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Master of Science

Development of a Tomographic Atmospheric Monitoring System based on Differential Optical Absorption Spectroscopy

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Acronyms

AP Air Pollution

CEM Continuous Emission Monitoring

COPD Chronic Obstructive Pulmonary Disease

CT Computed Tomography

DIAL Differential Absorption LIDAR

DOAS Differential Optical Absorption Spectroscopy

EEA European Environmental Agency

EPA Environmental Protection Agency (United States)

FBP Filtered BackProjection

FFF Forest Fire Finder

FST Fourier Slice Theorem

FT Fourier Transform

ICE Internal Combustion Engine

IFT Inverse Fourier Transform

ML Machine Learning

PM Particulate Matter

ROI Region Of Interest

RQ Research Question

SLR Systematic Literature Review

SMS Systematic Mapping Study

TDL Tunable Diode Laser

VOC Volatile Organic Compound

WHO World Health Organization

*

Background and Motivation

1.1 Context

The idea behind this thesis was born in 2015, at NGNS-IS (a Portuguese tech startup). At the time, the company's flagship product was the Forest Fire Finder (FFF). The FFF was a forest fire detection system, capable of mostly autonomous and automatic operation. The system was the first application of Differential Optical Absorption Spectroscopy DOAS for fire detection, and for that it was patented in 2007 (see [33, 34]). The FFF is a remote sensing device that scans the horizon for the presence of a smoke column, sequentially performing a chemical analysis of each azimuth, using the Sun as a light source for its spectroscopic operations [31].

The FFF was deployed in several "habitats", both nationally (Parque Nacional da Peneda-Gerês and Ourém) and internationally (Spain and Brazil). One of the company's clients at the time was interested in a pollution monitoring solution, and asked if the spectroscopic system would be capable of performing such a task. The challenge resonated through the company's structure and the idea that created this thesis was born. The team then started reading about the concept of Air Pollution AP and how both populations and entities were concerned about it. It became clear that, while there were already several methods to measure AP, there was a clear market drive for the development of a system that could leverage the large area capabilities of a DOAS device while being able to provide a more spatially resolved "picture" of the atmospheric status. With this in mind, the company managed to have the investigation financed through a PT2020 funding opportunity. This achievement was a clear validation of the project's goals and of the need there was for a system with the proposed capabilities. It was, however, not enough. FFF was a very good starting point, but there was still a lot of continuous research work needed before any of the goals that had been set were achieved. This led to the publication of this PhD project, in a tripartite consortium between FCT-NOVA, NGNS-IS and the Portuguese Foundation for Science and Technology. Its main goal was to develop an atmospheric monitoring system prototype that would be able to spectroscopically map pollutant concentrations

in a two-dimensional way.

1.2 The Problem

The first step in tackling the development of the proposed system was to understand the problem it should be dealing with. Air Pollution (AP) is one of the most present concerns of people around the industrialized modern world. In Europe, it is perceived to be the second most important threat to the environment. The first is climate change, which is great part caused by AP. Scientists in many countries have established it as a major cause for premature death, disease onset and hospital visits for some decades now. Regulatory bodies of many countries have been gathered to put some legislative pressure on industries and on society itself, in order to produce a decrease in the amount of Air Pollution to which people are exposed. These policies and measures have had a dramatic influence in air quality, which is very significantly improved throughout the years. In spite of this, official reports continue to highlight the importance of keeping a vigilant eye towards AP proliferation and its possible undiscovered health effects. A better introduction to the subject of AP is produced in Section 2.1.

Our spectacular progress as a species in the last few centuries has had some unforeseen adverse consequences. Mitigating them is not only a responsibility, but also a necessity. In some regards, as is the AP case, this mitigation is only achievable with intelligent and effective action. This of course demands that we understand, trace and measure it in as many ways as possible. This project aimed to create just that: another way in which to measure and map the behavior of certain pollutants.

1.3 Objectives

From the beginning of the project, the main objective has always been to design and develop a miniaturized spectroscopic environmental analysis device. The system would have to be small and portable enough to adapt to a drone, but should be able to function if adapted to any other surface, such as a car or even a fixed station. With time, however, the goal changed somewhat. The miniaturization and drone-adaptation were kept, but there was now the need to be able to map the pollutant concentration along a geographic region through the use of tomographic reconstruction algorithms. This meant that, while the device itself would be perfectly capable of operating without a drone, the tomographic capability would be lost, unless a prohibitively large number of spectroscopic systems were deployed in that region.

The concept evolved in such a way that the overarching goal of this thesis is now to theorize and design a two-dimensional mapping tool for trace atmospheric pollutants such as NO_x and SO_x, using passive DOAS as the measurement technique. In addition to this, it should be mentioned that the system must be small and portable; use tomographic reconstruction (and acquisition) algorithms to map the region; and that

it should use only one collection point (to reduce costs and instrumental complexity). From these objectives, the research questions, detailed in Section 2.2 were derived.

Research Question

2.1 Problem Introduction

AP is a very important topic of discussion in the current days, with scientists and researchers around the globe being very well aware of the potential effects it can have on the health of individuals and populations across all ecosystems [22]. After climate change (one of the largest capital threats to life on Earth, perhaps just behind nuclear apocalypse), AP is the biggest environmental concern for Europeans, and Europe's single largest environmental health hazard [11]. It has also been established by many authors as a major cause of premature death, cardiopulmonary disease onset and hospital visits [10, 11, 13, 35].

The growing concerns about Air Pollution and its effects on human health and the world in general is an indication for the importance of measuring it correctly and with great detail. The diversity of its effects and the sheer number of variables that need to be considered establish the problem of AP as one that can only be effectively tackled if approached intelligently, highlighting the need for smart devices for the measuring and monitoring atmospheric pollutants.

At the moment, there are several solutions that can be implemented for measuring atmospheric pollution. However, these solutions are limited in their application to either large area coverage and small details (DOAS ground stations, satellite data) or very detailed information in a very localized and fixed way (in-situ electrochemical sensors). To the best of our knowledge, there are no available systems that can monitor and map pollutant concentration without requiring infrastructure installation and capable of performing at various altitudes.

The answer to this lack could be a highly mobile tomographic DOAS system, that could bridge the gap between the local monitoring capabilities of in-situ electrochemical sensors and large-area spectroscopic ground stations, while maintaining portability and flexibility.

2.2 Research Question

In Chapter 1, I have introduced the reasons which led NGNS-IS to pursue the development of an atmospheric monitoring system, and that what set it apart from other systems was the ability to spectroscopically map pollutants concentrations using tomographic methods, thus defining a primary objective for this thesis.

Two secondary objectives were born from the necessary initial research, which had a very heavy influence over the adopted methods:

- To use a tomographic approach for the mapping procedure;

- To ensure the designed system would be small and highly mobile;

- To use a single light collection point, minimizing material costs.

Taking all the above into account, we arrive at the main Research Question (RQ), presented in Table 21.

Table 21: Main research question.

RQ1	*How to design a miniaturized tomographic atmosphere monitoring system based on DOAS?*

This is the main research question. It gave rise to four other more detailed research questions. These secondary questions allow a better delimitation of the work at hand and are important complements to RQ1. This questions are presented in Table 22

Table 22: Secondary research questions.

RQ1.1	*What would be the best strategy for the system to cover a small geographic region?*
RQ1.2	*What would be the necessary components for such a system?*
RQ1.3	*How will the system acquire the data?*
RQ1.4	*What should the tomographic reconstruction look like and how to perform it?*

2.3 Hypothesis and Approach

This work is based on the hypothesis that a system such as the one described in Chapter 1, which responds to the RQ in Table 21 and Table 22 can be achieved by careful selection of mathematical tomographic algorithms and instrumentation that is able to implement them correctly.

The first step in answering the entirety of the research questions should be to answer RQ1.1. In fact, it is not possible to make any other decision before this matter is settled. As with any technical problem, there are several ways to create a tomographic atmospheric monitoring tool. However, each and every one of them implies some kind of compromise, which determines the system's capabilities and requirements. Will the system use retro-reflection? Shall it move during the measurement? These are the kind of questions that determine the whole project.

When the measurement strategy is determined, one could start picking parts and components. However, a better first approach would be designing a software simulation. This simulator must include all major system features, so that it correctly mimics reality and is therefore able to mathematically validate the acquisition and reconstruction approach. The results obtained from the simulation will then dictate mechanical and control requirements.

One other aspect that needs addressing is the optical section. As mentioned before, the system will be inspired in FFF's basic optical capabilities. However, the smoke detector was not conceived with spatial restrictions in mind. This important set of components will thus need redesigning, so that it is in line with the size objectives of the new system.

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Literature Review

The work in this thesis involved dealing with many subjects. Air Pollution, tomographic algorithms and DOAS (in particular DOAS Tomography) were the most important. In this section, I provide a brief literary review covering the three.

3.1 Air pollution and pollutants

Daniel Vallero, in his book "Fundamentals of Air Pollution" [32] makes a very important observation: Air Pollution has no universal definition. Its meaning is intertwined with the context with which it is measured and observed, with the ecosystem in which it is perceived and even with the pollutant concentration (not every toxic compound is toxic at every concentration). The United States Environmental Protection Agency (EPA) defines Air Pollution as the following:

> *Air Pollution is the presence of contaminants or pollutant substances in the air that interfere with human health or welfare, or produce other harmful environmental effects.*

He then analyzes this definition through two possible lenses, the one that comes with the interference produced by air contaminants; and the one that comes from the harm they may cause. He notes that both points of view come with a heavy burden of ambiguity, incompatible with a scientific definition. We can thus observe that preferable to address the issue through its measurable effects and consequences. These are well-established and well known, and scientists all around the world have been publishing extensively about them for some decades now. The correlation between Air Pollution and an increased mortality in heavily industrialized areas was first established in Europe, in the 19th century, but the first time it was taken seriously was during the 1952 killer-smog incidents, in London [27]. At the time, a combination of very cold weather, an anticyclone and fireplace emissions caused a thick smog to fall over London, directly causing thousands of deaths and indirectly many more [1, 25]. The disastrous consequences of this incident had a huge impact in the civil society,

resulting in a series of policies and laws, among which the Clean Air Acts of 1956 and 1968.

More than 60 years have passed since the London-smog incident, but the influence it had on the whole Western world has prevailed in time. Almost every developed country in the world has laws and protocols in place to limit and decrease AP emissions over time. In the European Union, the European Environmental Agency (EEA) is responsible for providing sound and independent information to the ones involved developing, adopting, implementing and evaluating environmental policy [12]. The agency is also responsible for publishing reports on the state of air quality in Europe, which are made available to the general public. In their most recent report [11], one could see that, in general, rules and regulations put in place to control atmospheric emissions have caused a clear decreasing trend to appear on AP data (see Figure 31), although European productivity has been rising or stable across all sectors.

Reports like this one are very important in the current day Western world. In fact, Europeans have deemed Air Pollution to be their second largest environmental concern, after climate change [30], with which it is inexorably intertwined. The population's sensitivity to this subject is undoubtedly related to the growing knowledge that exists regarding human health implications of AP. It has been known for some time that there is a direct correlation between the emission level and premature mortality, especially due to cardiovascular complications [5, 13, 20, 21]. In Europe, poor air quality is an important cause of premature death, with a estimated toll of 400000 per year [11].

A comprehensive description of the effects of Air Pollution on the human and animal bodies would be a colossal task, much beyond the scope of this document or my whole thesis. It is, however, important to mention some of these effects, not only for demonstration purposes, but also as an introductory approach to the physiological importance of AP, which justify their social and societal significance as a public health menace. I will therefore address the phenomenon impact on the respiratory system, its importance as a precursor for cardiovascular diseases and its potential impact on the most vulnerable period of human life, gestation. The following discussion will once again be based around Vallero's work [32], complemented whenever necessary by other authors.

The respiratory system's main functions are the delivery of oxygen into the blood stream and the removal of carbon dioxide from the body. Air enters the body from the upper airways and flows to the alveolar region, where oxygen diffuses across the lung wall into the blood stream, from which it is transported to the tissues where it diffuses yet again and is made available to the mitochondria in the cells, that use it for cellular respiration [24]. The whole system is in permanent interaction with the atmosphere, and is therefore exposed to all kinds of air pollutants and trace gases, increasing the probability that some of them are delivered to this system.

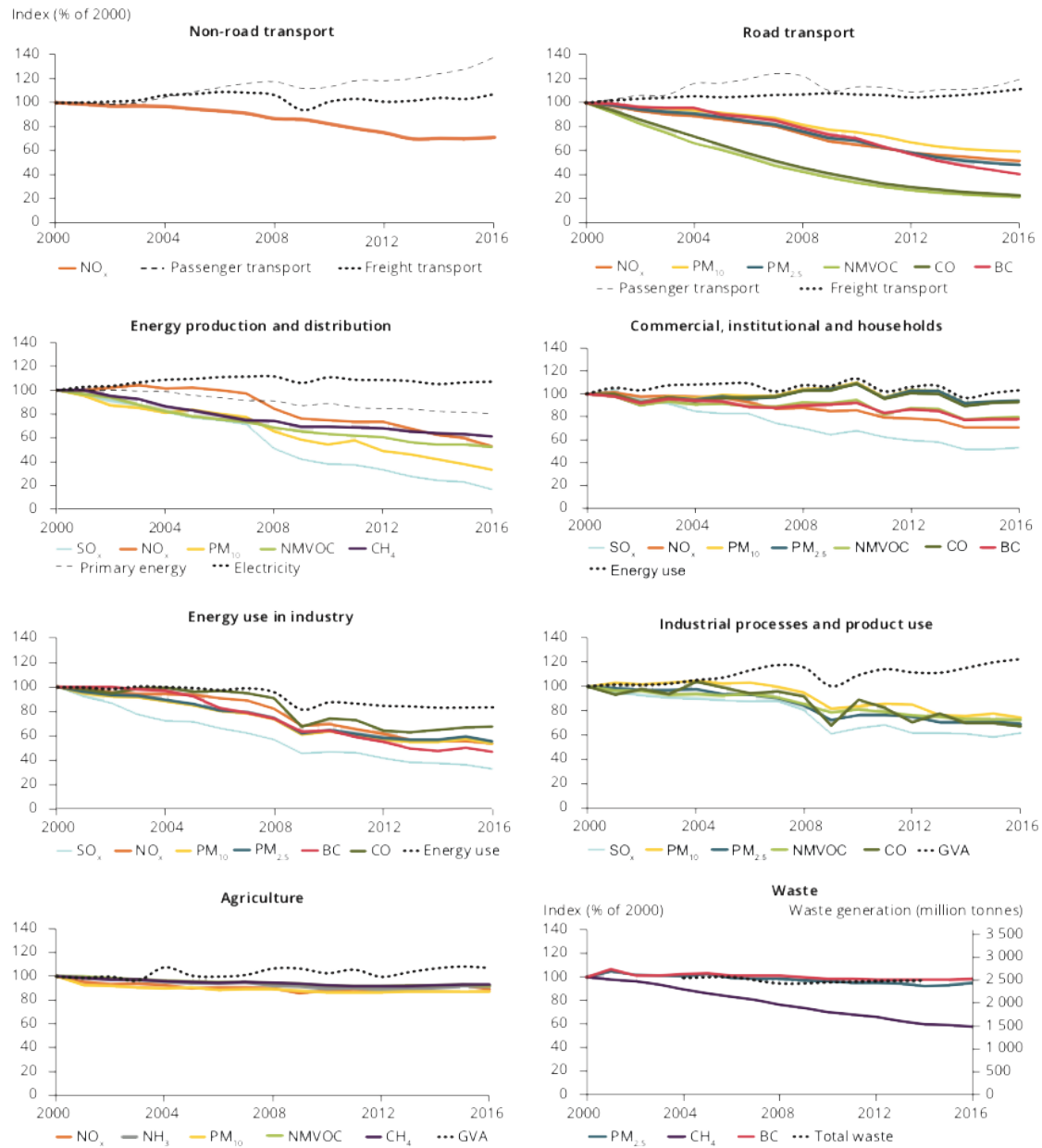Acute symptoms of AP exposure are very varied, and range from mild irritation

Figure 31: EU emissions evolution through time, since the year 2000, separated by source of emissions [11]. Notice the downward trend for emissions across all sources.

to complete respiratory failure, depending mostly on level of exposure and individual sensitivity to the chemical compound. On a chronic level, AP has been established as cause for Chronic Obstructive Pulmonary Disease (COPD), asthma, and lung and other cancers. In addition, by entering the body through the respiratory system, air pollutants and toxins are conveyed onto the other tissues, extending the range of their damage. The next system to be affected by AP is the cardiovascular system, which is the mechanism through which the oxygen, absorbed by the respiratory system, gets transported into all the other tissues. Oxygen is not the only molecule that is able to traverse the lung's wall and therefore it is possible for several air pollutants to contaminate the body through the same paths. The link between Air Pollution and cardiovascular effects started being made during the twentieth century, given a series of incidents (like London's 1952 killer-smog) that happened in the urban areas of industrialized countries. Nowadays, this link is perfectly established and we have alredy described several mechanisms by which AP is able to interfere with cardiovascular health. For instance, scientists and doctors have managed to establish at least three pathways between AP and cardiac arrhythmia, as depicted in Figure 32. One of the most important cardiovascular complications that arise from Air Pollution is CO poisoning. Carbon Monoxide is a tasteless, odorless and colorless gas that is a side product from an incomplete combustion of fuels containing carbon atoms. Its properties make it impossible to detect without some kind of instrument, since our senses cannot distinguish its presence. CO can easily enter the blood stream through the lungs. When in the body, it binds with hemoglobin. Its affinity to this transport molecule is about 200 times higher than oxygen's, and this means that it starts to starve the body organs from that important molecule. Continuous exposure to Carbon Monoxide is never beneficial. Low exposure levels can cause neuro-behavioral or developmental effects, but at higher concentrations, the most prominent symptoms are unconsciousness and death [26].

Mammals are in their life's most vulnerable stage while they are still developing inside their mother's womb. This is the time when there is a greater rate of tissue expansion and creation, which gives rise to the possibility of the appearance of some kind of morphological abnormality. This rate of development creates an enormous need for nutrients, provided by the mother through her blood. If the mother is exposed to a pollutant, and it gains access to the mother's blood stream, then the developing being is also exposed. The effects that come from *in utero* exposure are similar to those we see in other stages of life, but the dose at which they occur is significantly lower. Moreover, timing of exposure is also important, since there are stages to the fetus' development. Figure 33, taken from [32], illustrates what kind of developmental effects may come from Air Pollution exposure, and the influence of their timing.

The seriousness of the effects these chemicals produce create the need for quantification methods, so we can understand how we can deal with our surrounding atmosphere. The variability of this our environment, however, prevents the existence of any
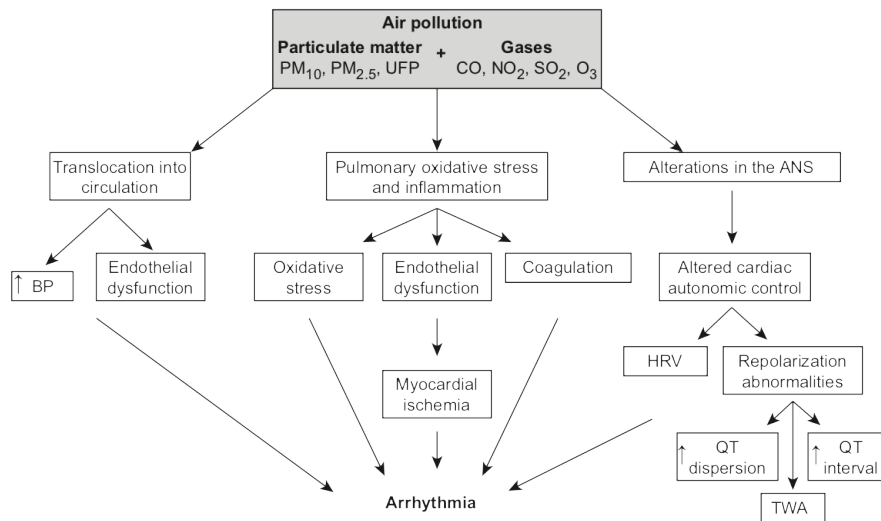
Figure 32: Physiological pathways to arrhythmia that stem from Air Pollution exposure [32].
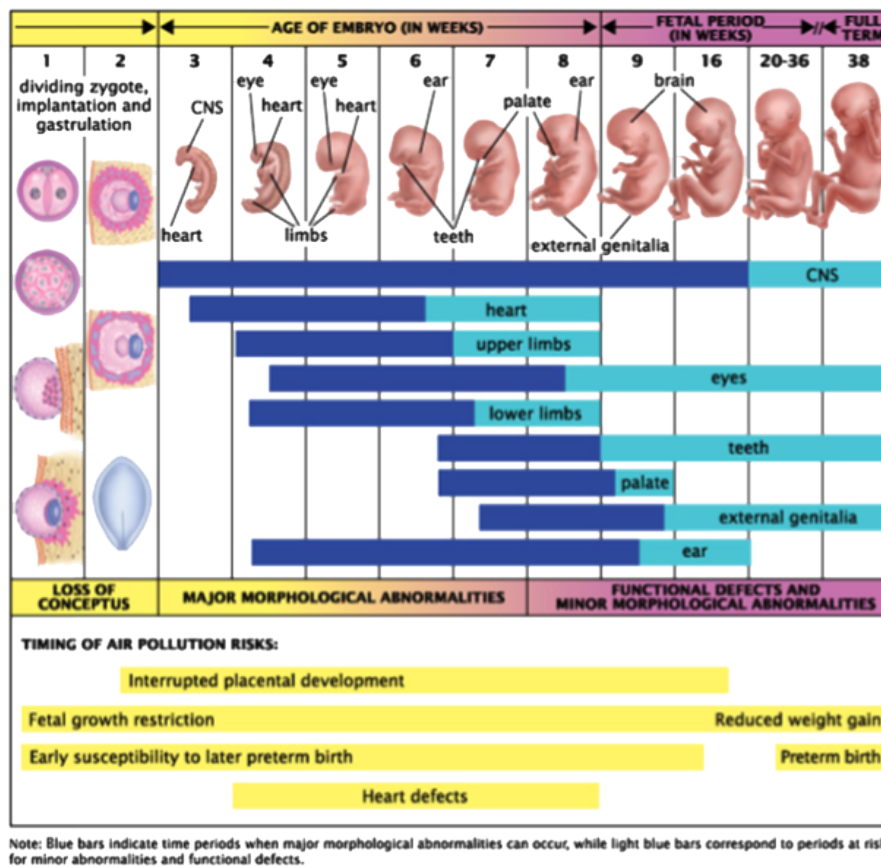

Figure 33: Possible abnormalities caused by AP exposure *in utero*. Notice that time of exposure is of critical importance [32].

one-size-fits-all solution. As a result, there are many techniques and methods with which we are nowadays able to measure pollution and airborne gaseous components. In the following discussion, I will address only open path monitoring systems, since these are the most relevant for the kind of project my thesis encompasses. A more curious reader is redirected to [7, 29, 32] for a more in depth review and presentation of emission monitoring technologies.

Open path atmospheric monitoring systems exploit interaction phenomena between light and the gaseous pollutants to detect and measure pollutant concentration. One of these technologies is Tunable Diode Laser (TDL), a technique in which light is emitted at a given wavelength (particularly in the infrared region of the spectrum) and its atmospheric absorption measured on the other end of the assembly. TDL has been used extensively for methane and NO measurements, and provides robust results in real-time, being an adequate solution for Continuous Emission Monitoring (CEM). One of the greater disadvantages of this technique is that, since only one wavelength is measured at a time, one has to have a light source for each target compound [2, 32]. Another one of these techniques is called Differential Absorption LIDAR (DIAL). In this method, light is pulsed in two different wavelengths, which must be close to one another. The first of these wavelengths corresponds to an absorption band of the substance in study, while the other is just off the absorption peak. The ratio between the two received signals (one from each emitted wavelengths) is proportional to the target pollutant concentration [29]. DIAL technology allows three-dimensional mapping of pollutant concentrations in a very flexible and versatile way. It is many times used for mapping pollutant concentration in urban settings. Its main drawbacks are the fact that it is limited to a number of components and that DIAL signals are hard to analyze and can be contaminated by parasite chemical compounds, which decrease the system's sensitivity to the intended pollutants. Finally, we reach the most important open path monitoring technology in this thesis, DOAS, which will be introduced in the next section, with much more detail.

3.2 DOAS

Differential Optical Absorption Spectroscopy is a well established absorption technique that is widely used in the field of atmospheric studies [27]. In this section, I present a short introduction to the field, extracted from [31], an article we have published in 2017, marking the conclusion of the initial studies for this PhD thesis.

There are two main families of DOAS assemblies, with different goals and capabilities:

- Active systems, of which a simple illustration is presented in Fig. 34, are characterized by relying on an artificial light source for their measurements. A spectrometer at the end of the light path performs spectroscopic detection. Active
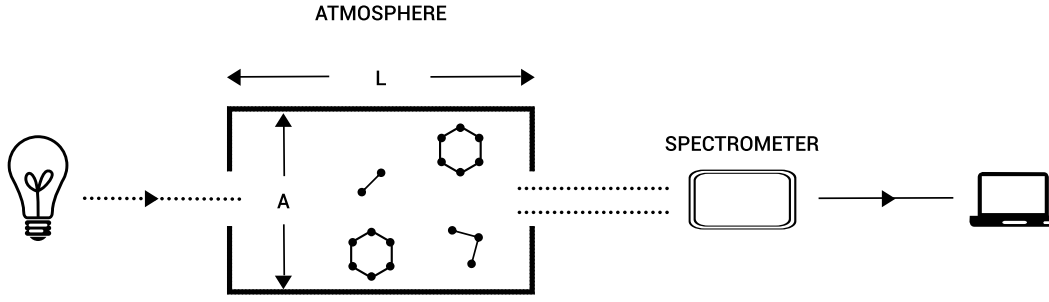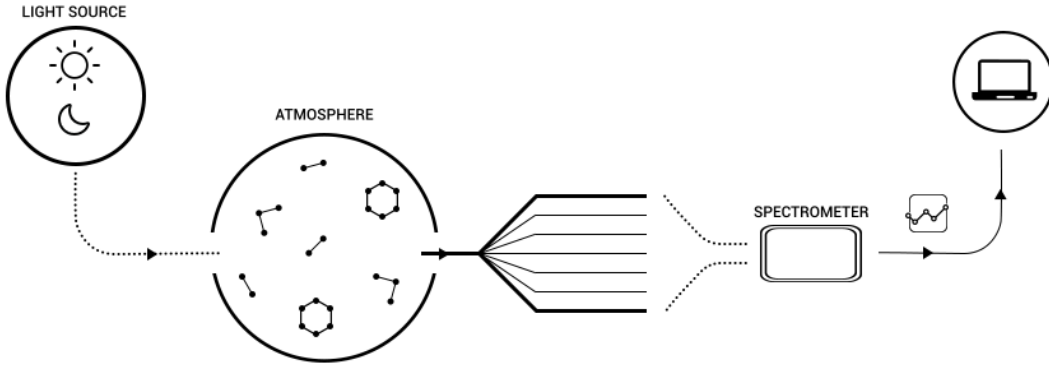
Figure 34: Active DOAS schematic.

Figure 35: Passive DOAS schematic.

DOAS techniques are very similar to traditional in-lab absorption spectroscopy techniques [27];

- Passive DOAS techniques, illustrated in Fig. 35, use natural light sources, such as the Sun and the moon, in their measurement process. An optical system is pointed in certain elevation and azimuth angles and sends the captured light into a spectrometer, connected to a computer. The system returns the total value of the light absorption in its path [23, 27].

DOAS itself is based on Lambert–Beer's law, which can be written as [27]

$$I(\lambda) = I_0(\lambda) \cdot \exp(-\sigma(\lambda) \cdot c \cdot L) \,, \tag{3.1}$$

Where λ is the wavelength of the emitted light; $I(\lambda)$ is the light intensity as measured by the system; $I_0(\lambda)$ is the intensity of the light as emitted by the source; and $\sigma(\lambda)$ is the absorption cross section of absorber, which is wavelength dependent; c is the concentration of the absorber we want to measure.

This law allows the definition of optical thickness (τ) [27]:

$$\tau(\lambda) = \ln\left(\frac{I_0(\lambda)}{I(\lambda)}\right) = \sigma(\lambda) \cdot c \cdot L. \tag{3.2}$$

In a laboratory setting, Eq. (3.1) or (3.2) can be used to directly calculate an absorber's concentration, provided there is knowledge of its cross section. In the open

atmosphere, however, absorption spectroscopy techniques are far more complex. On one hand, $I_0(\lambda)$ is not accessible since we measure from inside the medium we want to measure. On the other hand, there are several environmental and instrumental effects that influence measurement results. These effects include the following [27].

- Rayleigh scattering is due to small molecules present in the atmosphere and is heavily influenced by wavelength (hence the blue colour of the sky).

- Mie scattering is caused by particles and larger molecules suspended in the atmosphere and is not very dependent on the wavelength (hence the white colour of clouds).

- Instrumental and turbulence effects are the instrument's transmissivity and atmospheric turbulence in the optical path also limit light intensity.

In addition, we also have to take into account that, in the atmosphere, there are a number of trace gases that interfere with passing light.

Another aspect worth mentioning is that our device is never pointed directly at the light source (the Sun) but always processes light that has been scattered at some unknown point in the optical path. This means that the light that reaches our detector is only the scattered fraction of the sunlight, depending on the system's position and geometry, as well as wavelength.

The expansion of Lambert–Beer's equation to include all these effects results in Eq. (3.3).

$$
\begin{aligned}
I(\lambda) = {} & I_0(\lambda) \cdot A(\lambda, \ldots) \cdot S(\lambda) \\
& \cdot \exp\left[-\int \left[\left(\sum_i \sigma_i(\lambda, s) \cdot c_i(s) \right) + \epsilon_{\mathrm{M}}(\lambda, s) \right. \right. \\
& \left. \left. + \epsilon_{\mathrm{R}}(\lambda, s) \right] \mathrm{d}s \right],
\end{aligned} \tag{3.3}
$$

Where $A(\lambda, \ldots)$ is the fraction of scattered light that reaches the device, $S(\lambda)$ represents instrumental and turbulence effects, $\sigma_i(\lambda, s)$ is the absorption cross section of absorber i, c_i is the concentration of absorber i, $\epsilon_{\mathrm{R}}(\lambda)$ represents Rayleigh's extinction coefficient and $\epsilon_{\mathrm{M}}(\lambda)$ represents Mie's extinction coefficient.

The interest of this equation lies within the retrieval of c_i, a given absorber's concentration. Since the integral is taken along the total atmospheric path of the measured photons, and considering that their cross sections do not vary significantly in atmospheric conditions, it is possible to define the concept of slant column, which is of great importance [23].

$$
\mathrm{SC}_i = \int c_i(s)\mathrm{d}s \tag{3.4}
$$

This quantity, as Eq. (3.4) shows, equals the integral of an individual absorber's concentration along the atmospheric optical path of relevance.

Now, without knowledge of $I_0(\lambda)$, these equations cannot give us absolute concentration values. We can, however, use another scattered light spectrum as reference in Eq. (3.2). Instead of absolute densities, this will yield relative changes in the atmosphere. We thus arrive at Eq. (3.5).

$$
\begin{aligned}
\ln\left(\frac{I_{\text{ref}}}{I}(\lambda)\right) = {} & \ln\left(\frac{A_{\text{ref}}}{A}(\lambda,\dots)\right) + \ln\left(\frac{S_{\text{ref}}}{S}(\lambda)\right) \\
& + \sum_i (\sigma_i(\lambda) \cdot \Delta\text{SC}_i(\lambda)) + \Delta\tau_{\text{M}}(\lambda) \\
& + \Delta\tau_{\text{R}}(\lambda),
\end{aligned}
\tag{3.5}
$$

Where ΔSC_i is the relative slant column of absorber i; $\Delta\tau_{\text{M}}$ is the relative Mie scattering term, integrated to its optical thickness; and $\Delta\tau_{\text{R}}$ is the relative Rayleigh scattering term, integrated to its optical thickness.

This is where the principle of DOAS is applied. Instrument features, scattering and other atmospheric effects have broad absorption spectral profiles, which vary slowly with wavelength. Several trace absorbers have narrow and rapidly varying spectral signatures in at least a small section of the spectrum. By using Eq. (3.6), we can separate these contributions [8].

$$
\sigma(\lambda) = \sigma'(\lambda) + \sigma_0(\lambda)
\tag{3.6}
$$

Here, the broad part of the optical thickness ($\sigma_0(\lambda)$) can be separated from the narrow part ($\sigma'(\lambda)$ – differential) by approximating it by a low-order polynomial, resulting in Eq. (3.7).

$$
\ln\left(\frac{I_{\text{ref}}}{I}(\lambda)\right) = \sum_{i=1}^{n} \sigma_i{}'(\lambda) \cdot \Delta\text{SC}_i + \sum_{j=0}^{m} a_j \cdot \lambda^j,
\tag{3.7}
$$

Where $\sum_{i=1}^{n} \sigma_i{}'(\lambda) \cdot \Delta SC_i$ is the differential part (narrowband, rapidly varying with wavelength) and $\sum_{j=0}^{m} a_j \cdot \lambda^j$ is a low-order polynomial, used to remove the broadband spectral features resulting from atmospheric and instrumental phenomena.

In practice, the mathematical solving of Eq. (3.7) is not enough since it does not account for the Ring effect or the non-linearities that result from stray light and wavelength shift in measured and cross-section spectra.

The Ring effect is a consequence of rotational Raman scattering: molecules in the atmosphere do not absorb photons in a purely elastic (Rayleigh scattering) fashion. A small portion of the light–matter interaction is in fact inelastic [3, 23]. This changes the light source frequencies as seen from the detector. This phenomenon was first noticed by Grainger and Ring in 1962. At the time, they noticed that the well-known

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Fraunhofer lines would slightly change when one observed them by using moonlight instead of scattered daylight [14].

From the occurrence of these phenomena, it results that the mathematical procedure for DOAS measurements consists in solving a linear and a non-linear problem. The linear problem is solved by writing Eq. (3.7) in its matrix form:

$$\tau = \mathbf{A} \cdot X. \tag{3.8}$$

$\mathbf{A}$ is an $m \times n$ matrix, with its columns being the differential cross sections $\sigma_i'(\lambda)$ and the wavelength powers taking the polynomial $P(\lambda) = \sum_{j=0}^{m} a_j \cdot \lambda^j$ into account. Since the number of lines in A is much larger than the number of columns, the system is overdetermined and, in this case, we must use methods to numerically approximate a solution. It is common to use the least-squares approach, in which the best solution is the one that minimises $\chi^2 = [\tau - A \cdot X] \cdot [\tau - A \cdot X]^T$.

While the Ring effect is treated as a pseudo-absorber, a synthetically produced [6] cross section that is fitted just like any other absorber, non-linearities are addressed by applying Levenberg–Marquardt's approach to non-linear fitting problems to Eq. (3.9) [23, 28]:

$$\ln \left(\frac{I_{\text{ref}}(\lambda)}{I(\lambda + \text{shift}) + \text{offset}} \right) = \sum_{i=1}^{n} \sigma_i'(\lambda) \cdot \Delta\text{SC}_i$$
$$+ \sum_{j=0}^{m} a_j \cdot \lambda^j, \tag{3.9}$$

Where shift and offset, which represent spectral wavelength shifts and stray light offsets, respectively, are responsible for the non-linear character of the problem.

3.3 Tomographic algorithms and reconstruction techniques

3.3.1 Introduction

Tomography is the cross-sectional imaging of an object through the use of transmitted or reflected waves, captured by the object exposure to the waves from a set of known angles. It has many different applications in science, industry, and most prominently, medicine. Since the invention of the Computed Tomography (CT) machine in 1972, by Hounsfield [15], tomographic imaging techniques have had a revolutionary impact, allowing doctors to see inside their patients, without having to subject them to more invasive procedures [19].

Mathematical basis for tomography were set by Johannes Radon in 1917. At the time, he postulated that it is possible to represent a function written in $\mathbb{R}$ in the space

of straight lines, $\mathbb{L}$ through the function's line integrals. A line integral is an integral in which the function that is being integrated is evaluated along a curved path, a line. In the tomographic case, these line integrals represent a measurement on a ray that traverses the Region Of Interest (ROI). Each set of line integrals, characterized by an incidence angle, is called a projection (see Figure 36). To perform a tomographic reconstruction, the machine must take many projections around the object. To the set of projections arranged in matrix form by detector and projection angle, we call sinogram. All reconstruction methods, analytical and iterative, revolve around going from reality to sinogram to image [4, 9, 16–19].

Figure 36: A schematic representation of a projection acquisition. In this image, taken from [17], the clear line that comes down at a diagonal angle is a projection.

There are two broad algorithm families when it comes to tomographic reconstruction, regarding the physics of the problem. The problem can involve either non-diffracting sources (light travels in straight lines), such as the X-Rays in a conventional CT exam; or diffracting sources, such as micro-waves or ultrasound in more research-oriented applications [19]. In this document, I will not address the latter family, since I will not be applying them in my work. In the next few paragraphs, I will discuss the first family of algorithms, and describe how an image can be reconstructed from an object's projections when the radiation source is non-diffracting.

Let's consider the case in which we deal with a single ray of solar light entering the atmosphere at a given point. Since the atmosphere contains numerous absorbents and comparable atmospheric effects, the ray changes from the point where it enters the atmosphere to the point at which it is measured by a detector. Total absorption will depend on the pollutant species, their cross-section and their concentration, since it obeys Lambert-Beer's law. Looking from another angle, this absorption is also the line integral that we will use to reconstruct our image. With DOAS, it is possible to

measure several pollutants at the same time, but for simplicity (and since it is one of the most studied compounds in the field), let's consider that the single pollutant in our atmospheric mixture is NO_2.

3.3.2 Initial Considerations

The problem of tomographic reconstruction can be approached in a number of ways, depending mostly on the authors. In my literary search, I have found that Kak and Slaney [19] have certainly explained this problem in one of the clearer ways available. Therefore, I shall base the rest of my presentation in their writings, and complement with other authors' notes wherever necessary.

Considering the coordinate system displayed in Figure 37. In this schematic, the object is represented by the function $f(x, y)$. The (θ, t) parameters can be used to define any line in this schematic. Line AB in particular can be written:

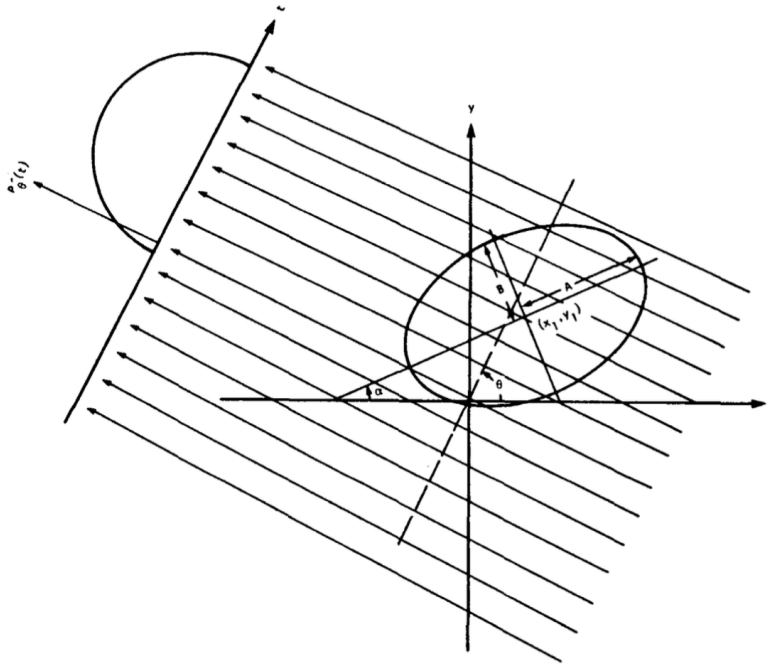$$x \cdot \cos(\theta) + y \cdot \sin(\theta) = t \tag{3.10}$$

Figure 37: Schematic representation for coordinate setting.

And if we were to write a line integral along this line, it would look like Equation 3.11, the Radon transform of function $f(x, y)$:

$$P_\theta(t) = \int_{-\infty}^{\infty} f(x, y) \cdot \delta(x \cdot \cos(\theta) + y \cdot \sin(\theta) - t) dx dy \tag{3.11}$$

Where δ, the delta function, is defined in Equation 3.12.

$$\delta(\phi) = \begin{cases} 1, & \phi = 0 \\ 0, & otherwise \end{cases} \tag{3.12}$$

As I have mentioned previously, a projection is a set of line integrals such as $P_\theta(t)$. Geometry plays a very important role in how the integrals are written and solved for reconstruction. The simplest case is the one where the set is acquired in a row, describing what is called a parallel geometry. Another more complex case is when a single point source is used as origin for all rays, forming a fan. This is called a fanbeam array. There are other possible geometries, but they fall out of the scope of this work and will therefore not be addressed any further.

3.3.3 The Fourier Slice Theorem

The Fourier Slice Theorem (FST) is the most important component of the most important algorithm in tomographic inversion, the Filtered BackProjection algorithm (FBP). FST is based on the equality relation between the two-dimensional Fourier Transform (FT) of the object function and the one-dimensional FT of the object's projection at an angle θ. Let's start by writing the 2D FT for the object function, Equation 3.13, and the 1D FT of projection P_θ, in Equation 3.14.

$$F(u, v) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x, y) \cdot \exp\left[-j2\pi(ux + vy)\right] dx dy \tag{3.13}$$

$$S_\theta(\omega) = \int_{-\infty}^{\infty} P_\theta \cdot \exp\left[-j2\pi\omega t\right] \tag{3.14}$$

For simplicity, let's consider the 2D FT at the line defined by $v = 0$ in the frequency domain. We rewrite the 2D FT integral as:

$$F(u, 0) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x, y) \cdot \exp\left[-j2\pi\omega ux\right] dx dy \tag{3.15}$$

Notice that y is not present in the phase factor of the FT expression anymore, and this means we can rearrange the integral as:

$$F(u, 0) = \int_{-\infty}^{\infty} \left[\int_{-\infty}^{\infty} \mathbf{f(x, y) dy}\right] \cdot \exp\left[-j2\pi\omega ux\right] dx \tag{3.16}$$

Now, the **bold** part of Equation 3.16 is similar to Equation 3.11. It is precisely that equation, considering $\theta = 0$ and a constant value of x, as in Equation 3.17.

$$P_{\theta=0}(x) = \int_{-\infty}^{\infty} f(x, y) dy \tag{3.17}$$

This in turn can be substituted in Equation 3.16, finally arriving at:

$$F(u, 0) = \int_{-\infty}^{\infty} P_{\theta=0}(x) \cdot \exp\left[-j2\pi ux\right] dx \tag{3.18}$$

And this is the one-dimensional FT for the projection at angle $\theta = 0$. Finally, the enunciation of the Fourier Slice Theorem:

> **The Fourier Transform of a parallel projection of an image** $f(x, y)$ **taken at angle** θ **gives a slice of the two-dimensional Fourier Transform,** $F(u, v)$**, subtending an angle** θ **with the** u-**axis (see Figure 38)**

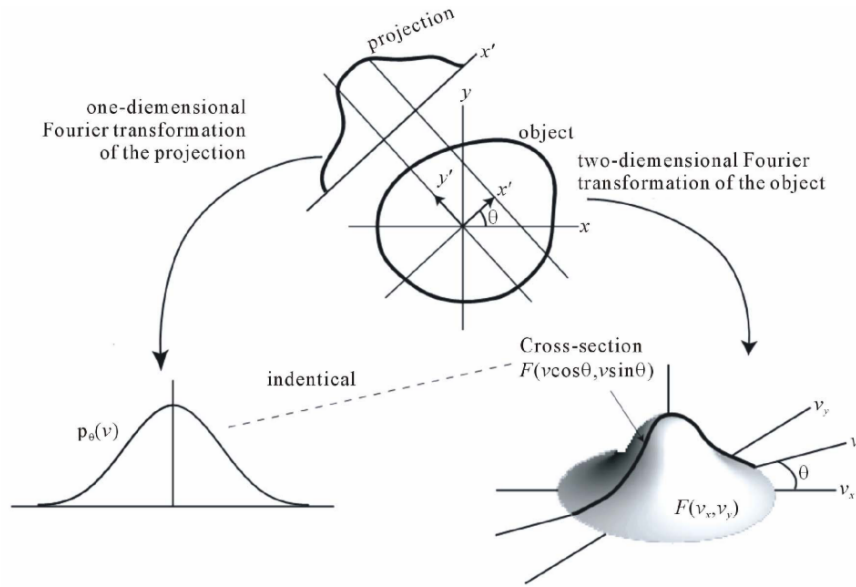

Figure 38: The FST, a schematic representation.

3.3.4   The Filtered BackProjection Algorithm

3.3.4.1   The rationale for FBP

If one takes the FST into account, the idea behind the FBP seems to appear almost naturally. Say one has a single projection and its Fourier transform. From the FST, this projection is the same as the object's two-dimensional FT in a single line. A crude reconstruction of the original object would result if someone were to place this projection in its right place in the Fourier domain and then perform a two-dimensional IFT, while assuming every other projection to be 0. The result, in the image space, would be as if someone had smeared the object in the projections direction.

What is really needed for a correct reconstruction is to do this many times, with many projections. This brings a problem with the method: smearing the object in all directions will clearly produce a wrong *accumulation* in the center of the image, since every projection passes through the middle (remember we are still talking about parallel geometry projections) and are summed on top of each other, but on the outer edges, this does not occur. If one does not address this, the image intensity levels

in the reconstructed image will be severely overestimated in the center and underestimated in the edges (due to normalization). The solution is conceptually easy: we multiply the Fourier transform by a weighting filter proportional to its frequency (ω) and that encompasses its relevance in the global scheme of projections. If there are K projections, then it is adequate for this value to be $\frac{2\pi|\omega|}{K}$. As an algorithm, FBP can be written as in Algorithm 1.

Algorithm 1 The Filtered BackProjection Algorithm

---

    for all $\theta, \theta \in \left\{0..180, \frac{180}{K}\right\}$ **do**
        Measure projection $P_\theta(t)$;
        FT($P_\theta(t)$), rendering $S_\theta(\omega)$
        Multiply by $\frac{2\pi|\omega|}{K}$;
        Sum the IFT of the result in the image space.
    end for

3.3.4.2 Fan Projections Reconstruction

Parallel projections, in which the object is scanned linearly from multiple directions, have the advantage of having a relatively simple reconstruction scheme. However, they usually result in acquisition times which are in the order of minutes. A faster way of collecting the data is one where all radiation emanates from a single point-source, which rotates around the target object (as well as the detectors). There are two types of fan beam projections: equiangular and equally spaced. In this project, I have only worked with equiangular processes, so I will not include an explanation for equally spaced fan beam projections. The reader may find this well described (much better than I would be able to) in [19] and [18].

Consider Figure 39. If our projection data were acquired through a parallel ray geometry, we would be able to say that ray SA belonged to a projection $P_\theta(t)$, in which θ and t would be written:

$$\theta = \beta + \gamma \quad \text{and} \quad t = D \cdot \sin \gamma \tag{3.19}$$

In Equation 3.19, D is the distance between the source S and the origin O; γ is the angle of a ray within a fan and β is the angle that the source S makes with a reference axis.

3.4 DOAS tomography

During the course of my PhD, I attended a course in the Computer Science Department of this Faculty called "Advanced Software Development". One of the assignments of this course was to write a Systematic Mapping Study (SMS) on this topic. This article is included in this document as an appendix (see A), and should be more than sufficient
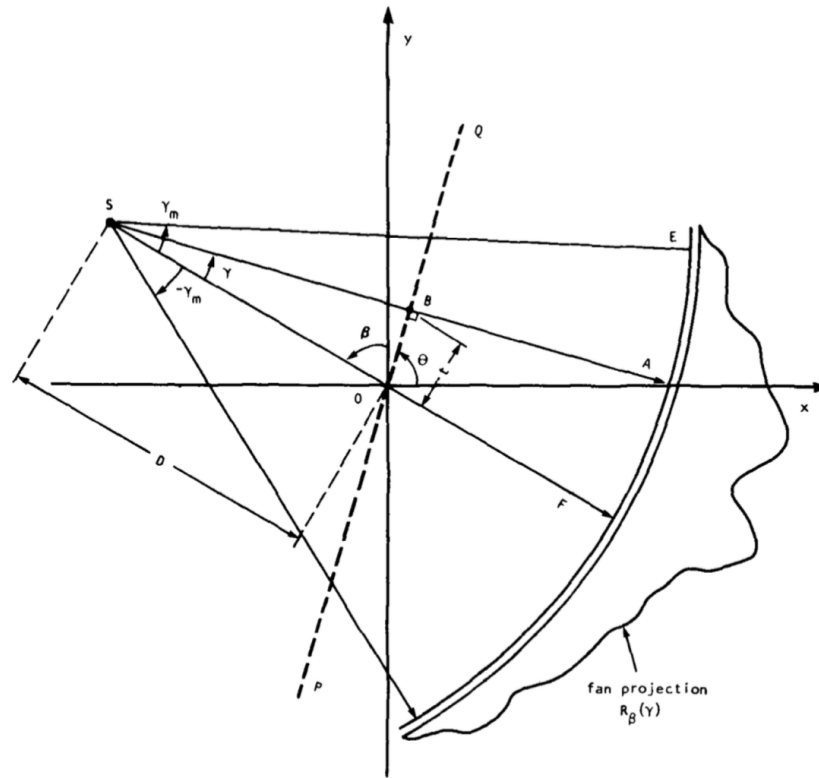
Figure 39: Schematic representation of an equiangular fan beam projection, taken from [19].

for detailing the literary scenario for active DOAS tomography. Passive DOAS systems, such as the ones that are frequently used in volcanology, are described in Section 3.4.1.

3.4.1 Passive DOAS tomography for volcanic plume studies

Research Methodology

4.1   Aimed contribution

This work aims to answer its main RQ by following and pursuing the proposed hypothesis (see Section 2.3). In doing so, I will contribute with a commercially viable (from a technical perspective) atmospheric monitoring system based on DOAS, capable of not only measuring pollutant contamination but also mapping their concentration in a given geographic region. This will generate several intermediate steps, which are themselves smaller contributions:

The first intermediate step will be the development of a tomographic strategy. This will of course include the selection of a sampling geometry (consider the ones presented in Section 3.3), but also the positioning of "sources and sensors" within the selected geometry. Since the system is designed to be a passive DOAS device (see Section 3.2), careful consideration must be taken in this respect. Spectral acquisition must be done in a way that allows tomographic reconstruction, but also respecting limitations and particularities that come from working with solar light. This step corresponds to answering the first secondary Research Question (see Table 22).

The next step will be to write a simulation tool for the tomographic procedure. The idea is for this tool to encompass the acquisition strategy that was defined in the previous step, in order to replicate the whole measurement process and then perform the reconstruction using one or more algorithms. The simulation tool has several functions. For one, it allows the fine-tuning of the approaches without having to expend any resources in purchasing material. Besides this, it also gives gives researchers the chance to experiment with different algorithms. The routine will be divided into two modules. The first module computes the projections for a given phantom, and the second performs the reconstruction with the projection data. The point is that one can write a tomographic reconstruction routine and plug it to the projection computation module, without any interference from one to the other.

Finally we reach the instrumentation definition phase. In this stage, I will have to select the optical components necessary to build this system, including telescope,

spectrometer and all the connection components. In order to maintain this system as small as possible, I will try to avoid using optical fibers, thus minimizing energy loss between telescope and spectrometer. In this stage, I will also have to design a mechanical support that allows a drone to be equipped with the optical system, respecting all positioning and pointing requirements that such a device must entail.

4.2   Detailed work plan and scheduling

In this section, I present the working plan for the proposed thesis. The complete work plan is depicted in Figure 41. It includes the 6 tasks, which take place in a period of 4 years of research activities and scientific writing. The order in which the tasks are performed is somewhat flexible (one could easily program the trajectory (task 5) before conducting the experiments (task 3)), but the presented sequence is the one that allows the best possible compromise between scientific results and project accomplishment, taking into account the hypothesis presented in Section 2.3.
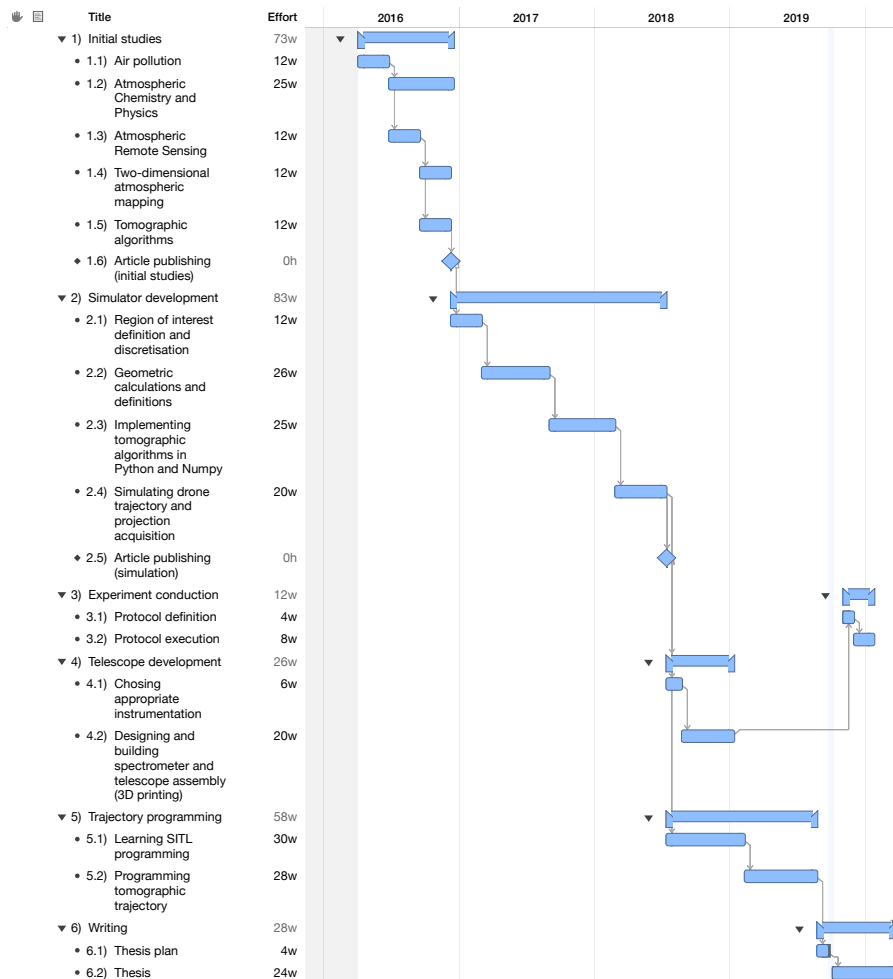

Figure 41: Gantt chart for the proposed thesis. Note the main milestones in 2017 and 2019, which correspond to publication moments.

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Task 1 is an exploratory task, in which I started reading the literature in order to gain a good level of sensitivity to the subjects implied. The task culminated in the writing of [31] in 2017.

Task 2 encompassed the development of a simulation module for the tomographic method with which I intended to retrieve a two-dimensional concentration mapping for certain atmospheric trace gases. The module includes a precise geometric description and error estimation (using Monte Carlo methods) and intends to simulate the formation of a fan-beam measurement using a specific circular trajectory. This task should result in one publication.

The third task concerns experiment conduction. These experiments are designed to verify the acquisition method hypothesis which was simulated in Task 2. Conducting this task shall require developing the experiment protocol as well as its final execution.

The spectral acquisition strategy for the proposed project involves the development of an optical assembly without any fiber-optics. In task 4, I shall choose the optical components for this assembly and design it using 3D CAD methods. Finally, the assembly is to be manufactured: first in a 3D printer and then using traditional metal milling methods.

4.3 Validation methodology

There are several ways to validate a piece of work as the one I present here. It is important to do this in more than one, to ensure not only the validity of the project, but also its relevancy.

Before going any further, I should mention that although my project was conducted as part of the pursuit of a doctoral degree, it was not a traditional PhD, in the sense that it was not done solely in a University setting. The grant that I was awarded by the Portuguese Foundation for Science and Technology was part of a PhD Program for degrees conducted in partnership between FCT NOVA and a group of companies, named NOVA Instrumentation for Health (NOVA I4H). This is relevant as it indicates that there is at least a commercial interest in developing the technology I propose with this thesis (a market validation of sorts). Otherwise, the project would not be viable for the company.

One important way in which I will validate this project is by publishing in significant peer reviewed publications. As illustrated in Figure 41, during the course of my PhD, I intend to publish two relevant articles in Web-of-Science-indexed publications. The first of these was published in 2017, at the end of the preliminary studies stage of the project. The second is currently in the finishing stages of writing and should be submitted before the end of September. Conference-wise, I plan to introduce my work to the scientific community in 2020, by participating in at least one acknowledged conference in the remote sensing or atmospheric monitoring community. Table 41 summarizes the project's dissemination plan.

Table 41: Dissemination plan for the PhD Project.

4.4 Integration with other research activities

As stated in Chapter 1, this project started as a direct evolution from the Forest Fire Finder system, an autonomous forest fire detection device. In 2017, NGNS-IS (the birthplace of FFF) was absorber by the Compta group, and FFF became Bee2Fire. As an extension to the Bee2Fire, this project is integrated in Compta's research efforts, namely in the remote sensing and artificial intelligence department.

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Bibliography

[1] M. L. Bell, D. L. Davis, and T. Fletcher. "A retrospective assessment of mortality from the london smog episode of 1952: The role of influenza and pollution." In: *Urban Ecology: An International Perspective on the Interaction Between Humans and Nature* 6.1 (2008), pp. 263–268. DOI: 10.1007/978-0-387-73412-5_15.

[2] G. P. Bishop, J. L. E. Flack, and M. Campbell. *Sensor Systems for Environmental Monitoring, Volume 2*. 1996. ISBN: 9789401065337.

[3] R. T. Brinkmann. "Rotational Raman scattering in planetary atmospheres." In: *Astrophys J* 154 (1968), pp. 1087–1093. ISSN: 0004-637X. DOI: 10.1086/149827.

[4] P. P. Bruyant. "Analytic and iterative reconstruction algorithms in SPECT." In: *Journal of nuclear medicine : official publication, Society of Nuclear Medicine* 43.10 (2002), pp. 1343–58. ISSN: 0161-5505. URL: http://jnm.snmjournals.org/cgi/content/abstract/43/10/1343%7B%5C%%7D5Cnhttp://jnm.snmjournals.org/cgi/content/full/43/10/1343%7B%5C%%7D5Cnhttp://www.ncbi.nlm.nih.gov/pubmed/12368373.

[5] M. Carugno, D. Consonni, G. Randi, D. Catelan, L. Grisotto, P. A. Bertazzi, A. Biggeri, and M. Baccini. "Air pollution exposure, cause-specific deaths and hospitalizations in a highly polluted Italian region." In: *Environmental Research* 147 (May 2016), pp. 415–424. ISSN: 00139351. DOI: 10.1016/j.envres.2016.03.003. URL: https://linkinghub.elsevier.com/retrieve/pii/S0013935116300834.

[6] K. V. Chance and R. J. D. Spurr. "Ring effect studies: Rayleigh scattering, including molecular parameters for rotational Raman scattering, and the Fraunhofer spectrum." In: *Applied Optics* 36.21 (July 1997), p. 5224. ISSN: 0003-6935. DOI: 10.1364/AO.36.005224. URL: https://www.osapublishing.org/abstract.cfm?URI=ao-36-21-5224.

[7] A. G. Clark. *Industrial Air Pollution Monitoring*. 1997. ISBN: 9789401071437. DOI: 10.1007/978-94-009-1435-3.

[8] T. Danckaert, C. Fayt, M. Van Roozendael, I. de Smedt, V. Letocart, A. Merlaud, and G. Pinardi. *QDOAS*. 2015. URL: http://uv-vis.aeronomie.be/software/QDOAS/.

[9] M. Defrise, P. E. Kinahan, and C. J. Michel. "4 Image Reconstruction Algorithms in PET * 2D Data Organization." In: (2003), pp. 91–114.

[10] EEA. *Air pollution in Europe 1990–2004*. Tech. rep. 2. European Environment Agency, 2007.

[11] EEA. *Air quality in Europe*. Tech. rep. 28. 2016, p. 83. DOI: doi:10.2800/413142.

[12] EEA. *European Environmental Agency*. 2019. URL: https://www.eea.europa.eu (visited on 09/23/2019).

[13] A. Ghorani-Azam, B. Riahi-Zanjani, and M. Balali-Mood. "Effects of air pollution on human health and practical measures for prevention in Iran." In: *Journal of Research in Medical Sciences* 21.1 (2016), p. 65. ISSN: 1735-1995. DOI: 10.4103/1735-1995.189646. URL: http://www.jmsjournal.net/text.asp?2016/21/1/65/189646.

[14] J. F. GRAINGER and J. RING. "Anomalous Fraunhofer Line Profiles." In: *Nature* 193.4817 (Feb. 1962), pp. 762–762. ISSN: 0028-0836. DOI: 10.1038/193762a0. URL: http://www.nature.com/doifinder/10.1038/193762a0.

[15] R. Gunderman. *Essential Radiology: Clinical Presentation, Pathophysiology, Imaging, 2nd ed.* 2nd ed. Thieme, 2006. ISBN: 9781588900821.

[16] G. T. Herman. "Image Reconstruction From Projections." In: *Real-Time Imaging* 1.1 (1995), pp. 3–18. ISSN: 10772014. DOI: 10.1006/rtim.1995.1002.

[17] G. T. Herman. *Fundamentals of Computerized Tomography*. Advances in Pattern Recognition. London: Springer London, 2009. ISBN: 978-1-85233-617-2. DOI: 10.1007/978-1-84628-723-7. URL: http://link.springer.com/10.1007/978-1-84628-723-7.

[18] G. T. Herman, A. Lent, and S. W. Rowland. "ART: Mathematics and applications. A report on the mathematical foundations and on the applicability to real data of the algebraic reconstruction techniques." In: *Journal of Theoretical Biology* 42.1 (1973). ISSN: 10958541. DOI: 10.1016/0022-5193(73)90145-8.

[19] A. C. Kak. "Algebraic Reconstruction Algorithms." In: *Computerized Tomographic Imaging*. 2001, pp. 275–296. ISBN: 978-0-89871-494-4. DOI: 10.1137/1.9780898719277.ch7.

[20] M. Kampa and E. Castanas. "Human health effects of air pollution." In: *Environmental Pollution* 151.2 (Jan. 2008), pp. 362–367. ISSN: 02697491. DOI: 10.1016/j.envpol.2007.06.012. URL: https://linkinghub.elsevier.com/retrieve/pii/S0269749107002849.

[21] V. Kollanus, P. Tiittanen, J. V. Niemi, and T. Lanki. "Effects of long-range transported air pollution from vegetation fires on daily mortality and hospital admissions in the Helsinki metropolitan area, Finland." In: *Environmental Research* 151 (Nov. 2016), pp. 351–358. ISSN: 00139351. DOI: 10.1016/j.envres.2016.08.003. URL: https://linkinghub.elsevier.com/retrieve/pii/S001393511630353X.

[22] G. M. Lovett, T. H. Tear, D. C. Evers, S. E. Findlay, B. J. Cosby, J. K. Dunscomb, C. T. Driscoll, and K. C. Weathers. "Effects of Air Pollution on Ecosystems and Biological Diversity in the Eastern United States." In: *Annals of the New York Academy of Sciences* 1162.1 (Apr. 2009), pp. 99–135. ISSN: 00778923. DOI: 10.1111/j.1749-6632.2009.04153.x. URL: http://doi.wiley.com/10.1111/j.1749-6632.2009.04153.x.

[23] A. Merlaud. *Development and use of compact instruments for tropospheric investigations based on optical spectroscopy from mobile platforms*. Louvain: Presses Universitaires de Louvain, 2013. ISBN: 978-2-87558-128-0. URL: http://books.google.com/books?hl=en%7B%5C%7Dlr=%7B%5C%7Did=inXVSyR82zwC%7B%5C%7Doi=fnd%7B%5C%7Dpg=PR3%7B%5C%7Ddq=Development+and+use+of+compact+instruments+for+tropospheric+investigations+based+on+optical+spectroscopy+from+mobile+platforms+sciences%7B%5C%7Dots=VdebeDBQMc%7B%5C%7Dsig=4GOeVEvthJXuqd8WI3IWjjVXuXc.

[24] G. E. Nilsson. *Respiratory Physiology of Vertebrates Life with and without oxygen*. Ed. by G. E. Nilsson. Oslo, Norway: Cambridge University Press, 2010. ISBN: 9780521878548.

[25] M. Office. *The Great Smog of 1952*. 2019. URL: https://www.metoffice.gov.uk/weather/learn-about/weather/case-studies/great-smog (visited on 09/23/2019).

[26] D. G. Penney. *Carbon Monoxide Poisoning*. CRC Press.

[27] U. Platt and J. Stutz. *Differential Optical Absorption Spectroscopy*. Heidelberg, Germany: Springer, 2007. ISBN: 9783540211938.

[28] W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery. *Numerical Recipes: The Art of Scientific Computing*. 3rd Editio. 2007. ISBN: 9788578110796. arXiv: arXiv:1011.1669v3.

[29] G. Stewart and M. Campbell. *Sensor Systems for Environmental Monitoring, Volume 1*. 1996. ISBN: 9789401072021. DOI: 10.1007/978-94-009-1571-8.

[30] The European Union. *Eurobarometer 468*. Tech. rep. Brussels: EU, 2017. URL: https://data.europa.eu/euodp/en/data/dataset/S2156%7B%5C_%7D88%7B%5C_%7D1%7B%5C_%7D468%7B%5C_%7DENG.

[31] R. Valente de Almeida and P. Vieira. "Forest Fire Finder – DOAS application to long-range forest fire detection." In: *Atmospheric Measurement Techniques* 10.6 (June 2017), pp. 2299–2311. ISSN: 1867-8548. DOI: 10.5194/amt-10-2299-2017. URL: https://www.atmos-meas-tech.net/10/2299/2017/.

[32] D. Vallero. *Fundamentals of air pollution*. 5th ed. Academic Press, 2014. ISBN: 9780124017337.

[33] P. Vieira and J. Matos. *SYSTEM FOR AUTOMATIC DETECTION OF FOREST FIRES THROUGHOPTC SPECTROSCOPY*. 2008.

[34] P. Vieira, J. Matos, and M. Mendes. *Sistema para a detecção automática de incêndios florestais por espectroscopia óptica*. 2007.

[35] World Health Organisation Europe. "Health Aspects of Air Pollution Results from the WHO Project "Systematic Review of Health Aspects of Air Pollution in Europe"." In: *World Health* (2004), p. 30.

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