the OEM to characterise the impact of TC on the retrieval of near-surface CO from IASI observations in terms of vertical sensitivity and errors (section 10.2). Finally, we investigate the potential improvement in monitoring CO in the lower troposphere using a synergy between nadir and limb observations (section 10.3).

# 10.1 IASI sensitivity to near-surface CO: detection of PBL enhancements

As we already mentioned, at global scale, CO is present over the whole troposphere, but near-surface CO enhancements occur locally close to sources. It is therefore instructive to evaluate the capability of IASI to detect such enhancements as a function of TC. This follows the idea of what we performed during the Master thesis for  $SO_2$  (Appendix B.1). Spectra have been simulated for two representative atmospheres, under varying conditions of TC. The first atmosphere (the reference) is characteristic of a non-polluted air mass (hereafter referred as background conditions). It has been simulated using the *a priori* profile of CO utilised in FORLI (Figure 4.2.1, (Hurtmans et al., 2012)), which has a mean VMR of 98.2 ppb in the 0-1 km layer. The second atmosphere is chosen to represent a polluted near-surface layer. Varying CO VMRs have been considered in this case for the 0–1 km layer, by scaling the background surface VMR. Figure 10.1.1 presents the range of CO VMRs considered at the surface (Table 10.1 includes the corresponding 0–1 km mean VMRs). The forward simulations have been performed considering an atmosphere discretised in 1 km-thick layers (0-60 km). The TC has been defined as the difference between the surface temperature and the mean temperature of the 0–1 km layer, which has been evaluated according to Curtis-Godson approximation<sup>1</sup> (Curtis, 1952; Godson, 1953). The parameters chosen for these simulations are summarised in Table 10.1.

<sup>&</sup>lt;sup>1</sup>The mean temperature is here calculated using equation (2.3.16) for which the density of air weights the average.



Figure 10.1.1: CO vertical profiles representative of background (blue) and polluted atmospheres (red). The background profile is the *a priori* profile of FORLI. For the polluted atmosphere, varying surface VMRs have been considered and are represented by the red dots (the corresponding 0–1 km VMRs are included in Table 10.1). For display purposes, only the profile associated to the largest surface VMR (1500 ppb) is shown.

Table 10.1: Range of atmospheric situations considered for the forward simulations used for the NRD calculation. Only the VMR of CO at the 0 km level has been varied, and the averaged VMRs for the 0–1 km layer are given.

Parameter	Values	Background
Spectral range	$2000-2250 \text{ cm}^{-1}$	
Satellite zenithal angle	0°	
0–1 km VMR (ppb) of CO	107.4–247.4, 10 ppb step 247.4–297.4, 25 ppb step 297.4–547.4, 50 ppb step 647.4 and 797.4	FORLI CO <i>a priori</i> (mean VMR of 98.2 ppb)
$TC (K)^1$	-20 to +20, 1 K step	
Temperature profile	US Standard model <sup>2</sup>	
$CO_2$ , $H_2O$ and $N_2O$ profiles	US Standard model <sup>2</sup>	
$O_3$ profile	FORLI a priori profile <sup>3</sup>	
Emissivity	1	

 $^{1}$  TC has been varied by changing the surface temperature. The temperature profile is kept fixed.

<sup>2</sup> Anderson et al. (1986).

<sup>3</sup> Hurtmans et al. (2012).

From the simulated spectra, a normalised radiance difference (NRD) is calculated as

$$NRD(\tilde{\nu}) = \frac{I(\tilde{\nu}, \theta, \text{TOA})_{polluted} - I(\tilde{\nu}, \theta, \text{TOA})_{background}}{RN(\tilde{\nu})}, \qquad (10.1.1)$$

where  $I(\tilde{\nu}, \theta, \text{TOA})_{polluted}$  and  $I(\tilde{\nu}, \theta, \text{TOA})_{background}$  are respectively the polluted and the background radiance spectra, for which the satellite zenith angle  $\theta$  has been taken as 0°, and  $RN(\tilde{\nu})$  is the IASI radiometric noise (Figure 4.1.4). The  $NRD(\tilde{\nu})$  thus represents the difference in the spectral signal detected by IASI due to an enhancement of CO abundance in the 0–1 km layer relative to the noise. A  $NRD(\tilde{\nu})$  larger than 1 characterises a situation for which IASI detects at wavenumber  $\tilde{\nu}$  a spectral signature above its noise level, which is due to the enhancement.

Figure 10.1.2 (left) presents the  $NRD(\tilde{\nu})$  as a function of TC considering a CO enhancement of around 200 ppb in the 0–1 km layer. The sign of the difference is opposite to TC. As we have seen in subsection 2.4.4, if the latter is positive, absorption occurs in the 0–1 km layer leading to negative NRD. Emissions from the 0–1 km layer occurs for negative TC, leading to positive NRD. From the left panel of Figure 10.1.2, we conclude that IASI is capable of detecting a 200 ppb enhancement of CO from 3 K of TC (in absolute value) in most channels corresponding to CO lines with low J values (between 2080 and 2190 cm<sup>-1</sup>). For weaker lines, mainly those at high J in both P- and R-branches, the detection is possible only for larger TC. As expected, in case of no TC, the NRD is 0 and the CO detection is not possible. In the right panel of Figure 10.1.2, the NRD is plotted as a function of the CO enhancement in the 0–1 km layer, for a constant TC of 10 K. For the strongest CO lines, if TC= 10 K, IASI is capable of detecting CO enhancement around 80 ppb. This value has to be higher (> 150 ppb) for the weaker lines.



Figure 10.1.2:  $NRD(\tilde{\nu})$  (color scale) calculated from the difference between polluted spectra and background spectra as function of TC (constant CO enhancement in the 0–1 km layer of around 200 ppb, left), and as function of CO enhancement in the 0–1 km layer (constant TC of 10 K, right).

Such simple calculations are useful to infer a detection threshold for CO enhancement in the PBL. To do this, for each IASI spectral channel and for each TC value, the minimum CO enhancement resulting in a *NRD* larger than 1 (i.e., CO PBL signal greater than radiometric noise) was calculated. The results are presented in the left panel of Figure 10.1.3, with the color scale corresponding to the detection threshold, plotted as a function of TC and wavenumber. As expected, smaller CO enhancements can be detected for larger TC, either positive or negative. For example, for most channels centered on the strongest CO lines, if the absolute value of TC is over 15 K, IASI can detect near-surface CO enhancements below 60 ppb. When moving away from the line centers towards the line wings, the CO threshold rapidly increases. For lower TC, the sensitivity of IASI to near-surface CO decreases and

only larger enhancements can be detected. At 4 K of TC, more than 150 ppb is needed to produce a sufficient spectral difference at the center of the strongest lines.



Figure 10.1.3: (Left) Minimum CO enhancement in the 0–1 km layer (ppb, color scale), calculated from the FORLI *a priori* background conditions, detectable by IASI as a function of TC and wavenumber. (Right) Detection threshold (ppb) for CO enhancement in the 0–1 km layer, calculated considering the spectral signal in the whole CO band, as a function of TC.

The detection thresholds discussed above are defined for individual spectral channel. We can of course expect lower thresholds if all the channels in the CO band are used. We have estimated this new threshold (TH) following the same method described above, but applying the more general relation (Rodgers, 2000):

$$TH = (\mathbf{K}_{01}^{\mathrm{T}} \mathbf{S}_{\boldsymbol{\epsilon}}^{-1} \mathbf{K}_{01})^{-1}, \qquad (10.1.2)$$

where  $\mathbf{K}_{01}$  is the Jacobian vector calculated with respect to CO in the 0–1 km layer, and is calculated for each channel of the 2000–2250 cm<sup>-1</sup> spectral range. As we explained in subsection 2.4.3, it is a measure of how large the spectral response in the 0–1 band of CO would be due to a change in CO concentration in the 0–1 km layer. The right panel of Figure 10.1.3 shows the threshold TH as a function of TC. Consistent with what was observed for a single channel, TH decreases for increasing TC (absolute value) but has comparatively lower values. TH drops for instance below 10 ppb for TC larger than 10 K (absolute value), which is significantly lower than the 80 ppb calculated for a single channel. The detection threshold reaches very large values when TC approaches 0 K, for which IASI is almost insensitive to CO located in the 0–1 km layer.

The results presented above provide the observational evidence on the capability of IASI to detect the radiance contribution of near-surface CO enhancement. However, they rely on

spectral differences and do not quantify the sensitivity of the measurements to near-surface CO relatively to the rest of the tropospheric column. In particular, these first simulations are not sufficient to evaluate how many independent pieces of information can be retrieved from the measurements. These diagnostics can be obtained using the OEM, as discussed in the next section.

# 10.2 Theoretical characterisation of CO retrievals from IASI observations

As we have seen in chapter 3, the OEM offers a very adequate framework to characterise the retrieval in terms of error (using the matrix  $\hat{\mathbf{S}}$ ) and vertical sensitivity (through the AVK functions). In this section, we use  $\hat{\mathbf{S}}$  and  $\mathbf{A}$  as diagnostics for the IASI sensitivity to near-surface CO. For this, Jacobians have been pre-calculated for different situations of TC, and are used to derive theoretical  $\hat{\mathbf{S}}$  and  $\mathbf{A}$  matrices (equations (3.1.15) and (3.1.20) respectively). These are then used to analyse the influence of TC on both the error budget and information content of the retrieved CO profile.

The forward simulations have been performed with the Atmopshit software. Table 10.2 summarises the parameters used for the calculation of the Jacobians,  $\hat{\mathbf{S}}$  and  $\mathbf{A}$  matrices. The atmosphere has been divided in 60 layers of 1 km thickness (0–60 km). The *a priori* profile and associated covariance matrix are those used in FORLI (Figure 4.2.1), as are also the spectral range and noise constraint (see Table 4.1 for comparison). Accordingly, the results presented in the following can also be seen as a characterisation of the FORLI-CO product. Figure 10.2.1 shows from left to right the reduction of the prior uncertainty for the 0–1 km layer as a function of TC, the averaging kernels expressed in VMR/VMR units<sup>2</sup> for the 0–1 km layer for different values of TC, and the DOFS as a function of TC. The total DOFS is represented in blue, and the first value of the 0–1 km averaging kernel is presented in red (hereafter we call it the 0–1 km DOFS). These quantities used as diagnostic are separately discussed in the following sub-sections. Note that the reduction of the prior uncertainty quantifies the contribution of the measurement in the retrieval of the atmospheric state (see chapter 3). A small reduction is in this sense understood as a minor gain of information on PBL CO after the measurement is made.

It is important to note that the pre-calculated Jacobians depend on the chosen retrieval settings summarised in Table 10.2. Although the results are strictly valid for the retrievals made under these same conditions, the general patterns of the error budget and of the vertical sensitivity of IASI to near-surface CO retrievals are more general.

#### 10.2.1 Reduction of prior uncertainty

The reduction of prior uncertainty for the 0–1 km CO column, calculated using the square root of the diagonal elements of the  $\hat{\mathbf{S}}$  and  $\mathbf{S_a}$  matrices  $([\hat{\sigma} - \sigma_a] \times 100/\sigma_a)$ , is shown in panel (a) of Figure 10.2.1. The smallest reduction of uncertainty for the 0–1 km layer is around 20% and occurs for TC= -7 K. This reduction increases for increasing TC values (absolute value), and reaches 53% for TC= -20 K and even a larger value for TC= +20 K (the most extreme TC values considered). Note that the prior uncertainty is around 63%.

According to the results shown in section 10.1, one would have expected the lowest uncertainty reduction to occur for TC=0 K. The fact that it is found at -7 K is explained by the correlation between layers, which is introduced in the *a priori* covariance matrix  $S_a$ 

<sup>&</sup>lt;sup>2</sup>Note that because Atmosphit retrieves scaling factors,  $\mathbf{K}$ ,  $\hat{\mathbf{S}}$  and  $\mathbf{A}$  are expressed at the output of the calculation in scaling factor units. They have been converted to VMR units *a posteriori*.

Table 10.2: Forward simulation parameters used for the calculations of Jacobians, and theoretical  $\hat{\mathbf{S}}$  and  $\mathbf{A}$  matrices. Those corresponding strictly to the retrieval settings of the FORLI algorithm are indicated.

Parameter	Values	FORLI settings
Spectral range	$2143-2181.25 \text{ cm}^{-1}$	$\checkmark$
Satellite zenithal angle	0°	
Instrumental noise	$2{\times}10^{-7}~{\rm W}/({\rm m^2~sr~m^{-1}}),$ diagonal ${\bf S}_{\boldsymbol{\epsilon}}$	
0-1  km layer CO VMR <sup>1</sup>	98.2 ppb	$\checkmark$
$TC (K)^2$	-20 to +20, 1 K step	
Temperature profile	US Standard model <sup>3</sup>	
${ m CO}_2,~{ m H}_2{ m O}~{ m and}~{ m N}_2{ m O}~{ m profiles}$	US Standard model <sup>3</sup>	
$O_3$ profile	FORLI a priori profile <sup>4</sup>	$\checkmark$
Emissivity	1	

 $^1$  The FORLI *a priori* profile is considered above the 0-1 km layer.

 $^2$  TC has been varied by changing the surface temperature.

<sup>3</sup> Anderson et al. (1986).

<sup>4</sup> Hurtmans et al. (2012).



Figure 10.2.1: Theoretical characterisation of CO retrievals from IASI at near-surface level: (a) Reduction of the prior uncertainty (%) of CO in the 0–1 km layer as a function of TC; the blue line is with the full  $\mathbf{S}_{\mathbf{a}}$  used in FORLI while the black dashed line corresponds to the error reduction for the 0–1 km layer in case of a diagonal  $\mathbf{S}_{\mathbf{a}}$ . (b) Averaging kernels (in VMR/VMR units) of the 0–1 km layer for different TC (K) conditions; (c) Total and 0–1 km DOFS as a function of TC.

with the non-diagonal elements. To demonstrate this, we have calculated the reduction of prior uncertainty on the 0–1 km CO column by considering a diagonal  $S_a$  matrix (black dashed line in panel (a) of Figure 10.2.1). The results show indeed that in the absence of correlation between layers, the error reduction has decreased (almost no reduction at all) at TC= 0 K. This experiment shows that in case of no TC (hence with no physical information on the CO concentrations in the 0–1 km layer), the error reduction is driven entirely by the upper layers, where the sensitivity of IASI is larger. This correlation between layers, which

share the vertical information, and the dependence of the PBL sensitivity on the value of TC, is of crucial importance when analysing CO retrieved columns, their spatial distributions and time evolution. They are important as well to properly assess the values of the IASI surface CO measurements in comparison with co-located measurements (see chapter 11).

#### 10.2.2 Near-surface sensitivity

Panel (b) of Figure 10.2.1 shows that for extreme TC values, e.g., -20 K, -15 K, +15 K and +20 K, the AVK of the 0–1 km layer peaks at the surface (values respectively of 0.57, 0.42, 0.28 and 0.32), meaning that the maximal sensitivity is well within the PBL. In these extreme situations, the AVKs drop close to 0 above 3 km in case of negative TC and above 6 km in case of positive TC, showing some correlation with the upper layers. The value of the averaging kernel at the surface decreases with decreasing TC (absolute value), and its maximum is shifted higher in the atmosphere. In these less favourable conditions for surface measurements, the sensitivity of IASI to CO is maximal in the middle troposphere, and this corresponds to the most common case (e.g., George et al., 2015). Most of the information on CO in the lowest layers is then inferred from higher up in the atmosphere. This is particularly the case for values of TC in the range -5 K to +5 K.

The total and 0–1 km DOFS values presented in panel (c) of Figure 10.2.1 confirm that increasing TC values favour the sensitivity to surface CO. For large absolute value of TC, the total DOFS is close to 2, which means that there are two independent pieces of information in the CO vertical profile. Figure 10.2.2 shows predicted averaging kernels (in VMR/VMR units) for three different TC values: -15 K (left), 0 K (middle) and +15 K (right). The right and left panels show that the averaging kernels peak at two different heights: close to the surface and in the 5–10 km range, consistent with two separate pieces of information. For TC= -15 K, these pieces correspond essentially to the 0–3 km and the 3–19 km layers, while for TC= +15 K, they are associated more to the 0–5 km and the 5–19 km layers. The total DOFS decreases with decreasing absolute values of TC and drops to 1.23 at -5 K. The averaging kernels, showed in the central panel of Figure 10.2.2 for TC= 0 K, illustrate this by being all similar for all the altitude (confirming a single piece of information) with a peak in the free troposphere and no sensitivity at the surface. As explained above, the smallest DOFS does not occur at TC= 0 K because of correlation between layers.



Figure 10.2.2: Predicted averaging kernels (in VMR/VMR units) for the ten first layers and for three different values of TC: -15 K (left), 0 K (middle), and +15 K (right).



Figure 10.2.3: From top to bottom: contributions to TOA radiance of the 0–1 km layer, the 1–2 km layer, the 2–3 km layer and the 7–8 km layer. They are expressed in brightness temperature (K). The contributions have been calculated following a method similar to the one presented in Clarisse et al. (2010) (and briefly explained in the case of SO<sub>2</sub> in section 7.1.2.2).

The 0-1 km DOFS follows the same trend as the total DOFS (panel (c) of Figure 10.2.1), and reaches its largest values of 0.57 and 0.32 for respectively high negative and positive TC, and its smallest value at -4 K of TC. The fact that the values of the 0-1 km DOFS never reach 1 indicates that the CO concentration in this layer is never retrieved independently from the concentration in the layers above.

An important result that comes out from this analysis is that large negative TC values provide the cases with the best decorrelation between the CO concentration in the low and

the high troposphere. This is indicated by the largest value of the 0-1 km DOFS for large negative TC but also from the shape of the averaging kernels shown in Figure 10.2.2. This result seems in contradiction with the one reported by Deeter et al. (2007) for MOPITT. However, in this earlier study with MOPITT, the largest negative TC value considered was only around -10 K. As Figure 10.2.1 demonstrates, this TC value is indeed associated with a small error reduction and a low DOFS compared to the corresponding positive TC value. What we show here is that the large decorrelation between the low and the high troposphere is found only for more negative TC values. In such cases, emission occurs in the first atmospheric layers, as illustrated in Figure 10.2.3 (two first panels), with the contribution of different layers to the TOA radiance. Absorption occurs in the higher layers of the troposphere (bottom two panels of Figure 10.2.3), and generally counterbalances the emission, resulting in net absorption at TOA. This is better seen on the top panels of Figure 10.2.4, where CO absorption lines are measured at TOA by IASI for both positive and negative TC. Note however that, in case of -15 K of TC, some spectral features still appear in emission at TOA; they correspond to  $H_2O$  lines, for which the surface contribution is very large (and thus for which emission is not completely compensated by absorption higher up).



Figure 10.2.4: For -15 K (left) and +15 K (right) values of TC: (top) simulated IASI spectrum at TOA in brightness temperature (K), the surface temperature is indicated in red; (bottom) Jacobians (expressed here in W m<sup>-2</sup> sr<sup>-1</sup> m per scaling factor, color scale) as function of height.

In summary, the simulations performed here show that it is the transition from emission to absorption that brings the decorrelation between the low and the high troposphere in case of temperature inversion. This is well seen again in Figure 10.2.3 and in the bottom panels of Figure 10.2.4, which represent the Jacobians for TC = -15 K and TC = +15 K as a function of altitude. In case of high positive TC (Figure 10.2.4, right), the Jacobians are negative, because an increase of CO concentration increases the strength of absorption in the TOA spectrum. They have constant high values and shape from ground to 6–7 km of height; this means that an identical change in CO concentration in one of these layers would

produce a similar effect in the IASI spectrum. In other words, the IASI sensitivity to CO is almost constant from the ground up to 6–7 km in case of large positive TC. For TC = -15 K (Figure 10.2.4, left), there is clear contrast (at around 3 km) in the shape of the Jacobians between low (0–2 km) and mid-upper troposphere (>3 km). Below 3 km, the Jacobians are positive due to emission in these layers (see the two first panels of Figure 10.2.3). Above 3 km, the Jacobians are negative due to the dominance of absorption. To sum up, a change of CO concentration below or above 3 km produces different spectral responses in the IASI spectrum. It is the latter, which comes from the transition between emission and absorption regimes, that allows decorrelating the low and the high troposphere in case of large negative TC.

## 10.3 Geometric synergy: Solar occultation - nadir

In this short section, we investigate theoretically the potential improvement on the retrieval of near-surface CO concentration brought by a L2-L1 synergy between nadir and limb sounders. By L2-L1 synergy, we mean that the profile measured by the limb sounder (from the high troposphere to the upper atmosphere generally) can be used as *a priori* for the CO retrieval from nadir co-located observations. The retrieval error associated to the limb measurement is in this case considered as the prior uncertainty and included in the  $S_a$  matrix. By doing this, we intend to constrain the retrieval of the upper part of the CO profile and to investigate if such *a priori* constraint can improve the retrieval of CO close to the ground<sup>3</sup>.

For this experiment, we have considered IASI and ACE-FTS instruments for nadir and limb sounders respectively. The analysis relies on the theoretical characterisation presented in previous section, but for which we have built a new  $S_a$  matrix (left panel of Figure 10.3.1) that reflects typical errors of ACE-FTS CO measurements in the upper atmosphere. More specifically, we have considered an error of 20% at 8 km of height, 15% at 9 km and finally 10% for the rest of the upper atmosphere following the work of Clerbaux et al. (2008b). The correlations between layers in this upper part of the atmosphere (8–19 km) have been set to 0 to reflect the high vertical resolution of ACE-FTS. Below 8 km, the FORLI  $S_a$ is considered. The other parameters used for the calculation of the Jacobians,  $\hat{S}$  and Amatrices are identical to those described in the section above (Table 10.2).

The middle panel of Figure 10.3.1 presents the reduction of the prior uncertainties on the 0-1 km column for the synergetic retrieval compared to the nadir-only retrieval as a function of TC. There is almost no gain from using the synergy for the retrieval: below TC= -16 K, the error reduction is improved only by a few percent (up to 5% for TC= -20 K), but for large positive TC, the reduction in uncertainties are similar. We also note a very small shift towards more negative TC is observed for the smallest reduction, which however stays close to 20%. Regarding the 0–1 km AVK, shown in the right panel of Figure 10.3.1, they are also very similar to those calculated for the nadir-only case (see middle panel of Figure 10.2.1). A small improvement is only observed for TC= -15 K and TC= -20 K, for which the values at the surface pass from 0.42 and 0.57 respectively to 0.48 and 0.68. Finally, Figure 10.3.2 shows predicted AVK functions of the ten first layers for the synergy for three TC conditions (-15 K, 0 K and +15 K). From 0 to 8 km, these do not show significant changes when compared to those obtained for the nadir (Figure 10.2.2), but the 8–9 and 9–10 km AVK are on the contrary very different: they are close to 0 and reflect the

<sup>&</sup>lt;sup>3</sup>Note that this work was done in the frame of the SIROCCO (Synergetic SWIR and IR retrievals of near-surface concentrations of  $CH_4$  and CO for Earth and Planetary atmospheres) project (funded by ESA, contract number 4000107088).



Figure 10.3.1: (Left)  $\mathbf{S}_{\mathbf{a}}$  matrix (%<sup>2</sup>/100) built for the synergy IASI-ACE. The typical error of ACE-FTS CO measurement have been considered in the upper atmosphere (8–19 km). (Middle) Reduction of the prior uncertainty (%) of CO in the 0–1 km layer as a function of TC for the synergy (blue) and non-synergy (red) cases. (Right) Averaging kernels (in VMR/VMR units) of the 0–1 km layer calculated for the synergy IASI-ACE for different TC conditions.



Figure 10.3.2: Predicted averaging kernels for the synergy IASI-ACE for three TC conditions: -15 K (left), 0 K (middle), and +15 K (right).

much stronger a priori constraint applied on the upper part of the CO profile.

In conclusion, based on the theoretical analysis, we can conclude that a synergy between co-located limb and nadir measurements would not improve significantly the retrieval of the CO concentrations in the free troposphere and certainly not in the PBL. This will be confirmed in the next chapter, where we test the synergy on real measurements.

# CHAPTER 11

### RETRIEVALS

After investigating theoretically the sensitivity of IASI to near-surface CO, we focus this chapter on real observations. More specifically, the capability of IASI to observe near-surface CO is evaluated by comparing the retrieved concentrations in the 0–1 km layer with co-located surface measurements. These include aircraft and in-situ measurements, taken respectively at airports (we analyse especially the data recorded above the airports of Windhoek and Frankfurt), and around Mexico City. The comparisons are discussed separately in sections 11.1 and 11.2.

# 11.1 Comparison with aircraft measurements at airports

In this section, near-surface CO retrievals from IASI observations are evaluated against MOZAIC aircraft measurements of CO close to the ground. The MOZAIC (Measurement of OZone, water vapour, carbon monoxide and nitrogen oxides by Airbus Inservice airCraft) program provides alborne in-situ measurements of different reactive gases, recorded at different stage of international flights (ascent, cruise phase, and descent) for the period going from August 1994 to November 2014. In this section, we have used the MOZAIC data recorded on both ascent and descent overpasses above the airports of Windhoek and Frankfurt, for the period 2008–2011. These are compared to the surface CO concentrations retrieved from IASI observations using FORLI (subsection 11.1.1). In a second step, they will be used also to verify that the limb-nadir synergy does not bring significant improvement to the retrieval of CO in the PBL (subsection 11.1.2)<sup>1</sup>.

#### 11.1.1 FORLI-CO evaluation for the near-surface layer

For the evaluation of the IASI CO near-surface retrieval, the 0-1 km CO VMRs derived with FORLI have been compared to the MOZAIC measurements recorded closest to the ground (1-2 km above ground). The comparison is done separately for morning and evening IASI overpasses. All IASI observations located in a box of  $1^{\circ} \times 1^{\circ}$  centered on the airport have been averaged. MOZAIC data have been separated in morning and in evening measurements,

<sup>&</sup>lt;sup>1</sup>This part of the work has been performed (with the help of Rosa Astoreca, ULB) in the frame of the SIROCCO project, for which MOZAIC data were provided. They are also freely accessible on http://mozaic.aero.obs-mip.fr/web/.

and compared to the mean 0-1 km VMR (equation (1.1.9)) calculated for IASI for the corresponding overpass. The comparisons for Windhoek and Frankfurt airports are discussed separately in the following.

#### 1. Windhoek

Figure 11.1.1 presents the comparison between IASI and MOZAIC surface CO VMRs as a time series for the period 2008–2011. Morning and evening measurements are respectively shown in top and bottom panels, and the mean TC values calculated for the  $1^{\circ} \times 1^{\circ}$  box centered on the airport are also indicated for IASI observations (color scale). We find that for the IASI morning overpass, the 0–1 km CO FORLI VMRs present a significant seasonality, with background values around 100 ppb (close to the a priori) between January and July. The largest VMRs, reaching up to 500 ppb, are retrieved from August to November. This period is associated to TCs larger than 10 K, which by enhancing the IASI sensitivity, allow catching with the retrieval the large CO surface VMRs. The seasonality observed by IASI is actually in very good agreement with the one of MOZAIC, which however measures somewhat smaller CO VMRs (maximum at around 400 ppb). This good agreement in the seasonality is not observed for the evening IASI overpass. The TC values remain around 5 K or below (absolute value) year-round, and limit the sensitivity of IASI to PBL CO; the large CO VMRs measured by MOZAIC between July and November are for this reason not captured by IASI. In low TC conditions, the FORLI-CO retrieved VMRs stay in fact close to the *a priori*.



Figure 11.1.1: For morning (top) and evening (bottom) overpasses: mean 0–1 km CO VMRs retrieved from IASI observations with FORLI (ppb) and surface VMRs measured by MOZAIC aircrafts (ppb, black dots) for the period 2008–2011 above Windhoek airport. All IASI observations located in a  $1^{\circ} \times 1^{\circ}$  box centered on the airport have been averaged. The associated mean TC (K), calculated for the same box, is indicated with the color scale.

The comparison between IASI and MOZAIC surface CO VMRs is shown differently in Figure 11.1.2, which presents the correlation between the two sets of data separately

for morning (left) and evening (right) overpasses as a function of TC. For the morning overpass, consistent with what we observe for the time series, a reasonable agreement is found between IASI and MOZAIC CO measurements. The linear regression calculated using all the data (black) shows a slope of 0.68, an intercept of 42.84, and is characterised by a Pearson's correlation coefficient of 0.58. To investigate the effect of TC on the correlation, two other linear regressions have been calculated using only data with 1) |TC| > 5 K and 2) |TC| > 10 K. With these criteria, we observe a significant improvement in the agreement between the two datasets. This is especially seen for the case |TC| > 10 K, for which the slope reaches 0.94, the intercept is almost divided by two, and the correlation coefficient is 0.65. This improvement with FORLI-CO is explained by a gain in sensitivity for TC values above 10 K. Regarding the evening overpass, the agreement between the IASI and MOZAIC measurements remains very poor, mainly because of low TC values. The linear regression calculated for the whole dataset lead to a slope of 0.13, a large intercept of 81.13, and a correlation coefficient of 0.27. A small improvement is found when only IASI measurement with |TC| > 7 K are considered<sup>2</sup>, with a correlation coefficient then reaching 0.46.



Figure 11.1.2: Comparison between the IASI mean 0–1 km CO VMRs (ppb) and surface MOZAIC CO VMRs (ppb), presented as a function of TC (K, colorscale), separately for morning (left) and evening (right) overpasses. For these, different linear regressions have been calculated using all data or part of it with a filter applied on the absolute value of TC. The red dashed lines represent the one-to-one lines.

#### 2. Frankfurt

Similarly to what has been done for Windhoek airport, the comparison between IASI and MOZAIC surface CO measurements is presented in Figure 11.1.3 as a time series. For the morning overpass (top), we find that IASI does not capture the pronounced seasonality in surface CO observed by MOZAIC. Especially, the large CO VMRs of up to 800–1200 ppb measured by MOZAIC during the end of fall and the winter are not reproduced, with the 0–1 km CO VMRs retrieved from IASI staying close to the *a priori* (around 100 ppb). This is explained by the low TC (a few K in absolute value)

<sup>&</sup>lt;sup>2</sup>Contrary to the morning overpass, there were not enough measurements with |TC| > 10 K to be statistically relevant in the calculation of the linear regression.

encountered at this period in Frankfurt that hampers the sensitivity of IASI to PBL CO. The agreement between IASI and MOZAIC data is somewhat better during the spring and the summer (April to September), which are associated to larger TC values (5–15 K): both instruments measure consistently surface CO VMRs in the range of 200–300 ppb. Regarding evening observations, IASI surface CO VMRs stay close to the *a priori* for almost the whole 2008–2011 period, mostly due to TC values below 5 K. IASI is therefore not able to catch the high CO VMRs measured by MOZAIC in winter.



Figure 11.1.3: Same as Figure 11.1.1 but for Frankfurt airport.

Correlation plots have also been analysed for Frankfurt airport (not shown). We find for both morning and evening overpasses a behaviour similar to that characterising the evening overpass above Windhoek (right panel of Figure 11.1.2), with Pearson's coefficients of only 0.1.

## 11.1.2 Evaluation of CO retrievals at the surface from the synergy nadir-limb

In section 10.3, we have shown theoretically that no significant improvement in the retrieval of near-surface CO concentrations was expected by a synergy L2–L1 between IASI and ACE sounders. This section verifies this on real data, using two IASI and ACE co-located observations. The two ACE observations selected were made in the region of the Frankfurt airport on 29<sup>th</sup> July 2009 and on 1<sup>st</sup> January 2011. These CO profiles retrieved from ACE probe the troposphere sufficiently deep to make a potential useful constrain on the IASI retrievals, and were recorded at a reasonable distance from the MOZAIC measurements. Their characteristics are summarised in Table 11.1. Regarding IASI, for each day, the closest observation to the available MOZAIC measurement has been selected (see Figure 11.1.4). The retrieval has been performed with Atmosphit using the retrieval settings shown in Table 10.2 (as explained there, most come from FORLI), except for the satellite zenith angle and the emissivity whose values are from, respectively, the measurement and the Zhou climatologies (Zhou et al., 2011). Two different *a priori* profiles have been applied (Figure 11.1.4): 1) the FORLI profile, 2) a combination of the FORLI profile and the colocated retrieved profile from ACE. For these two cases, the  $S_a$  are respectively the one of FORLI (right panel of Figure 4.2.1) and the one built specifically for the synergy with strong constrains on the upper part of the profile (shown in left panel of Figure 10.3.1).

Table 11.1: Characteristics of ACE observations used in the limb-nadir test experiment performed above Frankfurt airport (50.03°N, 8.56°E). The lower altitude at which the sounder has measured CO is indicated.

Name	Date	Latitude	Longitude	Lower altitude probed
ace.ss32100	2009-07-29 18:59:59.7	48.53°	$8.97^{\circ}$	$10.5 \mathrm{km}$
ace.sr39774	2011-01-01 07:32:50.03	$49.07^{\circ}$	$6.97^{\circ}$	$5.5 \mathrm{~km}$



Figure 11.1.4: *a priori* and derived CO profiles for retrievals performed with or without the limbnadir synergy, for 29<sup>th</sup> July 2009 (left) and 1<sup>st</sup> January 2011 (right). The surface CO MOZAIC measurements are shown with black dots. Relative difference (RD) between the IASI 0–1 km CO VMRs and the MOZAIC CO VMRs have been calculated and indicated.

The retrieved CO profiles using these different *a priori* settings are shown in Figure 11.1.4 for the two co-located measurements. We observe only a small difference in the first kilometres of height between the two types of retrieval. Above 8 km, the CO profile retrieved from IASI using the synergy almost equals the *a priori* profile, due to the limited *a priori* variability allowed. This is also the region where the largest differences between the two retrieved profile are observed. Focusing on the retrieval of the 0–1 km CO VMRs, we have calculated their relative differences with respect to MOZAIC measurements taken as the

truth (indicated in Figure 11.1.4). For 29<sup>th</sup> July 2009, we find a small improvement of 4% in the accuracy of the retrieved 0–1 km CO VMR when using the synergy. On the contrary, the relative difference increases by around 4.7% for 1<sup>st</sup> January 2011. As a final remark, the averaging kernels (not shown) obtained with and without the synergy are very similar in values and shape, particularly close to the surface (except for those associated to layers above 8 km, as explained in section 10.3). In conclusion, these results tend to confirm the theoretical findings that the use of a constrain on the upper part of the tropospheric CO profile (here from limb occultation measurements) does not provide significant improvement on the retrieval of near-surface CO concentrations from nadir measurements in the TIR.

# 11.2 Comparison with in-situ measurements: Mexico City test case

IASI measurements of near-surface CO are evaluated here through comparisons with groundbased in-situ measurements in the region of Mexico City. In contrast to previous section, the discussion also focuses on the characterisation of the retrievals, which will be used as a verification of the theoretical results presented in chapter 10. The region of Mexico City was chosen because: 1) it encounters persistent air pollution (e.g., Raga et al., 2001; Molina et al., 2007; De Foy et al., 2007; Stremme et al., 2013; Retama et al., 2015), 2) the TC in this area covers year-round a large range of different values (including extremes), 3) a dense local network of ground-based stations (RAMA, Red Automática de Monitoreo Atmosférico, http://www.aire.df.gob.mx) provides daily measurements of various pollutants, CO among them (Zhang et al., 2009). In the next subsections, we describe successively the retrieval procedure applied to IASI spectra recorded in the area (subsection 11.2.1), discuss the characterisation of the retrieved profiles (subsection 11.2.2), and compare the retrieved near-surface CO concentrations to ground measurements of RAMA network (subsection 11.2.3).

## 11.2.1 Retrieval procedure

Retrievals of CO profiles have been performed on IASI observations taken during 2013 using the Atmosphit software. Only measurements for which the cloud fraction is less than 20% and with available EUMETSAT L2 data have been considered. Table 11.2 summarises the retrieval settings; most are those also used in the FORLI algorithm. Mexico City is located in a basin of around 100 km of diameter, where the pollution remains trapped because of the surrounding high mountains (on South, West and East, see Figure 11.2.1). Therefore, to remove IASI observations located outside the polluted basin, only those having their centers inside the red rectangle (99.35–98.85°W/19.2–19.75°N) indicated in Figure 11.2.1 have been analysed. In total, 952 spectra have been adjusted, covering all months of 2013.

Moreover, the region of Mexico City is located at an altitude of around 2 km above sea level. To compare the theoretical results from section 10.2 to those obtained from real IASI measurements, the ground height is considered as the 0 level, i.e., the *a priori* CO profile shown in Figure 4.2.1 starts at the ground height instead of 0 km and the scale height of the associated  $S_a$  has been modified accordingly.

Note that the retrievals performed above Mexico will not allow to verify fully the theoretical calculations for the negative TC cases. Indeed while Mexico City experiences thermal inversions in winter (Molina et al., 2007) and some measurements associated to -5 K <TC < 0 K have been analysed, they remain modest and far from the most extreme values of -20 K investigated theoretically. This is unfortunately these that were found to be the

Table	11.2:	Settings	s used i	in the	retrieva	l of (	CO	profiles	from	IASI	obser	vations	recor	ded in	the
region	of Me	exico Cit	y. Note	e that	the 0 $k$	m ine	dica	ted her	e corr	espon	ds to	the gro	ound h	neight	(see
text).															

Parameter	Values / $a \ priori$	Layers and variability
Spectral range	$2143 - 2181.25 \text{ cm}^{-1}$	
Instrumental noise	$2{\times}10^{-7}~{\rm W}/({\rm m^2~sr~m^{-1}})$ diagonal ${\bf S}_{\boldsymbol{\epsilon}}$	
CO profile	FORLI (Figure $4.2.1$ )	$\mathbf{S_a}$ FORLI (Figure 4.2.1)
Surface temperature	L2 EUMETSAT PPF	2%
Temperature profile	L2 EUMETSAT PPF	Fixed
$\mathbf{CO}_2$	380  ppm constant	5% on the total column
$H_2O$	L2 EUMETSAT PPF	30% for the layers: 0–2 km, 2–4 km, 4–6 km, 6–8 km, 8–10 km, 10–15 km 15–20 km
$N_2O$	Tropical $model^1$	Fixed
$O_3$	FORLI a $priori^2$	Fixed
Emissivity	Zhou et al. (2011)	Fixed

 $^1$  Anderson et al. (1986);  $^2$  Hurtmans et al. (2012).

best cases for the decorrelation between the low and the high troposphere.

## 11.2.2 Characterisation of the retrievals

Figure 11.2.2 shows in three successive panels the reduction of the prior uncertainty on the retrieved 0–1 km CO VMRs, the DOFS for the entire profiles and for the 0–1 km layers. These three quantities are plotted against the TC, revealing a clear relation, consistent with the results from the previous chapter. The error reduction increases with increasing TC (absolute value), from around 25% for TC close to 0 K to more than 50% above 15 K. The DOFS increases from 1.2 to 1.9 (for the entire profile) and from 0 to 0.35 (for the 0–1 km layer) for TC varying from below 5 K to 30 K. These patterns can all be traced back to an increase of the IASI sensitivity to near-surface CO. Furthermore, these can be compared to those predicted in section 10.2 (Figure 10.2.1). A good consistency is found for both predicted prior uncertainty reduction and DOFS (total and 0–1 km).

To complete the evaluation, two IASI measurements over Mexico City representative of low and high TC conditions were analysed. The resulting retrieved CO profiles and their associated averaging kernels functions are shown in Figures 11.2.3 and 11.2.4. From Figure 11.2.3 (left), we see that, in case of low TC (here 3.17 K), the retrieved profile stays close to the *a priori* from the surface up to 19 km. The 0–1 km CO VMR is around 89 ppb and smoothly decreases to 63 ppb in the 11–12 km layer and to 31 ppb in the 18–19 km layer. The sensitivity of IASI to near-surface CO is limited in this case, as seen by the averaging kernels peaking at the same altitude of 6 km for all layers. The DOFS for the entire profile is 1.28, and expresses the fact that the retrieved CO concentration in the low troposphere is not independent at all on its concentration in the high troposphere.



Figure 11.2.1: Location of the RAMA ground-based stations (1 to 20), which provide hourly CO in-situ measurements, in the Mexico City basin. The name list of the stations is given in Table 11.3. The color scale indicates the CO VMRs (ppb) measured at each station for 1<sup>st</sup> February 2013 at 10:00 local time. The contour on the plot shows the terrain height in meters. The red rectangle defines the region for which IASI spectra have been selected.



Figure 11.2.2: Characterisation of CO retrieval above Mexico city as function of TC: (left) Reduction of prior uncertainty (%) on the derived 0–1 km CO VMR; (middle) DOFS for the entire profile; (right) DOFS for the 0–1 km layer.

The case of high positive TC (around 23.5 K), shown in Figure 11.2.4 has CO peaking at the surface with a retrieved VMR of 510 ppb. The three first averaging kernels (0–1, 1–2 and 2–3 km) peak at the surface, indicating that the information coming from the surface layer contribute indeed most to the retrieval of CO in these layers. The total DOFS equals 1.85, which means that almost two parts of the vertical profile of CO are retrieved independently. According to the shape of the averaging kernels (middle panel), these would correspond to the 0–5 km and 5–19 km layers. Note that these AVK are in a good agreement with those



Figure 11.2.3: (Left) Retrieved vertical profile of CO (blue, ppb) and *a priori* profile of CO (red, ppb) for a IASI measurement taken in low TC condition (3.17 K) above Mexico City. The error bars correspond to the retrieval error (blue) and the prior uncertainty (red). (Middle) Averaging kernel functions (in VMR/VMR units) for the ten first retrieved layers. (Right) Predicted averaging kernels (in VMR/VMR units) for the ten first layers for a TC of 3 K. The IASI observations has been made the 12/12/2013. The DOFS of the retrieval is 1.28.



Figure 11.2.4: Same as Figure 11.2.3 for a IASI measurement, taken in high TC condition (23.45 K). In the right panel, the predicted averaging kernels (in VMR/VMR units) are for a TC of 20 K. The IASI observation has been made the 09/03/2013. The DOFS of the retrieval is 1.85.

derived theoretically in the previous chapter (see right panel of Figure 11.2.4).

#### 11.2.3 Comparison to RAMA ground measurements

The CO VMRs retrieved from IASI at near-surface level can be evaluated against those measured at RAMA ground-based network. We have used the CO VMRs hourly recorded everyday by 20 stations, which are identified in Table 11.3. These stations are disseminated

in the area (as shown in Figure 11.2.1) at distances of up to 30 km from the city center. This distribution lead to very variable measured CO VMRs, which can differ of up to few ppm between the stations. This is shown in Figure 11.2.1 for the example of 1<sup>st</sup> February 2013 at 10:00 AM local time (LT), where we have 3 ppm for the largest VMR difference. For this reason, IASI observations which cover a large area have been compared to the mean CO VMR calculated for RAMA stations within the central part the footprint of the instrument (distance< 5 km). If all RAMA stations are located beyond 5 km from the footprint center, the closest one is selected for the comparison. Moreover, Mexico City encounters a strong diurnal cycle of surface CO VMRs, as reported by De Foy et al. (2007), Stremme et al. (2009) and Retama et al. (2015). A time window of ±30 minutes on IASI overpass has thus been applied for the selection of the RAMA reference measurements.

Name	Number on map	Longitude	Latitude
Acolman (ACO)	1	-98.912°	$19.6355^{\circ}$
Camarones (CAM)	2	$-99.1698^{\circ}$	$19.4684^{\circ}$
Cuajimalpa (CUA)	3	$-99.2917^{\circ}$	$19.3653^{\circ}$
FES Acatlán (FAC)	4	$-99.2435^{\circ}$	$19.4824^{\circ}$
Hospital General de México (HGM)	5	$-99.1522^{\circ}$	$19.4116^{\circ}$
Iztacalco (IZT)	6	$-99.1176^{\circ}$	$19.3844^{\circ}$
La Presa (LPR)	7	$-99.1177^{\circ}$	$19.5347^{\circ}$
Merced (MER)	8	-99.1196	$19.4246^{\circ}$
Nezahualcóyotl (NEZ)	9	$-99.0282^{\circ}$	$19.3937^{\circ}$
Pedregal (PED)	10	$-99.2041^{\circ}$	$19.3251^{\circ}$
Santa fe (SFE)	11	$-99.2629^{\circ}$	$19.3574^{\circ}$
San Juan Aragón (SJA)	12	$-99.0861^{\circ}$	$19.4526^{\circ}$
Santa Ursula (SUR)	13	$-99.15^{\circ}$	$19.3145^{\circ}$
Tlahuac (TAH)	14	$-99.0106^{\circ}$	$19.2465^{\circ}$
Tlalnepantla (TLA)	15	$-99.2046^{\circ}$	$19.5291^{\circ}$
Tultitlán (TLI)	16	$-99.1772^{\circ}$	$19.6025^{\circ}$
UAM Xochimilco (UAX)	17	$-99.1036^{\circ}$	$19.3044^{\circ}$
UAM Iztapalapa (UIZ)	18	$-99.0739^{\circ}$	$19.3608^{\circ}$
Villa de las Flores (VIF)	19	$-99.0966^{\circ}$	$19.6582^{\circ}$
Xalostoc (XAL)	20	$-99.0824^{\circ}$	$19.526^{\circ}$

Table 11.3: RAMA stations used for comparison with IASI CO measurements. They are represented in Figure 11.2.1 with the corresponding number.

The left panel of Figure 11.2.5 shows the correlation between IASI and co-located RAMA surface CO measurements as a function of TC. Two linear regressions have been calculated using 1) all data (black), and 2) IASI observations with TC > 15 K (pink). We find that IASI significantly underestimates the surface CO VMRs in the majority of the cases. The largest underestimation is observed for low TC values (between 0 and 5 K in absolute value), for which IASI provides 0–1 km VMRs around 100 ppb ( $\approx a \ priori$ ) whereas the RAMA stations report VMRs up to 2000 ppb. Observations associated to TC > 15 K tend to be less underestimated, as shown by the small improvement observed for the linear regression using only IASI observations with TC > 15 K. This is better seen with the right panel of Figure 11.2.5, which shows the relative difference between the two sets of CO measurements ((IASI-RAMA)/RAMA) as a function of TC. We find a clear decrease in the percent bias with increasing TC values. The averaged relative differences, calculated per bin of 5 K of

TC between -5 K and 25 K and indicated by red lines, decrease from averages up to 80% for TC lower than 15 K, to 60% for the 15–20 K bin and 40% for TC larger than 20 K. This decrease in the percent bias (absolute value) for increasing TC is consistent with the gain of IASI sensitivity to near-surface CO, which allows a more accurate estimation of its concentration close to the ground.



Figure 11.2.5: (Left) Comparison between 0–1 km CO VMRs (ppb) retrieved from IASI observations with surface RAMA CO VMRs (ppb), as a function of TC (K, color scale). The black and pink lines correspond to the linear regressions calculated considering respectively 1) all data and 2) IASI measurements with TC > 15 K. The equations and correlation coefficients are indicated (inset). The dashed red line is the one-to-one line. (Right) Relative difference (%) between the IASI and RAMA sets of surface measurements as a function of TC. The red lines indicate the mean differences calculated per bins of 5 K.

Although the agreement between IASI and RAMA data is improved in case of large TC, the CO VMRs measured by IASI are still significantly underestimated. This could be related for a part to the fact that IASI and RAMA surface measurements are different quantities. For IASI, we provide an averaged 0–1 km VMR calculated from the retrieved 0-1 km partial column of CO. Depending on the shape of the CO profile in the 0-1 km layer, this averaged retrieved VMR can be smaller than the surface VMR measured by the stations. This especially depends on the height of the mixing layer: low mixing height leads to accumulation of CO close to the ground (the 0–1 km VMR retrieved from IASI would be biased low compared to RAMA surface measurement), while a growth of the mixing layer is followed by a decrease of CO concentrations at the surface (RAMA and IASI VMRs would be more comparable quantities). Stremme et al. (2009) report strong diurnal variations of this height in Mexico City, which is the lowest during the early morning (and associated to the largest CO VMRs at the surface) and increases during the afternoon. The morning overpass time of IASI above Mexico City is around 10:00–11:00 LT, for which Stremme et al. (2009) measure a mixing height around 500 m. This narrow mixing layer could therefore partly explain the large discrepancies observed between IASI and RAMA datasets. Deeper investigation is however needed to confirm this effect.

Another possible origin of the underestimation of CO surface concentrations can be the choice of the *a priori* profile, which is not representative of a high CO pollution at the surface but rather describes a typical background concentration profile. Preliminary results

tend to show that the choice of a more polluted *a priori* profile has significant impact on CO retrievals (see also (George et al., 2015)). Further investigations are needed here to also estimate the gain in accuracy provided by a selection of a priori profile (and associated  $S_a$ ) representative of polluted megacities. Other retrieval adaptations could be also envisaged in high polluted cases, such as the use of more retrieved layers close to the surface. Finally, alternative minimisation approaches could be considered (e.g., Tikhonov-Phillips).

# CHAPTER 12

# SENSITIVITY OF IASI TO NEAR-SURFACE CO - CONCLUSION

# 12.1 Which TC conditions favour the sounding of PBL CO with IASI?

In this third part of the thesis, we have evaluated the performances of the IASI instrument to measure near-surface CO concentrations. Using theoretical analyses along with comparisons of IASI CO observations with co-located measurements, we have especially investigated the influence of TC on these performances. Following what we have done for  $SO_2$ , we have established the following conclusions on the impact of TC:

#### 1. IASI starts to be sensitive to near-surface CO from |TC| = 5 K.

This statement is supported by all the analyses we performed. Below |TC| = 5 K, we observe indeed a net loss of sensitivity, which translates into an increase in the detection threshold of CO surface enhancements (Figure 10.1.3). These TC values are also associated to 0–1 km AVK functions that peak in the mid-troposphere and have values close to 0 in the 0–1 km layer (Figures 10.2.1 and 11.2.3). Comparisons with MOZAIC aircraft measurements confirm that IASI is unable to capture the high CO concentrations above Frankfurt and Windhoek airports during periods associated to |TC| < 5 K (Figures 11.1.1 and 11.1.3).

#### 2. |TC| > 10 - 15 K favours the decorrelation of two parts of the profile.

This has been shown theoretically for both positive and negative TC, and the independent parts have been identified as the 0–3 km and the 3–19 km layers for negative TC, and the 0–5 km and the 5–19 km layers for positive TC (Figures 10.2.1 and 10.2.2). This has been confirmed also with retrievals on real data, corresponding to measurements performed above Mexico City for positive TC cases (Figures 11.2.2 and 11.2.4). The demonstration that the large negative TCs offer the most favourable conditions for the decorrelation is one of the important result that came out the theoretical analyses.

It is worth keeping in mind that these conclusions have been proposed based on retrievals performed using the (or most of) inversion settings of FORLI. Because the retrieval characterisation and retrieval results depend on these settings (notably on the  $S_a$ ), the conditions above are valid typically for the retrievals performed with FORLI software. The impact

of choosing other retrieval parameters was not evaluated. However, the conclusions should hold in their majority and give in all case an adequate representation of the patterns of IASI sensitivity to near-surface CO.

# 12.2 Concluding remarks

In addition to the conclusions made in previous section, some other important remarks have to be reported:

- 1. A noticeable result that came out the theoretical analysis is the significant impact of the *a priori* layer correlations on the retrieval. This impact has to be taken into account when analysing retrieved CO profiles from FORLI or other retrieval software that uses a full  $\mathbf{S}_{\mathbf{a}}$  matrix.
- 2. Although it has been theoretically proven, the fact that large negative TCs are the most favourable conditions to measure near-surface CO has not been shown using real IASI observations until now. This is currently being done using Barrow (Alaska) as test case.
- 3. The comparison between IASI and RAMA stations above Mexico City raises several issues that, we feel, should be investigated in the future. Firstly, the impact of the PBL/mixing height in comparisons of satellite and surface measurement of CO is non-negligible and should be quantified. Including explicit PBL height in the comparisons of VMRs is in particular required. Note that the use of other type of measurements, taken higher in the PBL, could be preferred for the evaluation of satellite near-surface CO retrievals. Secondly, in case of high polluted regions, it would be worth investigating if adaptations in the retrieval scheme allow to capture better the high CO concentrations at the surface and their time evolution.
- 4. The synergy between limb and nadir sounders have been investigated briefly, and our results suggest that it does not bring significant improvement on the retrieval of near-surface CO concentrations.

#### CONCLUSIONS AND PERSPECTIVES

Measuring the composition of the atmospheric boundary layer is of crucial importance to quantify the emissions of pollutants and to understand their impact on the environment and health. Considered for a long time inadequate to monitor near-surface pollution because of their poor sensitivity to the planetary boundary layer, TIR sounders were shown in this work to carry useful information on the near-surface composition in case of high thermal contrast. The demonstration was made in this thesis for the IASI instrument and for two pollutants:  $SO_2$  and CO. Throughout this work, different types of analysis, including theoretical simulations and retrievals performed on real observations, led us to revisit the IASI capabilities to measure  $SO_2$  and CO surface pollution, and more specifically, to establish the geophysical conditions that favour monitoring these gases in the lowest part of the atmosphere.

 $SO_2$ , an acidifying trace gases mainly emitted by anthropogenic sources, was the first pollutant on which this work has focused (part II). Given its short lifetime,  $SO_2$  remains mainly confined in the near-surface atmosphere. The first attempt to retrieve near-surface  $SO_2$  from IASI observations was performed above the industrial area of Norilsk, using a simplified scheme based on the optimal estimation method. We have demonstrated the possibility to capture the persistent  $SO_2$  pollution, related to heavy metals extraction activities in the region, using IASI observations during specific periods. This was shown especially for the winter, when strong temperature inversions develop. Furthermore, winter in Norilsk is characterised by low surface humidity. H<sub>2</sub>O content has been firmly identified as a limiting factor for the detection of PBL SO<sub>2</sub> in the  $\nu_3$  band spectral region, where the strong absorption of  $H_2O$  can render the near-surface atmosphere opaque. By exploiting the favourable conditions of thermal contrast and humidity occurring in winter in Norilsk, we were able to retrieve the 0-2 km columns of SO<sub>2</sub>, and to acquire the spatial distribution of the gas for February 2009: it shows up as a wide  $SO_2$  plume at very low altitude, with large columns of around 2 DU above the city, which decrease as the plume spreads away. The time series of the  $0-2 \text{ km SO}_2$  columns in Norilsk have been analysed for the period 2008–2011, according to seasonal variations of thermal contrast and humidity. Retrieval errors have been estimated independently of the optimal estimation characterisation, and their correlation with the thermal contrast values and the  $SO_2$  amount has also been assessed. Finally, a good agreement between IASI and OMI sounders was shown for both retrieved  $SO_2$  columns and  $SO_2$  emissions, which were calculated in this work using a simple box model. The complementary between both sounders was also well illustrated: due to lack of sensitivity during the summer, IASI provides  $SO_2$  measurements during the winter, whereas OMI is limited to the summer at these high latitudes due to the need of solar radiation.

A more extensive analysis of IASI's capability to measure near-surface  $SO_2$  was made possible thanks to the development of a retrieval scheme allowing deriving  $SO_2$  near-surface concentrations at global scale. This scheme relies on the calculation in the range 1300– 1410 cm<sup>-1</sup> of radiance indexes (called HRI), which represent the strength of the  $\nu_3$  band signal in IASI measurements. It consists of two successive steps, both using HRI: 1) the retrieval of the altitude of  $SO_2$  plumes and the selection of those located below 4 km of height (above ground), 2) for the low altitude plumes, the conversion of HRI values into  $SO_2$  columns using 4D look-up-tables, linking the  $SO_2$  columns to the thermal contrast, the  $H_2O$  total column, and the HRI values. The zenithal angle of the satellite was also taken into account by building angle-dependent tables. Using this retrieval scheme, we have acquired a first global distribution of near-surface SO<sub>2</sub> from IASI. Anthropogenic hotspots including the large SO<sub>2</sub> emitters, such as China or Norilsk, along with smaller sources, like power plants located in Turkey and Bulgaria, have been identified. By combining monthly global distributions of near-surface  $SO_2$ , thermal contrast and  $H_2O$  total column, we have assessed for each identified anthropogenic source the seasonal variation of IASI sensitivity to near-surface  $SO_2$  in terms of the temporal variations of thermal contrast and humidity.

More generally, the analyses performed in the thesis have conducted us to firmly establish the geophysical conditions that favour monitoring SO<sub>2</sub> pollution in the  $\nu_3$  band spectral range using IASI observations. These are:

- 1. TC larger than 5 K in absolute value,
- 2. H<sub>2</sub>O total column below  $4 \times 10^{22}$  molecules/cm<sup>2</sup>, and H<sub>2</sub>O VMR at the surface below 4 g/kg.

Considering among other the various degrees of  $SO_2$  pollution, these conditions should not be considered as strict requirements, but more as indications.

In part III of the thesis, we have investigated the capability of IASI to measure nearsurface CO. This was done combining theoretical evaluations and real retrievals performed on IASI observations. We have first investigated the influence of thermal contrast on the detection of surface CO enhancements with IASI, by calculating differences between simulated spectra for background and polluted CO conditions. Using this approach, we have shown that there were three main factors driving IASI sensitivity to CO surface enhancements, namely: 1) the thermal contrast, 2) the enhancement of CO itself, and 3) the wavenumber. We have shown indeed that IASI is more sensitive to near-surface CO at the center of the rotational lines, where CO enhancements smaller than 80 ppb can be observed from 10 K (in absolute value) of TC. For lower TC, e.g. at 4 K, the smallest detectable enhancement is about 150 ppb. These thresholds significantly decrease by exploiting the whole 1–0 band of CO, and we suggest that enhancement as low as 10 ppb can be detected.

Compared to SO<sub>2</sub>, the difficulty to measure near-surface CO is the need to decorrelate its concentration in the lower troposphere from that in the higher troposphere. The extent with which this can be achieved has been investigated using the general framework of the optimal estimation method. In case of high negative (positive) TC, we have demonstrated that it was possible to retrieve the 0–3 (0–5) km and 3–19 (5–19) km mean VMRs independently. An important result was to show that large negative TCs, corresponding to temperature inversions, are in fact the most favourable conditions for this decorrelation of two tropospheric layers. We have explained this by the transition between emission in the first atmospheric layers and absorption in higher layers. Another important result is the shift of minimal error reduction/DOFS from vanishing TC towards negative values, when using a non-diagonal  $S_a$  matrix. This has been attributed to the correlation between the atmospheric layers, which

have therefore to be taken into account carefully when interpreting the error budget and information content of real retrievals of CO abundance in the near-surface atmosphere.

In a final step, we have performed a series of comparisons between the IASI retrieved 0–1 km CO averaged VMRs and co-located aircraft and in-situ measurements. Comparisons with MOZAIC aircraft data have confirmed the capability of IASI to capture high surface CO concentrations above Windhoek airport in the morning from August to November, a period associated to large positive thermal contrast. The sensitivity of the instrument was however shown to be hampered in low thermal contrast situations. This explains the poor performances of IASI for measuring the seasonal cycle of CO concentrations above Frankfurt airport (especially to observe the high CO surface VMRs recorded by MOZAIC aircraft during the winter), and its generally reduced sensitivity during the evening overpass. Retrievals performed above Mexico City also confirmed the results from the theoretical characterisation for positive thermal contrast. In particular, the comparison with RAMA ground-based in-situ measurements has shown the clear dependence of IASI retrievals to thermal contrast, with relative biases decreasing with increasing thermal contrast. A remaining absolute bias of IASI with respect to RAMA was, however, found even for high thermal contrast. The strong diurnal variation of the mixing height in Mexico City was suggested to be one possible explanation of these discrepancies. The use of a background-like CO a priori profile in FORLI, not representative of the high pollution levels of the city, could also contribute to this underestimation.

As for  $SO_2$ , the analyses performed for CO led us to the following conclusions with regard to the impact of thermal contrast on the capability of IASI to measure near-surface concentrations:

- 1. IASI starts to be sensitive to near-surface CO from |TC| = 5 K,
- 2. |TC| > 10 15 K favours the retrieval of two independent parts of the profile,
- 3. Large negative thermal contrasts offer more value for the decorrelation between CO concentration in the lower and upper troposphere.

These thermal contrast conditions often occur above the continents, and this suggests that IASI observations recorded above land could be exploited in air quality applications.

Different questions and issues have been raised throughout the thesis, and we feel that they should be the object of future developments and/or investigations. These are listed below in two categories, which are discussed separately.

#### 1. Methodology

Several methodological developments for the retrieval of near-surface  $SO_2$  or CO deserve more work.

(a) SO<sub>2</sub> - Use of  $\nu_1$  band

The limiting factor due to  $H_2O$  absorption identified in this work is specific to the use of the  $\nu_3$  band in the SO<sub>2</sub> retrieval. The  $\nu_1$  band (1100–1200 cm<sup>-1</sup>) is much less impacted by  $H_2O$  absorption and thus less subjected to opacity in the PBL. Although the  $\nu_1$  band has a lower intensity, it could be worth using it to retrieve near-surface SO<sub>2</sub> in case of large pollution event under moderate/high humidity. One possible way for exploiting the  $\nu_1$  band could be the building of LUTs for the conversion of radiance indexes calculated in this spectral range. Incorporating these radiance indexes in a neural network could be another possibility (see below). (b)  $SO_2$  - Including variety of real situations in LUTs

It was shown in chapter 7 that the LUTs developed for the  $SO_2$  retrievals do not include all the variety of geophysical conditions encountered, especially of temperature profiles. This led to the rejection of a large amount of data with no correspondence in the existing LUTs. This was made responsible for the large concentration differences between day and night measurements of IASI. Including more temperature profiles in the LUTs could avoid this shortcoming in the future. Alternative approaches could also be envisaged. Neural networks are particularly appealing and have been successively applied in the group recently for the retrieval of  $NH_3$  (Whitburn et al., 2016). This method would allow including different input parameters in the conversion of HRI values in  $SO_2$  columns.

(c)  $SO_2$  - Averaging and filters

Due to the large variability of IASI sensitivity, averaging near-surface  $SO_2$  measurements is not straightforward. It can be done in several ways, which would lead to different results. We have decided in this work to average only measurements with less than 25% relative error and 10 DU absolute error. By selecting mostly large  $SO_2$  columns, this caused an overestimation of the  $SO_2$  means and made the comparison with OMI observations complicated. Establishing the best averaging procedure should be part of future investigations.

(d) CO - Adaptation of retrieval settings

In case of high pollution levels, the potential underestimation of near-surface CO concentrations, retrieved using the FORLI *a priori*, should be quantified. In the same way, retrieval adaptations could be envisaged to improve the retrieval in high pollution situations. For instance, we could analyse if a dedicated set of *a priori* profile and  $\mathbf{S}_{\mathbf{a}}$ , built from reference data for high pollution, could improve the retrieval of PBL CO above megacities such as Mexico City. The potential improvement in the capture of high CO surface concentrations provided by increasing the number of retrieved layers between 0 and 1 km should be explored. Increasing this number could allow including a larger variability in the  $\mathbf{S}_{\mathbf{a}}$  for the layers close to the surface. Alternative retrieval approaches, such as the Tikhonov minimisation method, could be also envisaged (Tikhonov, 1963).

#### 2. Characterisation of the sensitivity

In addition to methodologies, the characterisation of IASI sensitivity to the nearsurface atmospheric composition can be improved in several ways.

(a) CO - Effect of large negative thermal contrast

Although it has been theoretically proven, the fact that large negative TCs are the most favourable conditions to measure near-surface CO has not been shown using real IASI observations. This is something that should be done in the future for a complete demonstration.

(b)  $SO_2$  - Use of  $H_2O$  total column or near-surface VMR?

The main impact of  $H_2O$  absorption on  $SO_2$  retrievals is located in the lowest part of the troposphere. We extensively used the  $H_2O$  total column to characterise the IASI sensitivity to near-surface  $SO_2$ , but this is maybe not the most adequate choice. Surface  $H_2O$  VMR could be used instead (as done for the Norilsk study). The shape of the  $H_2O$  profile could have an influence, especially if it presents an inversion (right panel of Figure 6.1.2), and this could be investigated in the future. (c)  $SO_2$  and CO - PBL height

In this work, we discussed extensively the problem of retrieving  $SO_2$  and CO concentrations in the lower part of the troposphere, but we never touched upon the issue of the PBL height. To clarify the capabilities of IASI for retrieving near-surface composition, this parameter could be included in future characterisation. As it also affects the vertical distributions of trace gases in the near-surface atmosphere, the PBL height should be included when assessing retrieval performances using comparisons with ground-based measurements.

(d) SO<sub>2</sub> and CO - Impacts of errors

Although we have taken care in our work to quantify errors, we did not analyse the impact of uncertainties on some important parameters, such as the thermal contrast. For instance, underestimation of the thermal contrast leads to overestimated concentrations and inversely. Such assessment will first require determining what are the typical uncertainties on such quantities. There is little litterature results documenting these. This is especially true for thermal inversions, whose errors are not known.

(e)  $SO_2$  and CO - Impact of the thermal contrast definition

In this work, the thermal contrast has been mainly calculated from the difference between the surface temperature and the temperature at 500 m. In the future, we could investigate if this definition is the best to describe the IASI sensitivity. The altitude of the PBL could be used as another reference to define the average temperature of air close to the surface.

(f)  $SO_2$  and CO - Inclusion of other parameters

More generally, in addition to thermal contrast (and humidity in the case of  $SO_2$ ), the impact of other parameters could be included in the analysis of TIR sounders sensitivity to near-surface composition. These parameters are for instance the spectral resolution, the radiometric noise or the spectral range used for the retrievals. We indeed expect an increase in the sensitivity for increasing spectral resolution and spectral range, and for decreasing radiometric noise. These effects should be quantified, and would be relevant especially for preparing future satellite missions.

(g) Extension of the work

As this work has well demonstrated for  $SO_2$  and CO, the PBL retrievals difficulty and quality depend on the targeted species. It would be interesting to extend he characterisation of the IASI PBL sensitivity to other atmospheric constituents, such as  $O_3$  that causes pollution episodes, or  $CH_4$  released by the melting of the permafrost. Also, as mentioned above, retrieval performances depend on the instrumental design and characteristics. To evaluate the sensitivity/retrieval differences between TIR sounders, this work could be extended to other instruments, current or future.

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# Appendices

# APPENDIX A

#### RADIATIVE TRANSFER FOR A TWO-LEVEL SYSTEM

#### A.1 Spectral radiant energy density function

As mentioned in subsection 2.1.2, the Planck function takes different forms depending on whether it is expressed as a function of wavelength, frequency or wavenumber. From equation (2.1.4), the Planck functions in frequency ( $\nu$ ) and wavenumber ( $\tilde{\nu}$ ) units are calculated as

$$B(\nu,T) = B(\lambda,T)_{\lambda \to \nu} \left| \frac{\mathrm{d}\lambda}{\mathrm{d}\nu} \right| = \frac{2h\nu^3}{c^2 \left[ \exp\left(\frac{h\nu}{k_B T}\right) - 1 \right]} \qquad \text{units} : \mathrm{Js}^{-1}\mathrm{m}^{-2}\mathrm{sr}^{-1}\mathrm{Hz}^{-1}, \ (A.1.1)$$

$$B(\tilde{\nu},T) = B(\lambda,T)_{\lambda \to \tilde{\nu}} \left| \frac{\mathrm{d}\lambda}{\mathrm{d}\tilde{\nu}} \right| = \frac{2hc^2\tilde{\nu}^3}{\exp\left(\frac{hc\tilde{\nu}}{k_BT}\right) - 1} \qquad \text{units}: \mathrm{Js}^{-1}\mathrm{m}^{-2}\mathrm{sr}^{-1}\mathrm{m}.$$
(A.1.2)

Because the radiation emitted by a blackbody is isotropic, the *spectral radiant energy* density function  $\rho$  of the latter can be calculated as

$$\varrho = \frac{4\pi}{c}B,\tag{A.1.3}$$

and this gives the following relations respectively in wavelength, frequency and wavenumber units:

$$\varrho(\lambda, T) = \frac{8\pi hc}{\lambda^5 \left[ \exp\left(\frac{hc}{\lambda k_B T}\right) - 1 \right]} \quad \text{units} : \text{Jm}^{-3}\text{m}^{-1}, \quad (A.1.4)$$

$$\varrho(\nu,T) = \frac{8\pi h\nu^3}{c^3 \left[\exp\left(\frac{h\nu}{k_B T}\right) - 1\right]} \quad \text{units} : \text{Jm}^{-3}\text{Hz}^{-1}, \quad (A.1.5)$$

$$\varrho(\tilde{\nu}, T) = \frac{8\pi h c \tilde{\nu}^3}{\exp\left(\frac{h c \tilde{\nu}}{k_B T}\right) - 1} \qquad \text{units} : \text{Jm}^{-3}\text{m.}$$
(A.1.6)

Finally, by integrating  $\rho$  over the whole spectral domain, we obtain the *total radiant energy* density function  $\rho_{tot}(T)$ :

$$\varrho_{tot}(T) = \int_0^\infty \varrho(\lambda, T) \,\mathrm{d}\lambda = \int_0^\infty \varrho(\nu, T) \,\mathrm{d}\nu = \int_0^\infty \varrho(\tilde{\nu}, T) \,\mathrm{d}\tilde{\nu}. \tag{A.1.7}$$

## A.2 Einstein coefficients

The probability of a transition between two energy states can be expressed using the Einstein coefficients<sup>1</sup> (Thorne et al., 1999). Considering two levels of energy  $E_i$  and  $E_j$ , with  $E_i < E_j$ , of a system with populations  $N_i$  and  $N_j$  respectively, we distinguish three radiative processes that allow the system to pass from one level to the other (Figure A.2.1):

1. Absorption: In the presence of radiation of spectral radiant energy density  $\rho(\tilde{\nu}_{ij})$ , the system can absorb a photon of energy  $hc\tilde{\nu}_{ij}$ , and passes from level *i* to *j*. The probability of this process is given by  $B_{ji} \rho(\tilde{\nu}_{ij})$ , and the number of transitions per second is calculated as

$$\left(\frac{\mathrm{d}N_i}{\mathrm{d}t}\right)_{abs} = -B_{ji}\,\varrho(\tilde{\nu}_{ij})\,N_i,\tag{A.2.1}$$

where  $B_{ji}$  (units: J<sup>-1</sup> m<sup>2</sup> s<sup>-1</sup>) is the Einstein coefficient associated to the absorption.

2. Stimulated emission: In the presence of radiation of spectral radiant energy density  $\rho(\tilde{\nu}_{ij})$ , the system can undergo stimulated emission, and passes from level j to level i with emission of a photon of energy  $hc\tilde{\nu}_{ij}$ . The probability of this process is given by  $B_{ij} \rho(\tilde{\nu}_{ij})$ , and the number of transitions per second is calculated as

$$\left(\frac{\mathrm{d}N_j}{\mathrm{d}t}\right)_{stim} = -B_{ij}\,\varrho(\tilde{\nu}_{ij})\,N_j,\tag{A.2.2}$$

where  $B_{ij}$  (units:  $J^{-1} m^2 s^{-1}$ ) is the Einstein coefficient associated to the stimulated emission.

3. **Spontaneous emission**: The system can spontaneously undergo a transition from level j to level i, with the emission of a photon of energy  $hc\tilde{\nu}_{ij}$ . The probability of such process is given by the Einstein coefficient  $A_{ij}$  (units:  $s^{-1}$ ) associated to spontaneous emission, and the number of transitions is calculated using

$$\left(\frac{\mathrm{d}N_j}{\mathrm{d}t}\right)_{spont} = -A_{ij} N_j. \tag{A.2.3}$$

By assuming that the system is at the thermodynamic equilibrium, we can derive the relations between the Einstein coefficients. At the equilibrium, the rate at which atoms/molecules of the system reach one level is equal to the rate at which they leave the other level:

$$\left(\frac{\mathrm{d}N_i}{\mathrm{d}t}\right)_{abs} = \left(\frac{\mathrm{d}N_j}{\mathrm{d}t}\right)_{stim} + \left(\frac{\mathrm{d}N_j}{\mathrm{d}t}\right)_{spont},\tag{A.2.4}$$

which leads to

$$B_{ji} \,\varrho(\tilde{\nu}_{ij}) \,N_i = B_{ij} \,\varrho(\tilde{\nu}_{ij}) \,N_j + A_{ij} \,N_j. \tag{A.2.5}$$

<sup>&</sup>lt;sup>1</sup>Note that the presented development is done in wavenumber units.



Figure A.2.1: Radiative processes responsible for the transition of a system between two energy states  $E_i$  and  $E_j$ . We distinguish the spontaneous emission  $(A_{ij})$ , the absorption  $(B_{ji})$ , and the stimulated emission  $(B_{ij})$ .  $N_i$  and  $N_j$  represent the populations of levels *i* and *j* respectively, and  $\rho(\tilde{\nu}_{ij})$  is the spectral radiant energy density function at wavenumber  $\tilde{\nu}_{ij}$ .

By rearranging equation (A.2.5), we obtain

$$\varrho(\tilde{\nu}_{ij}) = \frac{A_{ij}}{B_{ji} \frac{N_i}{N_j} - B_{ij}}.$$
(A.2.6)

At thermodynamic equilibrium, the populations of levels i and j are given by the Boltzmann equation:

$$N_{i} = g_{i} \exp\left(-\frac{E_{i}}{k_{B}T}\right),$$

$$N_{j} = g_{j} \exp\left(-\frac{E_{j}}{k_{B}T}\right),$$
(A.2.7)

where  $g_i$  and  $g_j$  are the respective degeneracies of levels *i* and *j*. From the above equations, we have

$$\frac{N_i}{N_j} = \frac{g_i}{g_j} \exp\left(-\frac{E_i - E_j}{k_B T}\right) = \frac{g_i}{g_j} \exp\left(\frac{hc\tilde{\nu}_{ij}}{k_B T}\right),\tag{A.2.8}$$

and by replacing in equation (A.2.6), we obtain

$$\varrho(\tilde{\nu}_{ij}) = \frac{A_{ij}}{B_{ji} \frac{g_i}{g_j} \exp\left(\frac{hc\tilde{\nu}_{ij}}{k_BT}\right) - B_{ij}},$$

$$= \frac{A_{ij}}{B_{ij}} \frac{1}{\frac{B_{ji} g_i}{B_{ij} g_j} \exp\left(\frac{hc\tilde{\nu}_{ij}}{k_BT}\right) - 1}.$$
(A.2.9)

Finally, by comparing this last equation with equation (A.1.6), we find the relations between the Einstein coefficients:

$$A_{ij} = 8\pi h c \tilde{\nu}_{ij}^3 B_{ij} \tag{A.2.10}$$

$$B_{ji} g_i = B_{ij} g_j. \tag{A.2.11}$$

#### A.3 Radiative transfer for a two-level system

Using the definitions of the Einstein coefficients, we can now derive the radiative transfer equation at a microscopic scale for a two-level system. This allows us to express the absorption and emission coefficients in terms of the Einstein coefficients. For this, we consider the same system as section A.2, with two energy states  $E_i$  and  $E_j$ , and submitted to an incoming radiation of spectral radiant energy density  $\rho(\tilde{\nu}_{ij})$ . The rate at which the total radiant energy density function varies can be calculated as the product between the number of transitions and the loss/gain of energy associated to the transitions. Thus, we can write

$$\frac{\mathrm{d}\varrho}{\mathrm{d}t} = B_{ij}\,\varrho(\tilde{\nu}_{ij})\,N_j\,hc\tilde{\nu}_{ij} + A_{ij}\,N_j\,hc\tilde{\nu}_{ij} - B_{ji}\,\varrho(\tilde{\nu}_{ij})\,N_i\,hc\tilde{\nu}_{ij}.\tag{A.3.1}$$

Recalling equation (A.1.7), by taking the derivative of  $\frac{d\varrho}{dt}$  with respect to the wavenumber, we can express the rate at which the spectral radiant energy density function varies as

$$\frac{\mathrm{d}\varrho(\tilde{\nu}_{ij})}{\mathrm{d}t} = B_{ij}\,\varrho(\tilde{\nu}_{ij})\,N_j\,hc + A_{ij}\,N_j\,hc - B_{ji}\,\varrho(\tilde{\nu}_{ij})\,N_i\,hc. \tag{A.3.2}$$

From the above equation, following what we have done in section 2.2, we need to determine the net change of radiance due to the absorption and emission by the system. We therefore need first of all to convert the spectral radiant energy density functions  $(\varrho(\tilde{\nu}_{ij}))$  in radiance  $(I(\tilde{\nu}_{ij}))$ . Recalling equation (A.1.3), we can write

$$\frac{4\pi}{c} \frac{\mathrm{d}I(\tilde{\nu}_{ij})}{\mathrm{d}t} = 4\pi h \, B_{ij} \, I(\tilde{\nu}_{ij}) \, N_j + A_{ij} \, N_j \, hc - 4\pi h \, B_{ji} \, I(\tilde{\nu}_{ij}) \, N_i. \tag{A.3.3}$$

Then, with the chain rule, we have

$$\frac{\mathrm{d}I(\tilde{\nu}_{ij})}{\mathrm{d}t} = \frac{\mathrm{d}I(\tilde{\nu}_{ij})}{\mathrm{d}s}\frac{\mathrm{d}s}{\mathrm{d}t} = c\frac{\mathrm{d}I(\tilde{\nu}_{ij})}{\mathrm{d}s}.$$
(A.3.4)

Using this relation and by rearranging terms of equation (A.3.3), we obtain the radiative transfer equation at the infinitesimal scale as a function of the Einstein coefficients:

$$\frac{\mathrm{d}I(\tilde{\nu}_{ij})}{\mathrm{d}s} = h \left[ B_{ij} N_j - B_{ji} N_i \right] I(\tilde{\nu}_{ij}) + \frac{hc}{4\pi} A_{ij} N_j \,. \tag{A.3.5}$$

Equation (A.3.5) is equivalent to equation (2.2.3), and by comparing the two, we can find an expression for the absorption coefficient  $\alpha_{tot}(\tilde{\nu}_{ij})$ . Because we have considered a two-level system,  $\alpha_{tot}(\tilde{\nu}_{ij})$  is in this case equal to  $\alpha(\tilde{\nu}_{ij})$ , and is expressed as

$$\alpha_{tot}(\tilde{\nu}_{ij}) = \alpha(\tilde{\nu}_{ij})$$
  
=  $-h \left[ B_{ij} N_j - B_{ji} N_i \right]$   
=  $h B_{ji} N_i \left( 1 - \frac{B_{ij} N_j}{B_{ji} N_i} \right).$  (A.3.6)

Using equations (A.2.8) and (A.2.11), we find the following expression for the absorption coefficient:

$$\alpha_{tot}(\tilde{\nu}_{ij}) = h B_{ji} N_i \left[ 1 - \exp\left(\frac{-hc\tilde{\nu}_{ij}}{k_B T}\right) \right].$$
(A.3.7)

Similarly, by equating the second terms of the right hand sides of equations (2.2.3) and (A.3.5), we can express the emission coefficient  $J(\tilde{\nu}_{ij})$  as

$$J(\tilde{\nu}_{ij}) = \frac{hc}{4\pi} A_{ij} N_j \,. \tag{A.3.8}$$

Finally, using equations (A.3.7) and (A.3.8), the source function  $S(\tilde{\nu}_i j)$  can be expressed as

$$S(\tilde{\nu}_{ij}) = \frac{J(\nu)}{\alpha_{tot}(\tilde{\nu})}$$
$$= \frac{c}{4\pi} \frac{N_j A_{ij}}{N_i B_{ji}} \frac{1}{\left[1 - \exp\left(\frac{-hc\tilde{\nu}_{ij}}{k_B T}\right)\right]}.$$
(A.3.9)

From the relations between the Einstein coefficients (equations (A.2.10) and (A.2.11)), we can derive

$$A_{ij} = 8\pi h c \tilde{\nu}_{ij}^3 B_{ji} \frac{g_i}{g_j},$$
 (A.3.10)

and by replacing this equation and equation (A.2.8) in the source function expression ((A.3.9)), we finally obtain

$$S(\tilde{\nu}_{ij}) = \frac{2hc^2\tilde{\nu}_{ij}^3}{\exp\left(\frac{hc\tilde{\nu}_{ij}}{k_BT}\right) - 1},$$
(A.3.11)

which corresponds to the Planck function in wavenumber units (equation (A.1.2)).

# APPENDIX B

#### SUMMARY OF THE MASTER THESIS RESULTS

# B.1 IASI sensitivity to surface SO<sub>2</sub> in Norilsk: forward simulation analyses

The idea of the forward simulations performed during the Master thesis was to determine the influence of the TC on the capability of IASI to measure an enhancement of  $SO_2$  in the PBL. To do so, spectra have been simulated for two representative atmospheres, under varying conditions of TC. The first reference atmosphere is characteristic of a non-polluted air mass (hereafter called background spectrum), for which we have considered Arctic atmospheric models, one for the winter and one for the summer (Anderson et al., 1986). The second reference atmosphere has an increased  $SO_2$  PBL concentration and is chosen to represent a polluted near-surface layer. The PBL has been defined as the 0–1 km layer. We have considered a mean background VMR for this layer of about 0.3 ppb for both winter and summer models, and a polluted VMR of 100 ppb (SO<sub>2</sub> well-mixed in the 0-1 km). The TC has been defined as the difference between the surface temperature and the temperature of the air at 500 m. TC values in the range -15 K and 15 K, per 1 K step, have been considered. The forward simulations have been performed using Atmosphit, considering an atmosphere discretised in 1 km-thick layers (0–60 km) and over the spectral range 1000– 1450 cm<sup>-1</sup>, which includes both  $\nu_3$  and  $\nu_1$  bands. An emissivity of 1 and a satellite viewing angle of 0° have been considered. From simulated spectra, we have calculated a normalised BTD  $(BTD_{norm})$  as

$$BTD_{norm}(\tilde{\nu}) = \frac{BT(\tilde{\nu}, \text{TOA})_{polluted} - BT(\tilde{\nu}, \text{TOA})_{background}}{Ne\Delta T},$$
(B.1.1)

where  $BT(\tilde{\nu}, \text{TOA})_{polluted}$  and  $BT(\tilde{\nu}, \text{TOA})_{background}$  are respectively the polluted and the background spectra expressed in BT, and  $Ne\Delta T$  is the noise equivalent temperature difference at 280 K (see subsection 4.1.1). The  $BTD_{norm}(\tilde{\nu})$  thus represents the difference in the spectral signal detected by IASI due to an enhancement of 100 ppb of SO<sub>2</sub> in the 0–1 km layer relative to the noise. A  $BTD_{norm}(\tilde{\nu})$  larger than 1 characterises a situation for which IASI detects at wavenumber  $\tilde{\nu}$  a spectral signature above its noise level, which is due to this enhancement.

Figure B.1.1 presents the calculated  $BTD_{norm}$  (color scale) as a function of TC and wavenumber, for both winter (top panel) and summer (bottom panel) in the Arctic. Spectral



Figure B.1.1:  $BTD_{norm}$  (color scale) calculated from the difference between polluted (enhancement of 100 ppb of SO<sub>2</sub> well-mixed in the 0–1 km) and background spectra as a function of TC and wavenumber, for winter (top) and for summer (bottom) in the Arctic.

features located between 1100 cm<sup>-1</sup> and 1200 cm<sup>-1</sup> are those of the  $\nu_1$  band, and between 1300 cm<sup>-1</sup> and 1400 cm<sup>-1</sup> are those of the  $\nu_3$  band. In winter, there is a clear difference in the sensitivity of IASI to the two SO<sub>2</sub> bands. The strongest lines of the  $\nu_3$  band are detectable from absolute values of TC larger than 1 K. Almost the entire band is detectable in case of 5 K of TC. On the contrary, because it is weaker, the observation of the  $\nu_1$  band requires larger TC values; a signal becomes detectable in some spectral channels for TC larger than 10 K (absolute value). At an absolute value of 15 K, the  $\nu_1$  remains only partially observed. In summer, the results are completely different. The  $\nu_3$  band is undetectable for all the TC values considered. This is explained by the larger humidity during summer (almost 10 times larger than in winter if we compare the H<sub>2</sub>O profiles of the two Arctic models). The strong absorption of H<sub>2</sub>O ( $\nu_2$  band, see subsection 4.1.1) renders thus the lowest layers of the atmosphere opaque in the spectral region of the  $\nu_3$  band of SO<sub>2</sub>. Contrary to the  $\nu_3$  band, the  $\nu_1$  band is less influenced by H<sub>2</sub>O absorption, but is still hardly detected; only few spectral channels are observed for absolute values of TC around 15 K and more.

For constant conditions of TC and H<sub>2</sub>O, the detection of the vibrational bands of SO<sub>2</sub> obviously depends on its enhancement in the 0–1 km layer. Forward simulations have been performed for different levels of SO<sub>2</sub> pollution for the winter model only, and new  $BTD_{norm}$  have been calculated following the same procedure as described above. Table B.1 summarises the results obtained for both  $\nu_3$  and  $\nu_1$  bands. As expected, larger SO<sub>2</sub> enhancements can be detected for lower values of TC.

$SO_2$ enhancement (ppb)	$ \mathbf{TC} $ threshold for $\nu_3$	$ { m TC} $ threshold for $ u_1$
20	$> 5 \mathrm{~K}$	>> 15 K
40	5 K	$> 15 {\rm ~K}$
60	3 K	$> 15 {\rm ~K}$
80	2 K	15 K
120	1 K	$> 10 \ {\rm K}$
140	1 K	10 K
160	1 K	8 K
180	1 K	$> 5 \mathrm{~K}$
200	1 K	5 K
250	1 K	4 K
300	1 K	4 K

Table B.1: Influence of the SO<sub>2</sub> enhancement in the 0–1 km on its detection by IASI. For each enhancement considered, the absolute value of TC from which a spectral signal starts to be detected (at least one channel) are indicated for both  $\nu_3$  and  $\nu_1$  bands.

## B.2 Spatial distributions and time series

In the Master thesis, in addition to perform forward simulations in order to theoretically investigate the influence of TC on the IASI sensitivity to PBL  $SO_2$ , we retrieved  $SO_2$  nearsurface columns from IASI observations taken above the area of Norilsk. Following the results obtained in the theoretical study, we have chosen to analyse only spectra recorded in winter (November-March) during the period 2009–2011. Due to the long computation time associated to the OEM, only observations located in the area  $68-70^{\circ}N/87-89^{\circ}E$  for which a BTD (see subsection 5.1.1) larger than 0.25 K (indication of the presence of SO<sub>2</sub>) were analysed. Moreover, only those associated to a cloud coverage lower than 25% were selected. The retrievals were performed over the spectral range 1285–1400 cm<sup>-1</sup>, excluding the 1290–1308 cm<sup>-1</sup> range that includes the Q-branch of CH<sub>4</sub>. The temperature and humidity profiles, the surface temperature and the emissivity used in the analysis were the ones of EUMETSAT L2 PPF. In case they were not available, daily average profiles were used instead, and the surface temperature was calculated as the average of six clear spectral channels (857.50, 866.25, 868.50, 879.00, 892.75, 966.00 cm<sup>-1</sup>). The retrieval was performed in three steps, considering different *a priori* variabilities to maximise the number of convergent adjustments. All the inversion settings are summarised in Table B.2.

Parameters	Retrieve layers	a priori	a priori variability
$H_2O$	0–2, 2–4, 4–6, 6–8, 8–10, 10–15, 15–20 km	EUMETSAT L2 PPF	$1^{st}$ step: 30% $2^{nd}$ - $3^{rd}$ steps: 20%
$\mathbf{CH}_4$	$0{-}10 \mathrm{~km}$	Arctic winter model	$1^{\rm st}$ step: 10% $2^{\rm nd}$ - $3^{\rm rd}$ steps: 20%
$\mathbf{SO}_2$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Arctic winter model	1 <sup>st</sup> step: 50% 2 <sup>nd</sup> step: 40% 3 <sup>rd</sup> step: 25%
$\mathbf{T}_{ ext{surf}}$	-	EUMETSAT L2 PPF	All steps: $2\%$

Table B.2: Inversion settings used to retrieve the near-surface  $SO_2$  column. Three successive procedures are indicated, considering different *a priori* variability were performed.

In the top panel of Figure B.2.1, daily (grey dots), monthly (blue filled circles) and winter (orange triangles) averaged 0–1 km VMRs of SO<sub>2</sub> are presented for the period 2009–2011. They were calculated using only retrievals with a RMS smaller than  $2 \times 10^{-6}$  W m<sup>-2</sup> sr<sup>-1</sup> m (the instrument noise is around  $4 \times 10^{-7}$  W m<sup>-2</sup> sr<sup>-1</sup> m in this spectral range), and with an associated absolute value of TC larger than 5 K (20 ppb  $SO_2$  are in this case observable). In this figure, it is worth noticing first the large variability of the daily averages, which vary from around 0 ppb (the *a priori*) to 237 ppb. Monthly and winter averages are on the contrary more stable in the range 20–30 ppb. Among the monthly means presented, those of November 2010, March 2011, November 2011 and December 2011 stand out (shown in red in top panel of Figure B.2.1). We found that these months were associated to a very small amount of measurements (less than 35 retrieved VMRs for the entire month and entire area), and we decided to exclude these of the main analysis. Similarly, the winter average of the end of 2011 was also rejected (pink triangle). When these data are removed, we find a small decrease of the  $SO_2$  VMR in the 0–1 km layer over the period 2009–2011. This was done with a linear regression  $(y = -0.013x + 3.2 \times 10^4, R^2 = 0.48)$  over the monthly averages (weighted by the standard deviation), which is shown in green in top panel of Figure B.2.1.

A spatial distribution of the polluted  $SO_2$  plumes in the area of Norilsk is shown in the bottom panel of Figure B.2.1. It was built from the average of retrieved 0–1 km VMRs for the entire period. The area covered by the plume therefore is driven by transport and chemistry. The largest VMRs are observed around the cities of Norilsk and Kayerkan, where the smelters for the extraction of copper are located.  $SO_2$  is not seen in the region of the Plutorana Plateau, suggesting that the gas is mainly located close to the surface.



Figure B.2.1: (Top) Daily (grey dots), monthly (filled blue circles), and winter (orange triangles) averaged 0–1 km VMRs of SO<sub>2</sub> for the period 2009–2011. The vertical bars represent the standard deviations. The filled red circles correspond to the monthly means that have been rejected from the linear regression analysis. Similarly, the pink triangle corresponds to the rejected winter average. The green line corresponds to the linear regression performed on the monthly averages. (Bottom) Spatial distribution of the 0–1 km VMR of SO<sub>2</sub> calculated over the period 2009–2011.