NOVA SCHOOL OF
SCIENCE & TECHNOLOGY

DEPARTMENT
OF PHYSICS

DEVELOPMENT OF A TOMOGRAPHIC ATMOSPHERIC MONITORING SYSTEM BASED ON DIFFERENTIAL OPTICAL ABSORPTION SPECTROSCOPY

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BIOMEDICAL ENGINEERING

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To my parents.

Acknowledgements

First and foremost, I need to thank FCT NOVA and FutureCompta, for having me and letting me work with them and develop this thesis. In addition, I want to acknowledge the contribution from the Portugues Foundation for Science and Technology, who funded this work through the NOVA I4H doctoral programme, grant PDE/BDE/114549/2016.

I would also like to thank my advisor, Prof. Pedro Vieira, for all the support he has given me, on many levels and throughout the years.

To my friends, old and new, I extend my utmost gratitude for helping me tilt my head back and laugh once in a while.

Finally, to my family, without whom I would have never been able to do anything, much less something as significant as what I present in this dissertation.

“I know the pieces fit, ’cause I watched them fall away. ”
(TOOL - Schism)

“Silenzio, Bruno! ” (Luca Paguro)

Abstract

The aim of this thesis is to describe the design and development of a proof of concept for a commercially viable large are atmospheric analysis tool, for use in trace gas concentration mapping and quantification.

Atmospheric monitoring is a very well researched field, with dozens of available analytical systems and subsystems. However, current systems require a very important compromise between spatial and operational complexity. We address this issue asking how we could integrate the Differential Optical Absorption Spectroscopy (DOAS) atmospheric analysis technique in a Unmanned Aerial Vehicle (UAV) with tomographic capabilities.

Using a two-part methodology, I proposed two hypothesis for proving the possibility of a miniaturised tomographic system, both related to how the spectroscopic data is acquired. The first hypothesis addresses the projection forming aspect of the acquisition, its matrix assembly and the resolution of the consequent equations. This hypothesis was confirmed theoretically by the development of a simulation platform for the reconstruction of a trace gas concentration mapping.

The second hypothesis deals with the way in which data is collected in spectroscopic terms. I proposed that with currently available equipment, it should be possible to leverage a consequence of the Beer-Lambert law to produce molecular density fields for trace gases using passive DOAS. This hypothesis was partially confirmed, with definite conclusions being possible only through the use of complex autonomous systems for improved accuracy.

This work has been a very important first step in the establishment of DOAS tomography as a commercially viable solution for atmospheric monitoring, although further studies are required for definite results. Moreover, this thesis has conducted to the development of a DOAS software library for Python that is currently being used in a production environment. Finally, it is important to mention that two journal articles were published from pursuing this work, both in important journals with Impact Factors over 3.0.

Keywords: DOAS, tomography, UAV, drones

Resumo

Era o objectivo deste trabalho descrever o processo de desenho e implementação de uma prova de conceito para um sistema de avaliação atmosférica comercialmente viável, para uso no mapeamento das concentrações de compostos traço na atmosfera.

A avaliação atmosférica é um campo muito estudado, estando no presente momento disponíveis para instalação diversos sistemas e subsistemas com estas capacidades. No entanto, é marcante o compromisso que se verifica entre a resolução espacial e a complexidade operacional destes equipamentos. Nesta tese, desafio este problema e levanto a questão sobre como se poderia desenvolver um sistema com os mesmos fins, mas sem este premente compromisso.

Usando uma metodologia a duas partes, proponho duas hipóteses para comprovar a exequibilidade deste sistema. A primeira diz respeito à formação da matriz tomográfica e à resolução das equações que dela derivam e que formam a imagem que se pretende. Confirmei esta hipótese teoricamente através do desenvolvimento de uma plataforma de simulação para a reconstrução tomográfica de um campo de concentrações fantoma.

A segunda é dirigida a aquisição de dados espectroscópicos. Proponho que com o material presentemente disponível comercialmente, deverá ser possível aproveitar uma consequência da lei de Beer-Lambert para retirar os valores de concentração molecular de gases traço na atmosfera. Foi apenas possível validar esta hipótese parcialmente, sendo que resultados mais conclusivos necessitariam de equipamentos automatizados dos quais não foi possível dispôr.

No final, este trabalho constitui um importante primeiro passo no estabelecimento da técnica de DOAS tomográfico como uma alternativa comercialmente viável para a análise atmosférica. Ademais, o desenvolvimento desta tese levou à escrita de uma biblioteca em Python para análise de dados DOAS actualmente usada em ambiente de produção. Por fim, importa realçar que dos trabalhos realizados no decorrer da tese foram publicados dois artigos em revistas científicas com *Impact Factor* acima de 3.

Palavras-chave: DOAS, tomografia, drones

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Acronyms

ALRI	Acute Lower Respiratory Infections 9
ANS	Autonomic Nervous System 10
AP	Air Pollution ix, x, 1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 18, 19, 20, 21, 22, 23
BAEP	Brainstem Auditory-Evoked Potentials 12
BTU	British Thermal Unit 18
CNS	Central Nervous System 12, 13
CO	Carbon Monoxide 4, 21
CO_2	Carbon Dioxide x, 18, 20
COPD	Chronic Obstructive Pulmonary Disease 9, 12
CVD	Cardiovascular Disease 10
CVM	Cardiovascular Mortality 10
DIAL	Differential Absorption LIDAR 25
DOAS	Differential Optical Absorption Spectroscopy vii, viii, 1, 2, 3, 4, 7, 25
EEA	European Environmental Agency 4, 5, 7, 21
EPA	Environmental Protection Agency (United States) 3, 4
ESCAPE	European Study of Cohorts for Air Pollution Effects 9
FFF	Forest Fire Finder 1, 2
FP7	European Union's Seventh Framework Programme 9
GDP	Gross Domestic Product x, 20, 21
H_2S	Hydrogen Sulfide 15
ICE	Internal Combustion Engine 7, 20, 21
IOT	Internet Of Things 2

LIDAR	Light Detection and Ranging 25
LPG	Liquefied Petroleum Gas 21
NH_3	Ammonia 21
NO	Nitrogen Oxide 7
NO_2	Nitrogen Dioxide xi, 4, 6, 7, 9, 11, 14, 26, 27
NO_X	Nitrogen Oxides 7, 21
O_2	Oxygen 7, 24
O_3	Ozone 4, 5, 7, 11, 14
OP-FTIR	Open Path Fourier Transform Infrared Spectroscopy xi, 25, 26
PAH	Polycyclic Aromatic Hydrocarbons 12
PM	Particulate Matter x, 4, 7, 9, 10, 11, 15, 16, 17, 25
Project ATMOS	ATmosphere MOnitoring System Project 1, 2
PT2020	Portugal2020 1, 2
RQ	Research Question 2
SGA	Small for Gestation Age 11
SO_2	Sulfur Dioxide 4, 6, 11, 14, 15
TDL	Tunable Diode Laser 25
UAV	Unmanned Aerial Vehicle vii
VOC	Volatile Organic Compound 5, 17
WHO	World Health Organization 5

Todo list

1

Background, Motivation and Introduction

1.1 Starting Points

This thesis describes the work that I have done in the past 4 years on the design and development of a miniaturized system for atmospheric monitoring based on optical spectroscopy. The project itself was the major part of the ATmosphere MOnitoring System Project (Project ATMOS), an initiative that was contemplated with European funding through a Portugal2020 (PT2020) initiative and came as a response to the growing weight that AP has in the whole Western World.

The potential impact of AP on human health is amply documented. Numerous papers have, for decades, established many links between air quality and several common ailments like respiratory syndromes and cardiovascular diseases. Similar connections have also been found regarding the probability of gestational malformations and several types of cancer. On a different level, and of perhaps less immediate concern, are the effects that have been observed on ecosystems. Frequently these effects are difficult to predict (and timely mitigate) and in some cases have been known to interfere with people's livelihood. If not addressed, these interferences will certainly hinder economies and limit the quality of life of populations globally. The severity of this problem makes it clear that we need to tackle it intelligently, and this approach requires that we can measure, trace and track AP effectively, which beckons engineers and scientists to create more technology for this specific purpose.

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 DOAS for fire detection, and for that it was patented in 2007 (see [40, 39]). 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 [37].

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 team then started reading about the concept of 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.

In April 2017, NGNS-IS was integrated in the Compta group, one of the oldest IT groups operating in Portugal. Despite its age, this company is one of the main presences in some of the most modern industrial fields, like Internet Of Things (IOT) applications. Project ATMOS's pollutant tracing capabilities made it an almost perfect fit in one of IOT's most resounding niches, the *Smart Cities* trend. Unfortunately, the transition between one company and the other, regardless of the project's adequacy, was anything but smooth. Almost two years later, in the beginning of 2019, engulfed in a sea of endless bureaucracy and ill intent on behalf of the managing governmental authorities (who seemed always more interested in seeing the project fail than anything else), Project ATMOS was terminated and financing was cut.

Obviously, this was a very hard blow to recover from, especially from the perspective of this thesis. After all, most of the work that was planned implied the use of very expensive equipment that was on the verge of being purchased. Since this was not going to be possible, we had to reimagine it. How could the Research Question (RQ) presented in Section 1.2 still be answered when we could not use drones or buy any more telescopes or spectrometers? The point of the thesis thus became to present a modeled proof of concept for the initially proposed system, instead of a minimum viable product.

1.2 Research Questions

This thesis had the defining primary objective of modelling a proof of concept for a spectroscopy-based pollution monitoring system that can be fitted onto a highly mobile platform, such as a drone. The other defining characteristic of the system is that it needs to be able to cover large areas (which could be remote and / or inaccessible) and have a good spatial resolution.

Early in the project's life, the team reached a conceptual milestone: what if it was possible to perform an atmospheric tomographic scan? Preliminary research into the literature indicated this had already been done (focused literature review available in Chapter **??**). This started to systematise our objectives.

- 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.

The main research question was thus formed, and is presented in Table 1.1. From it, four secondary research questions are derived, which are presented in Table 1.2.

Table 1.1: Main research question.

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

Table 1.2: 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?*

1.3 Air Pollution

Daniel Vallero, in his book "Fundamentals of Air Pollution" [38] 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 Environmental Protection Agency (United States) (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 19^{th} century, but the first time it was taken seriously was during the 1952 killer-smog incidents, in London [31]. 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 [3, 28]. 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, which are broadly considered to be some of the first actions to decrease pollution in human societies. Much work has been done, and it has resulted in remarkable progress since the definition of those two policies. We are in fact in a much better place than we were some years or decades ago, but pollution is still a part of everyday reality for the whole of civilization. In the current day and age, both European and American regulatory and surveillance bodies (the European Environmental Agency (EEA) and the EPA, respectively) have identified a group of six *criteria pollutants* that need to be monitored effectively.

1.3.1 Criteria Pollutants

Criteria pollutants are a group of six chemical species, commonly found mixed in air, that constitute a serious hazard for human, animal, and general environment health. These pollutants were defined in 1970, through the Clean Air Act in the United States, but have since been widely adopted. These six pollutants are:

1. Particulate Matter;
2. Ozone;
3. Carbon Monoxide;
4. Sulfur Dioxide;
5. Nitrogen Dioxide;
6. Lead (Pb);

They are collectively addressed as criteria pollutants, solely because environmental agencies around the world have since been using them, and their atmospheric concentrations as criteria for setting standards. Of the 6 criteria pollutants, 4 are of direct importance for this dissertation, as DOAS can be used to measure and quantify them. They are PM, Ozone (O_3), Sulfur Dioxide (SO_2) and NO_2. This section aims to provide a brief presentation of these four species.

1.3.1.1 Particulate Matter

Particles are aggregates of many molecules, that can be similar of different. There are several processes in which particles can be formed, and they can be chemically active or, for instance, act as surfaces on which trace gases may condense. The chemical composition of a particle is immensely variable, and it can even be difficult to determine, since one particle sample (usually collected over a period of some hours) can have thousands of species, namely hydrocarbons. One interesting aspect of PM is that its volume distribution is bimodal, having two clear maxima below 1μm and another

Table 1.3: Main avenues for the formation of ozone in the troposphere.

around 10μm. The reason for this separation is the way in which the particles were formed. Coagulations and condensation tend to form the smaller particles, while the larger peak is comprised mostly of crustal (as in from the Earth's crust) and sea solids, together with some smaller aggregated particles – smaller particles that have adhered onto one another. Figure 1.1 illustrates this bimodal distribution and the responsible formation phenomena.

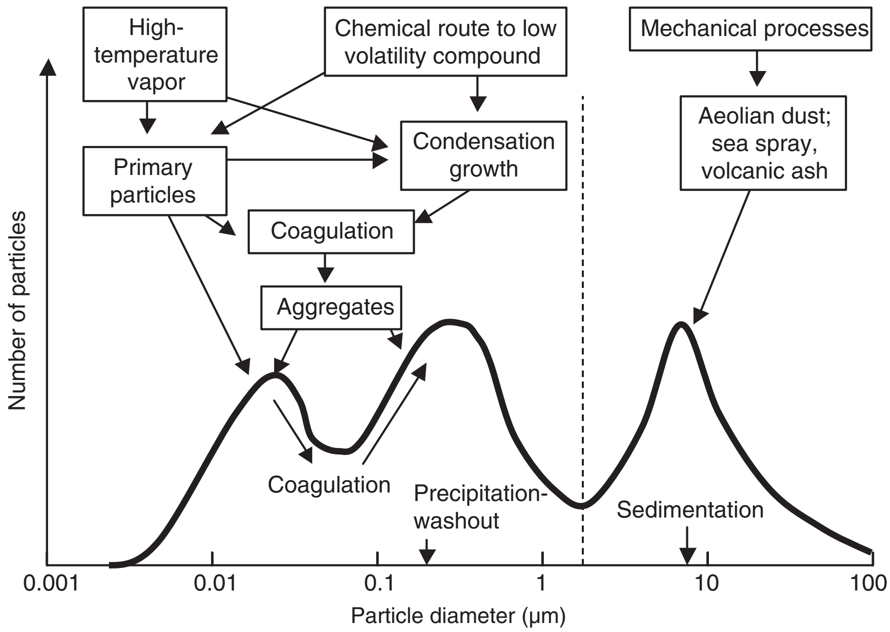

Figure 1.1: Bimodal distribution for particle volume and the phenomena that lead to their formation [38]

1.3.1.2 Tropospheric Ozone

Ozone is one of the most important trace gases in the atmosphere, in functional terms. The O_3 concentration in lower troposphere has had a sharp rise in recent decades, which indicates that this rise is anthropogenic in nature [4]. In the last EEA reports, European concentrations of O_3 have remained approximately stable and just above the World Health Organization (WHO)-set limit for the protection of human life [14, 21]. In both reports, the EEA states that although ozone precursor concentrations have been steadily declining, concentrations for O_3 remain the same, although the amplitude of peak events is shown to be decreasing (see Figure 1.2)

Ozone formation in the lower atmosphere is also interesting. While other pollutants are directly emitted by its sources, O_3 is a secondary pollutant, which means that it is formed through chemical reactions that its precursors endure. With the exception of Volatile Organic Compound (VOC), these precursors are results from human activity. There innumerable pathways for ozone formation. Table 1.3 summarizes the main avenues.

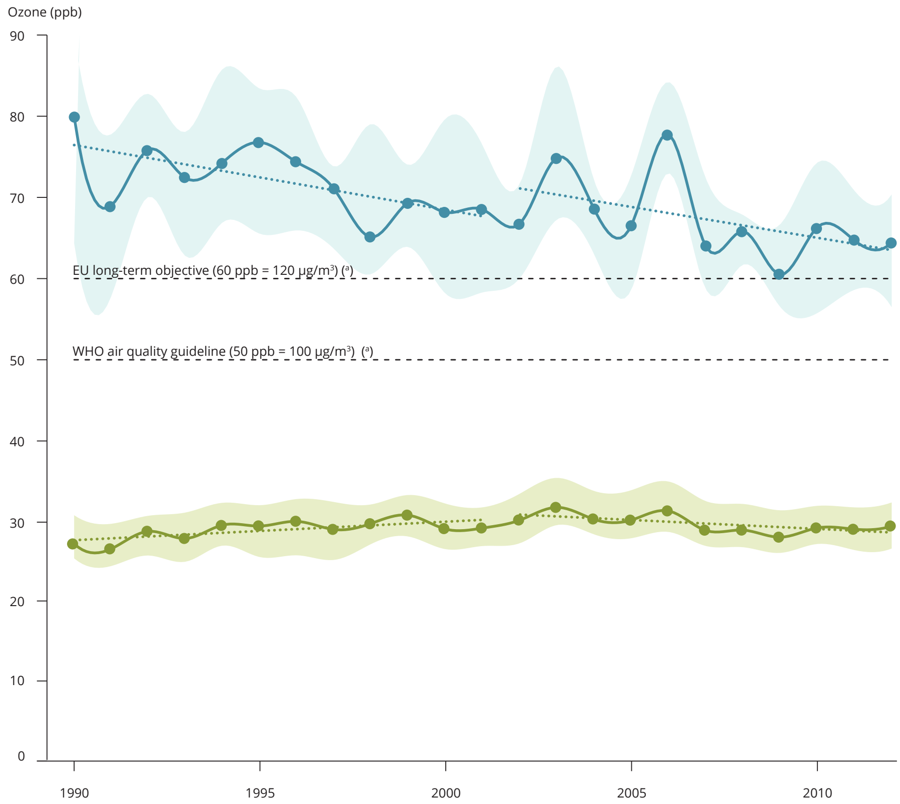

Figure 1.2: Ozone mean and peaks in European rural sites. Peaks are plotted blue, mean is plotted green. Note the decrease in peak concentration and the steadyness of the mean signal.

1.3.1.3 Sulfur Dioxide

Nitrogen, Sulphur, Phosphorous and Potassium are very familiar to those accustomed to dealing with plant life. For plants, these 4 chemicals are. Their life depends on them. However, from an AP point of view, sulphur and nitrogen compounds are common issues and have to be addressed separately. We will deal with NO_2 in Section 1.3.1.4. Sulphur compounds are released into the atmosphere primarily through anthropogenic activities (for instance, diesel-powered engines), although marine biogenic gases represent a significant proportion of the emitted sulphuric species.

These compounds can be released in reduced and oxidised forms, although reduced forms are generally oxidised onto SO_2. SO_2 has many complex atmospheric chemical reactions, but proceeds to the sulphate ion through at least three pathways. If given enough time, sulphur oxidises into SO_4^-, usually forming sulphuric acid. This reacts readily with ammonia in the atmosphere, and produces ammonium sulphates that, together with their precursor sulphuric acid, are readily dissolved in water [4].

1.3.1.4 Nitrogen Dioxide

NO_2 is the most important atmospheric trace gas as far as this thesis is concerned, for reasons that will become clear in Section **??**. Nitrogen oxides are toxic, but that is not the only reason why they are problematic. In fact, they are one of the main precursors of tropospheric ozone, namely through photolysis, as described in Equation 1.1.

$$NO_2 + h\nu \rightarrow NO + OO + O_2 + M \rightarrow O_3 \tag{1.1}$$

M, in the case of Equation 1.1, is any third body that absorbs excess vibration energy and can stabilise the newly formed molecule. But O_3 can go on to react with Nitrogen Oxide (NO) and regenerate NO_2 and Oxygen (O_2), as in Equation 1.2.

$$O_3 + NO \rightarrow NO_2 + O_2 \tag{1.2}$$

Now, these reactions and several others that involve nitrogen species occur whether there is pollution or not, which results in an equilibrium O_3 concentration of 30 ppb. In a polluted atmosphere, say by Internal Combustion Engine (ICE), this balance is destroyed. Fossil fuel combustion increases Nitrogen Oxides (NO_X) concentration, but also concentrations of hydrocarbons through incomplete combustion. This means that in addition to the balanced atmospheric reactions of nitrogen species, we now have to consider the oxidation of these long hydrocarbon chains, which produce NO_2 without destroying O_3, thus upsetting the initial balace.

1.3.2 Air Pollution Effects on Human Health

Arguably, there is no medium in which it is more important to consider AP by its effects than in the human body. However, even this has its caveats. The body's response to any given substance changes with the dose that is administered to it, something which has been known to us for centuries:

> *What is it that is not poison? All things are poison and nothing is without poison. It is the dose alone that makes a thing not poison.*
>
> – Paracelsus

This quote, originally in the writings of one of the fathers of modern medicine, the Swiss Paracelsus, was taken from Patricia Frank's book called *The Dose Makes The Poison* [18] and is one of the core tenets of toxicology even today. There are, however, some substances which do not need anything close to a high dose to cause harm to human health, and in general, atmospheric pollutants fall in that category. According to the EEA, heart disease and stroke are the most common causes of premature death due to Air Pollution. The same organization states that the most prominent atmospheric pollutants in terms of the effects they have on human health are PM, NO_2 and O_3 [14, 13]. In this thesis, I will focus mostly on them, not only because of their health importance, but also because of their spectral nature, which allows us to detect them using DOAS [31]. Of course, a complete description of how AP affects the human body is a colossal task which is well beyond the scope of this thesis. Therefore, I will focus my attention on the more prominent symptoms that are results of these chemicals: respiratory syndromes, cardiovascular diseases, problems during gestation and finally, neurologic consequences of AP.

1.3.2.1 Respiratory effects of Air Pollution

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 [27]. The whole system is in permanent interaction with the atmosphere, and is therefore exposed to all kinds of air pollutants and trace gases, and therefore it is only natural that respiratory effects are among the most direct health complications originating in AP [38].

The region in which a given pollutant is, within the respiratory system (see Figure 1.3), is of great importance. After the air is inhaled through the nose, the air is heated or cooled to body temperature, as well as humidified, in the upper airways. The trachea leads the air into the bronchi, where flow is divided several times before reaching the alveoli, where oxygen is supposed to enter circulation. Since air flows within the different regions of the pulmonary system are completely different, AP is also handled differently among them. Moreover, it is also important to consider that pollutants also vary according to their own physical properties, and pollutant absorption is also a function of this. Particles' absorption depends on their aerodynamic characteristics, as well as soluble fraction and density. Gaseous pollutants are dependent exclusively on their vapor pressure, solubility and density [27, 38].

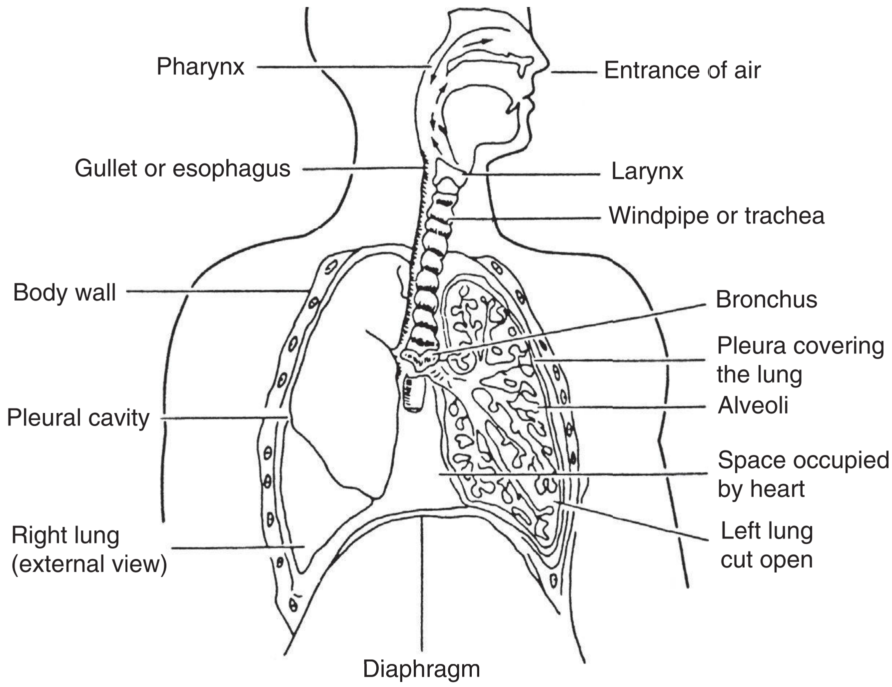

Figure 1.3: Annotated anatomy of the respiratory system [38].

The respiratory system has several (imperfect) mechanisms in place to prevent particles from reaching the blood stream. Larger particles are deposited in the nose, by impaction on the hairs and bends of the nose. Smaller particles are immune to this first barrier, and manage to get to the trachea and bronchi, where they are filtered also by impaction, this time on the walls of the innumerable bifurcations of the bronchial tree. The smallest particles are removed through Brownian motion, which ends up pushing them against the alveolar membrane. Deposited substances are then removed through the action of cilia in the pulmonary system's walls or by coughing, sneezing or blowing one's nose [38].

While the body is quite efficient at filtering out particles from the respiration process, the same cannot be said about gaseous pollutants. Removal of these compounds can only be achieved through absorption, which depends almost exclusively in the gases' solubility. High solubility compounds are absorbed directly in the upper airways (SO_2, for instance), while less soluble gases (such as O_3 and NO_2) are absorbed in the lungs themselves. Irritant gases trigger a variety of responses, in which one can include sneezing, coughing or bronchoconstriction. These gaseous compounds are then diffused through to the bloodstream or the lungs themselves try to convert them into other substances via biochemical processes. In some cases, this attempt to detoxify a pollutant can lead to much more problematic circumstances. For instance, the lung is known to active procarcinogenics, substances that are only carcinogenic after being metabolized in a certain way [38].

Acute symptoms of AP exposure are very varied, and range from mild irritation to complete respiratory failure, depending mostly on level of exposure and individual sensitivity to the chemical compound. One of the most important acute manifestations of AP exposure are encompassed within the Acute Lower Respiratory Infections (ALRI) group. There are several studies in which the relationship between this issue and AP is deducted and explained, mostly in developing countries, and it remains as one of the major causes for infantile death [8, 36]. Children are one of the most affected demographics by AP [14], and one of the chief reasons for this is that the human respiratory system is till developing in this stage of life.

In a 2016 review [20], the authors searched the literature for childhood adverse effects of AP, with a particular focus on respiratory problems. They have found evidence for a number of respiratory complications and diseases that were previously reported in the literature caused or exacerbated by AP. Effects are many, and vary immensely in nature, severity and affected populations. Short term effects, like coughing and wheezing were found for the three types of major pollutant and several others; several papers mention an association between the occurrence of respiratory infections and exposure to AP, namely concerning PM and NO_2. The same review found reports of decreased lung function in children and asthma exacerbation in children due to Air Pollution. Moreover, a person exposed to high levels of AP during childhood are also more likely to develop syndromes like Chronic Obstructive Pulmonary Disease (COPD), and to have exacerbated symptoms of this disease. Finally, and perhaps more concerning, the carcinogenic nature of several of the constituents of AP leads to findings relating the appearance of respiratory cancers to exposure levels during childhood. Many of the conclusions of this review come from a large-scale European effort called European Study of Cohorts for Air Pollution Effects (ESCAPE), that intended to investigate long-term health effects of AP in Europe. ESCAPE was an European Union's Seventh Framework Programme (FP7) initiative that ended in 2014.

1.3.2.2 Air Pollution and cardiovascular issues

After being absorbed by the respiratory system, oxygen is distributed to all cells of the body through the cardiovascular system. Air pollutants, like particles and trace gases, are also capable of penetrating the lung barrier and therefore share the same fate. There are several pathways with which AP and negatively affect the cardiovascular system. The most immediate of which is probably an imbalance in the Autonomic Nervous System (ANS) caused by direct inflammation and oxidative stress in the respiratory system. The second most immediate pathway is systemic inflammation caused by Air Pollution. Finally, soluble AP compounds in the bloodstream also contribute to Cardiovascular Disease (CVD) by increasing inflammation and oxidative stress in the cardiovascular system [7, 38].

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, Cardiovascular Mortality (CVM) has been shown to be intricately connected to AP. In fact, in a 2013 review indicated that an annual increase of $10\mu g/m^3$ in fine PM and NO_2 led to an increase of 11% and 13% respectively in terms of CVM and premature atherosclerosis, in spite of absolute AP concentrations were maintained below the European policy-recommended thresholds. Road traffic exposure studies have reported similar findings, with subjects having increased coronary calcium scores [5].

Arrhythmia is one of the other cardiovascular issues that might be caused by AP. There is still some debate regarding whether or not there is a causal relationship between the two, but there have been several studies in which increased levels of Air Pollution were correlated with arrhythmia-related hospital admissions. Moreover, there seems to be a correlation between low heart rate variability and AP, which is considered a marker for ANS imbalance and an important risk factor for CVM[5].

The risk of stroke is also clearly exacerbated by the presence of increased levels of AP. In fact, it is currently thought that AP is responsible for about 29% of the burden of stroke, globally. Studies have shown that an increase of 5 $\mu g/m^3$ in the annual $PM_{2.5}$ concentration leads to a remarkable 19% increase in the risk of stroke, which was found to be more significant in non-smokers. A positive correlation was also found between gaseous pollutants (no_2, CO and SO_2) concentration and the risk of stroke or stroke mortality.

Short term effects of AP on the cardiovascular system seem to be predominantly the triggering acute coronary incidents. For instance, a positive correlation was found between short term increases in AP and non-fatal myocardial infarctions.

1.3.2.3 Gestational and developmental complications

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, creating an enormous need for nutrients. These are supplied by the mother's blood, crossing the placenta and reaching the fetus through its umbilical cord. High rates of tissue formation and proliferation render the forming being unstable and therefore more susceptible to the appearance of some kind of morphological abnormality. At this time, there is no separation between the mother's blood and the fetus, meaning that whatever chemical reaches the progenitor's bloodstream also reaches the growing fetus. If the mother is exposed, so is the fetus [38].

There are numerous chemicals that can affect the female reproductive system, of which some are habitual components of AP. They have been associated to several highly adverse affects, and interfere with such things as the processes by which the body is able to produce eggs, or other processes that enable the formation of a single cell by the union of the sperm and the egg (the zygote). After conception, AP has been known to reduce uterine nurturing capabilities, and hinder the new being's development. Some of them are even teratogens, meaning that they induce birth defects. Figure 1.4 illustrates the kind of defects that come with exposure, according to the time at which the mother was exposed.

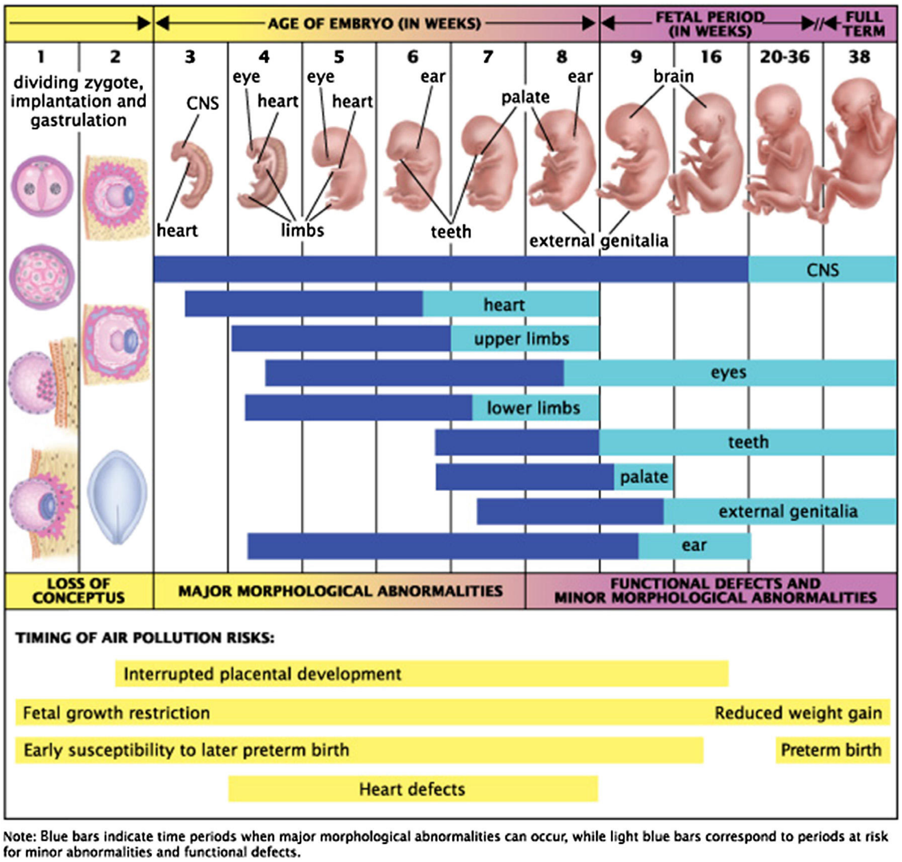

Figure 1.4: Possible abnormalities caused by AP exposure *in utero*. Notice that time of exposure is of critical importance [38].

There are already several studies that correlate higher AP exposure levels to birth defects or the probability of negative outcomes. For instance, in [25], researchers have studied the association between AP exposure levels (for the mother) and the appearance of premature Small for Gestation Age (SGA) by collecting more than 40000 births in Changzhou Maternity (China) and studying the mother's typical environment. This study has found a positive association between SGA and exposure to $PM_{2.5}$ in two or three pollutants models of AP (with NO_2 and SO_2), during the third trimester of gestation. Another, perhaps more comprehensive study, was performed using Swedish data from 1997 to 2007, and found that there was a positive association between O_3 exposure and the appearance of pre-eclampsia (a potentially deadly complication of pregnancy), estimating that about 1 in 20 pre-eclampsia cases were caused by AP [29].

Besides uterine development compromises, birth defects and reproductive difficulties, Air Pollution has also been associated with hindrances to the child's neurodevelopment. In a New York study was able to associate lower levels of mental development at age 3, in African-American children with valid prenatal Polycyclic Aromatic Hydrocarbons (PAH) exposure data. In another study from the neighboring Boston, AP was associated with generally lower cognitive test scores, even when correcting for several influencing factors. On a different level, AP was shown to produce significant delays in the central conduction times of Brainstem Auditory-Evoked Potentials (BAEP) tests in children, indicating that there might be important repercussions of AP to vestibular and auditory development.

Although most other systems are affected by AP, it does have a particularly heavy toll on the respiratory development. This is because the lungs are not completely developed at birth, and are only finished in the late teens. The level to which AP affects the respiratory system development varies greatly with the staeg of life in which the effect is produced, and severity is also very varied. Acute negative effects range from respiratory death to chronic cough [38]. Moreover, childhood (and prenatal) exposure to AP has been associated with the emergence of conditions such as COPD and asthma.

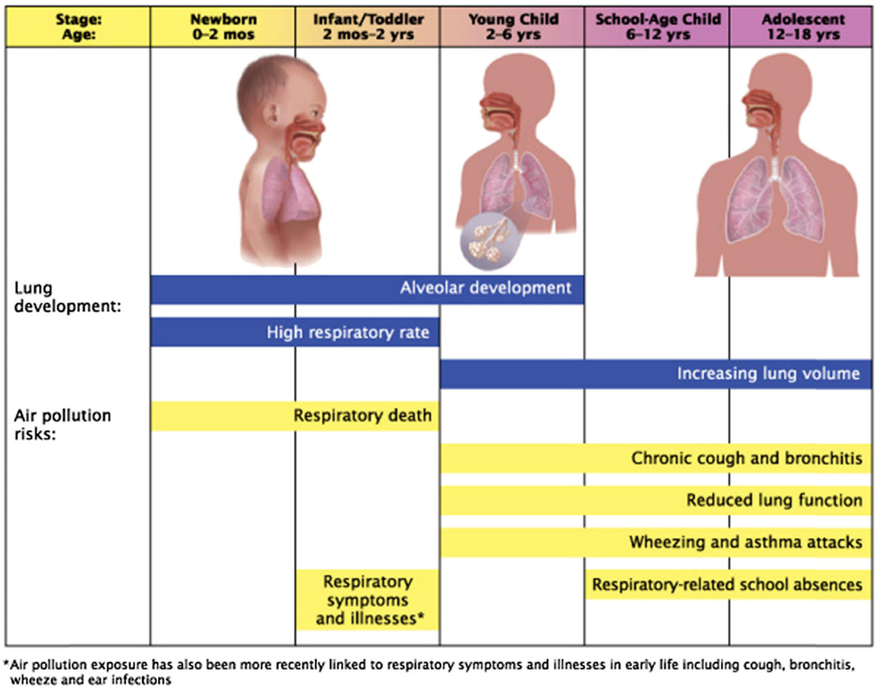

Figure 1.5: Developmental stages of the lung throughout life vs the risks of AP exposure in each stage [38].

1.3.2.4 Neurological disorders

The brain and the Central Nervous System (CNS) were one of the last to be included in the range of organs that are affected by AP. While the effects of AP on the respiratory and cardiovascular systems are quite broad and include some "surprises", the fact that these systems were affected by Air Pollution was evident and expectable, given the type of exposure these systems endure. The CNS, on the other hand, has a more difficult to express relationship with AP, and has required more sophisticated methods to detect [38, 19]. It was in the beginning of this century that the first connections between AP and the emergence of neurological disorders started to be made, and from then on, we have progressed into thinking that not only are they related, but also that AP might be one of the key driving forces in the onset of certain neurological diseases, including the most dreaded of them all, Alzheimer's and Parkinson's [19, 11, 9].

The reason why AP is able to reach and damage the CNS is a continuation (or even an extension) of the ways in which it affects the cardiovascular system. By crossing the alveolar barrier into the bloodstream, AP acts as an oxidative stress source. As it can also do in lung tissue, Air Pollution creates some local proinflammatory effects in the cardiovascular system, affecting the vascular endothelium cells. This can lead to a systemic inflammatory status, which is accompanied by the production of proinflammatory cytokines (a type of message-protein that is used by organisms to trigger certain types of response, like inflammation [44]). Now, since blood vessels in the brain are extremely responsive to this kind of message, their presence can activate cerebral endothelial cells and disrupt the blood-brain barrier [19].

In 2018, a consortium of several Spanish universities and researchers wrote a review detailing the until-then-published articles dealing with the neurological implications of AP [11]. This review identifies several articles that connect the long-term exposure to Air Pollution with adverse impacts on the brain and brain structures. *In vitro* and *in vivo* studies, focusing on traffic related emissions and their effect on gray matter cells, have found that these display significant alterations. On other studies identified by the review, it was shown that white matter, the myelinated part of the brain, is particularly sensitive to AP and its volume is significantly decreased both in the elderly and children, as consequence of prolonged exposure to it.

There are also several articles that show that there is an association between exposure to air pollutants and impairments on brain function. In Section 1.3.2.3, I have already mentioned a study that was conducted in New York, and that found that the children that they were using as subjects were found to have measurable cognitive deficits in comparison with children of the same age living in less polluted areas which are compatible with the affected areas of the brain that were detected through neuroimaging studies [11].

1.3.3 Air Pollution effects on ecosystems

The Earth is home to an almost unbelievable number of different ecosystems. The ubiquitousness of AP means that all of them are in some way or another affected by this problem. In general terms, the threat posed by AP to any given habitat is a function of its biodiversity, defined as the number of different living beings that inhabit a certain environment (in all biological kingdoms) [30]. Living beings within an ecosystem are like nodes in a graph, with many connections to any particular node. More biodiversity corresponds to a greater number of nodes and an even larger number of links, which means that there is a greater probability that some of those links become disrupted by Air Pollution in some way.

Water based environments are greatly affected by AP. Material deposition on the surface of the water can have serious consequences in terms of habitat conditions for holding life. In this regard, the most important air pollutants are NO_2 and SO_2, which significantly decreases the water's pH. On its own, this represents a major problem. The acidifying effects of nitrogen and sulfur deposition became very pronounced in Scandinavia (among other places). Thousands of this territory's lakes, once teeming with wildlife, became effectively lifeless. Those that did not reach this point, have seen the number of fish living on their waters dwindle to numbers from which there may be no return [41]. Sulfur and nitrogen depositions also enrich surface waters, altering the solubility and other physical aspects on the surface of the water, which in turn inevitably leads to disruptions in species abundance and diversity. Moreover, indirect effects may also take their tolls. For instance, O_3 does not play any significant role in the chemical behavior of a water body, but it can influence the number of predators around this habitat, which will compromise the predator-prey balance of the aquatic environment [38, 26].

In terrestrial ecosystems, AP effects are not smaller in importance or complexity, and they are different for each type of being. To the Flora, AP can have a subtle to deadly effect, depending on variables like pollutant chemical species, exposure time, or plant life stage in which exposure happens. For instance, O_3 is especially poisonous to plants. Even small concentrations of this gas will cause plant growth to decrease significantly. It enters the plant through the stomata and reduces photosynthesis through increased oxidative stress. Many times, although concentrations are not enough to outright kill the plant, they are enough to make them more susceptible to other attacks like pathogens, insects or environmental conditions. Ozone is commonly responsible for huge financial losses that come from the diminished agricultural yields. And while it is true that due to several policies, AP is in a clear downward trend since the 1980s in urban regions, it is also true that in many rural areas, these changes have been smaller or non-existent, making these losses even more relevant [26, 38].

Forests are among the most susceptible environments to AP. They suffer from the previously described mechanisms of AP damage, like acidic deposition, but also suffer from other, less direct pollution risks. Emission of greenhouse gases can induce changes in humidity, temperature, and general climate profile of a forest. The combination of direct and indirect risks result in an exacerbation of both, leading to more and more forest losses due to Air Pollution. The damage done to forests all around the world is especially problematic given the biodiversity that these ecosystems contain within themselves. Rainforests in particular are thought to contain more than half of the world's terrestrial species. These species have many times adapted to a particular kind of microhabitat which only exists in the specific rainforest in which it lives. Changes in these specific conditions, whether caused by Air Pollution or any other cause, are leading to alarming extinction rates in forests and rainforests globally [38, 26].

Of course it is not only the flora that suffers with Air Pollution. Direct implications of AP on animals approximate those that fall upon humans. We are an animal species, after all. Our main difference is the adaptation capabilities that our superior intellect grants us, which allows us to escape more or less unscathed for a longer period of time, and to combat what we cannot escape from in ways which are simply unaccessible to other animal species. So, although AP has direct effects on all animals that are exposed to it, ecosystem damage and eventual destruction remains the most perilous factor for this biological realm [38, 26].

1.3.4 Air Pollution Sources

There are almost as many AP sources as there are pollutants. The first major division between these sources is whether they are natural or anthropogenic. However, this separation is not always clear, as one source can lead to another and boundaries become fuzzy within their own context. The most prominent example of such is the case of accidental fires. While they are most of the times classified as a natural source of AP, their origin lies most of the times in human activities. In this section, I will present a selection of the most important naturally occurring air pollutants and examples of how they have affected human lives throughout the times. The selection itself does not intend to be complete description of pollution sources, but rather paint a general picture of the subject.

1.3.4.1 Natural Sources of Air Pollution

Although people, governments and institutions tend to speak far more seldomly of them than of their man-made counterparts, natural sources of air pollutant are not only abundant, but also important. One of the main natural sources of AP are volcanic eruptions. These phenomena are responsible for the emission of immense quantities of PM and gases such as SO_2, Hydrogen Sulfide (H_2S) and methane. Depending on the type of volcanic eruption, the emitted cloud of gas and PM can remain airborne for long periods of time, even disrupting modern life at times, namely in what concerns air travel. The last eruption to happen in Portuguese soil took place in the remote Azorian island of Faial. In September 1957, the Earth shook almost continuously for around two weeks. Finally, on the 27th, 100 m Northeast the Capelinhos islands, the sea was seen to boil and project vapor and volcanic material hundreds of meters into the air. In the following hours, the underwater volcano finally exploded, emitting large quantities of volcanic ash and gases into the atmosphere. The phenomenon lasted for more than a year, and the final ejection of lava took place in October 1958 (see Figure 1.6). The eruption had a significant social impact, in addition to its ecologic importance. In the end, 40% of Faial's population left the island as a result [38, 35].

Oceans are also a significant source of AP. Aerosol particles of salt are continuously emitted from these large masses of salt water, which damage many human created structures, namely metallic constructions. In certain parts of the world, another important source of Particulate Matter (especially because of its consequences in the inhabitants' daily life) are dust storms. The most famous of these events, and one of the most deadly storms in the recorded history of the US territory was the infamous *Black Sunday* dust storm. Starting on Palm Sunday, 14 April, this sky-blackening dust storm punished the peoples from the panhandles of Texas and Oklahoma, burying entire houses (see Figure 1.7) under the dust and destroying the livelihoods of thousands of Americans. Dust storms were an important part of the US history during the 1930s and led to the creation of the Soil Conservation Service, a branch of the US Department of Agriculture [38, 2, 33].

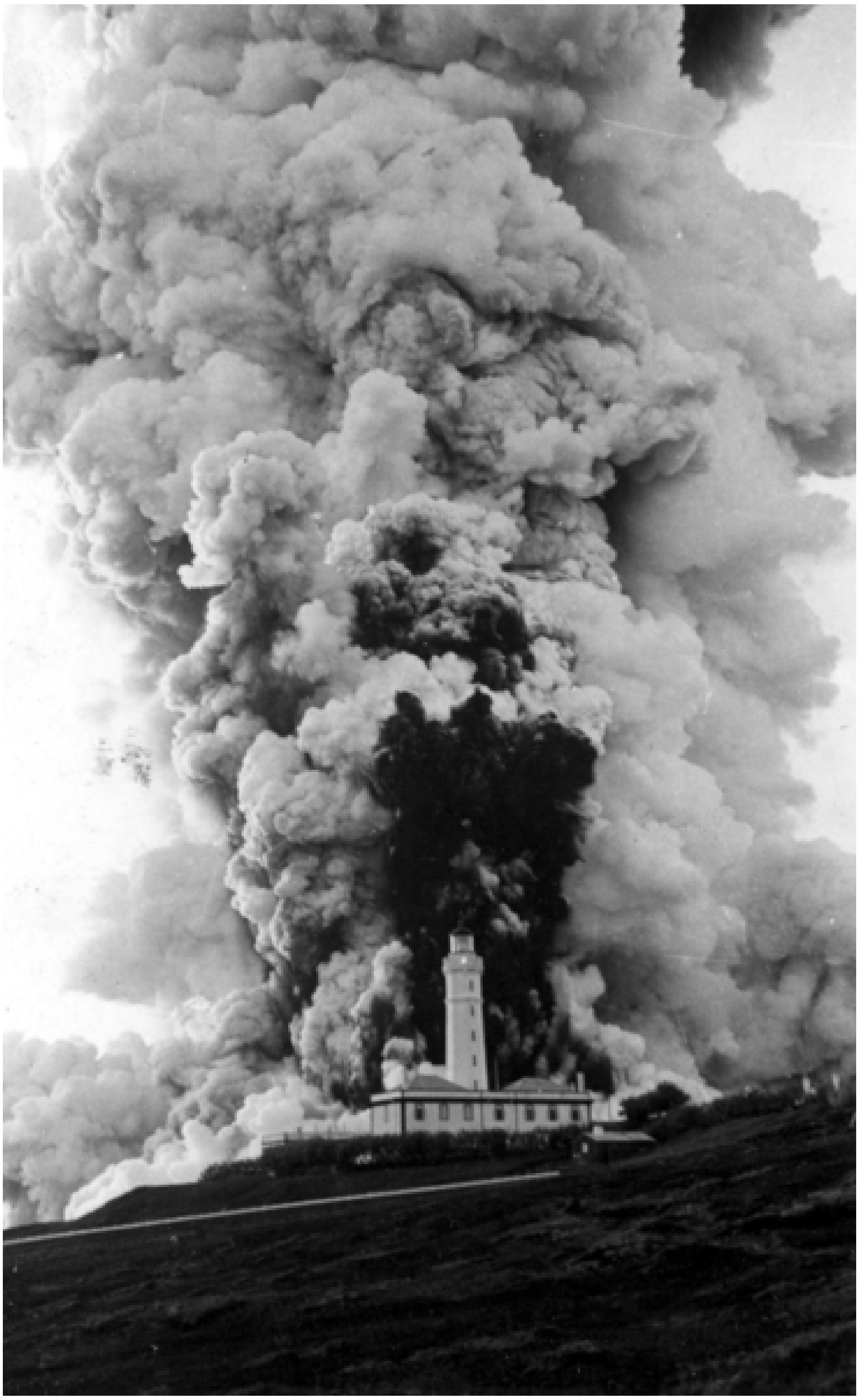

Figure 1.6: Dramatic photograph depicting the Capelinhos' lighthouse, half a kilometer from the eruption site, surrounded by a cloud of ash PM, volcanic gas and water vapor with more than 1km in height[35].

Figure 1.7: House almost completely buried by the Black Sunday dust storm. Several houses were entirely swallowed during this storm, trapping people inside, as if a big blizzard had hit them. Unlike a blizzard though, there was nothing anyone could do to keep the dirt outside, and all surfaces were covered black [33].

Fires are also one of the largest sources of natural air pollution in the world. The uncontrolled burning of organic matter that is a large forest fire creates a large quantity of air pollutants that range from smoke to unburned (or partially burned) hydrocarbons, nitrogen and carbon oxides, and ash particles. Besides the obvious dangers of this kind of burnings for human life and activities, forest fires can also cause indirect damages, such as disruptions in supplies and travel due to reduced visibility [38].

Trees and forests in themselves are also responsible for a certain quantity of air pollution. Although they have the main part in the carbon dioxide conversion into oxygen, through photosynthesis, plants and trees are still the largest emitters of hydrocarbons in the planet, as attested by the blue haze that is visible on top heavily forested areas, resulting from chemical reactions between VOCs produced by the trees. This counter-intuitive fact was in the origin of the infamous Ronald Reagan speech in which he "blamed"trees for much of AP, in a time when anthropogenic AP was at its apogee in the US and Europe.Plants are also the emitters of another kind of PM, which is of particular importance both to themselves and humans, which are the pollens. This is a bio-aerosol - a type of aerosol that is or was part of a living being - associated with a number of diseases [38].

Finally, I will discuss Radon gas. This is a natural occurring radioactive gas that is part of the radiative decay of Uranium present in all rocks. Although chemically inert, Radon is radioactive and, as all radioactive substances, emits particles when it decays. Although present virtually everywhere, outdoor concentrations of Radon are typically too small to cause any problems. The problem with this gas comes essentially from indoor concentrations, namely at home. Being a gas, Radon is able to enter people's houses, exposing the inhabitants. Prolonged exposure to Radon gas is the second biggest cause of lung cancer and authorities estimate that between 3 and 14% of lung cancer cases are caused by this gas. In Portugal, Radon concentrations were found to be below the European prescribed limit in two thirds of the houses in a 2001 study, but in 17% of the cases, concentrations were not only above this limit, but also over the highest tolerable limit [38, 43, 32].

1.3.4.2 Anthropogenic Sources of Air Pollution

Air Pollution that originates from human activities is called anthropogenic. Since the first industrial revolution, mankind has been using more and more resources to fuel our progress and continuously improving way of life. Of course, the consumption of natural resources has some unpleasant and sometimes dangerous consequences. The most important of which, looking from the lens of this thesis, is the incredible increase in the levels of AP. If one had any doubts whatsoever, all it would take would be a look into the atmospheric CO_2 concentration chart (Figure 1.8) from a few centuries back to the current day to completely dissipate them.

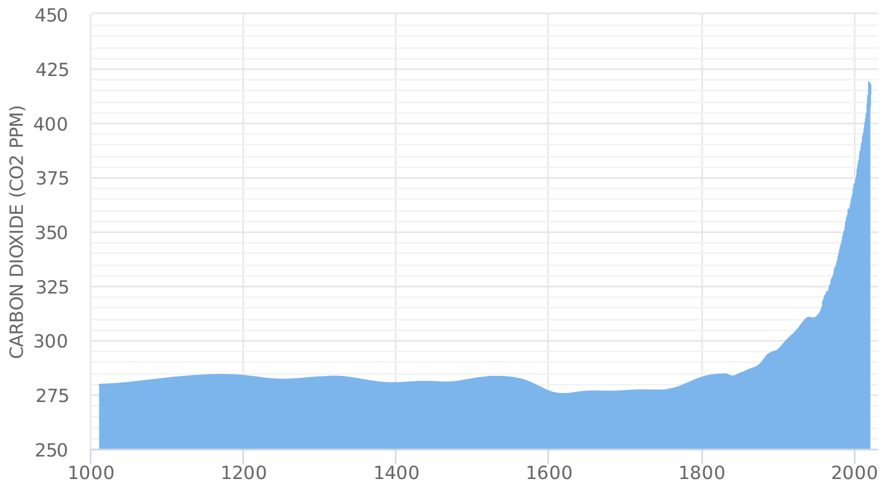

Figure 1.8: Carbon Dioxide atmospheric concentrations since the year 1000. Note the seemingly exponential increase since the 1800s. Plotted and published by the 2 Degrees Institute [1] with data from ice cores [17] and in situ monitors [34].

There are literally hundreds of sources of AP, but it is possible to categorize them into 4 main *families*: industrial processes, energy (includes transportation), agriculture and forestry, and waste. Of these 4 broad categories, as displayed in Figure 1.9. The most prominent is without a doubt the energy sector, although we also have to bear in mind that any and all combustion used in the other sectors is counted as energy production [23, 8].

From 2002 to 2011, fossil fuel combustion has been responsible for an average of 8.3 petagrams of carbon per year. This truly gigantic carbon footprint is in its majority explained by the worlds energy needs, which are ever increasing up to now. In 1990, total energy demand was situated at 356 quadrillion British Thermal Unit (BTU), having grown to 410 quadrillion BTU in 2010. In 2020, energy demand estimates are located at 600 quadrillion BTU, of which almost a quarter was expended by China [8].

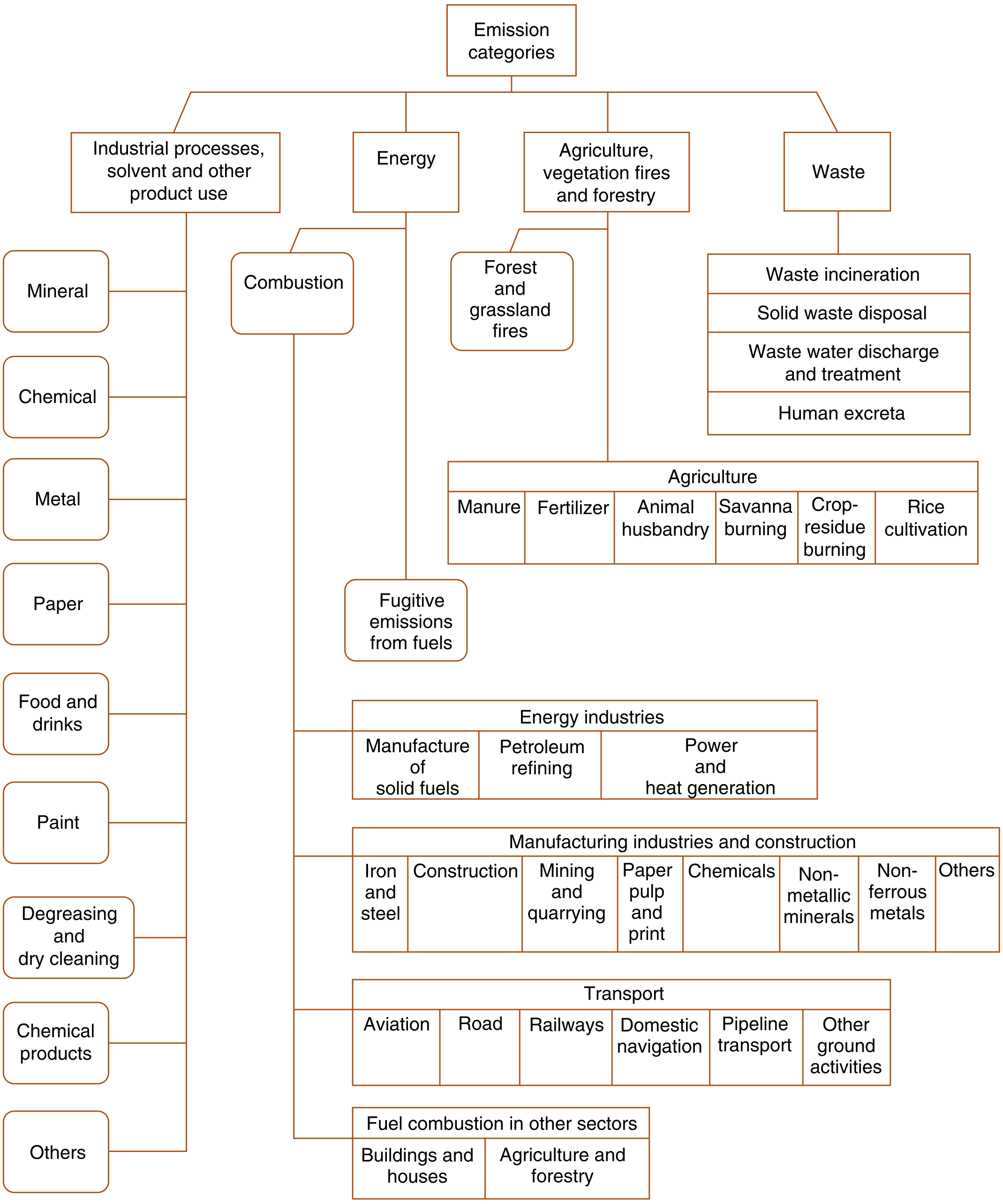

Figure 1.9: Schematic presentation on the sources of anthropogenic pollution and its categorisation according to the IPCC. Adapted from [8]

It is important that we focus a little bit more on the Chinese case. It is now somewhat near commonsense to regard China as the factory of the world, and this of course is tied to Chinese energy consumption and production. On the same line of reasoning, this must mean that in some way, the country's energy expenditure is connected to the amount of financial resources that it produces, the GDP. Looking at the plots in Figure 1.10, one can see that all these numbers are highly correlated. When we ponder on the case of Chinese AP, and wonder why has this problem not been addressed previously, given its imposing dimensions and growing importance, one must take into account that, given the indirect importance of AP on Chinese people's gains, it is highly likely that the country's governments will be reluctant to decrease it in any expedient form [8, 22, 42].

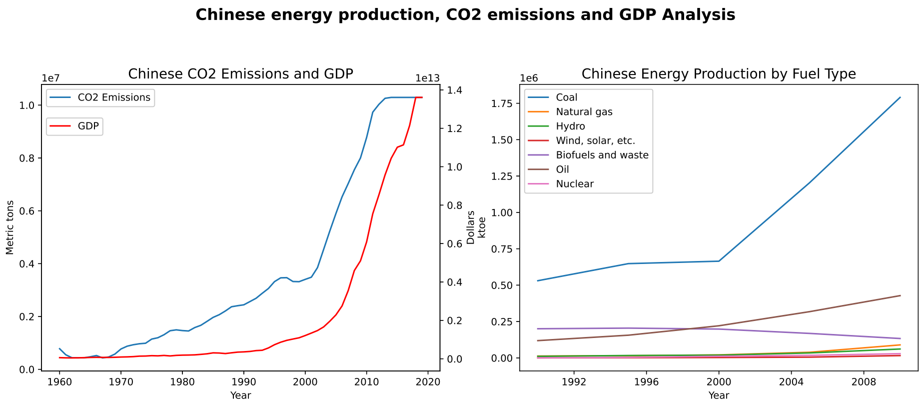

Figure 1.10: Chinese energy production, GDP and CO_2 emissions. Data collected from the World Bank and International Energy Agency websites [42, 22]

Another important conclusion that we can take from the plot in Figure 1.10 is that China has a large and historical dependence on the use of coal as fuel for energy production. This adds to the problem described in the above paragraphs, as coal is the single most damaging fossil fuel available. Not only does China get most of its energy from coal burning, but is also responsible for more than half of the worlds production and consumption of this substance (see Table 1.4).

Table 1.4: Global energy production, divided according to the fuel used to obtain it and the production country.

Country	**Liq. Fuel** (M barrels / day)	**Coal** (BTU)	**Nat. Gas** (T cu. ft)	**Renew.** (BTU)	**Nuc.** (b kWh)
China	10,6	80,6	5,1	10,6	93
USA	18,5	17,3	25,5	7,8	769
Europe	14,4	12,5	17,9	11,7	837
Middle East	16	0,1	14,8	0,2	1
India	3,6	12,6	2,1	3,5	30
Russia	3,4	4,5	15,7	1,7	166
Africa	3,5	4,3	2,7	4,7	12
Brazil	3,3	0,5	1,1	6,8	15
World	91,4	153,9	120,8	63,7	2345

ICE are the single most important means for powering human transportation.

Almost every vehicle in the world uses a kind of ICE. These motors operation is an application of the Otto cycle, in which the chemical energy in the fuel is converted to mechanical energy. These engines are as ubiquitous as the fossil fuels that have powered them since the beginning of the automobile revolution, in the early 20^{th} century. Fossil fuels have several features that make them ideal to power our vehicles. Their energy density is high, they are incredibly safe to manipulate and use, and fossil fuel infrastructure can be found in almost every far corner of the Earth. However, using them releases a number of gaseous and particle-condensed side products into the atmosphere, and this makes traffic one of the most important sources of AP. For instance, traffic pollution is the main responsible for human exposure to NO_X gases. Without countermeasures, gasoline ICE equipping passenger vehicles emit around 1.8 g/km of these gases, while diesel emits 2.8 g/km and Liquefied Petroleum Gas (LPG) around 2.1 g/km. On heavy duty engines, like on trucks and tractors, these figures skyrocket to 14.7 g/km for diesel engines and around 5.1 g/km for LPG [8].

Energy production (including transportation) is clearly the single largest contributor to global AP. This does not mean that other human activities do not pollute or produce air pollutants. Pollutant contributions from the industry, the agricultural activities and waste disposal are also non-negligible. In fact, industries around the world are responsible for the production and emission of all the criteria pollutants. It is important to single out one particular activity, which is the burning of forest for land-use changes. Carbon Monoxide (CO) emissions for this purpose are very high due to the nature of the burning material, which emits more than 50 times more CO than fuel or coal [8].

1.3.4.3 The European Case

Europe has for long been on the forefront of the fight against AP emissions. The European Union has put in place a number of policies aiming at cutting (or even eliminating) emissions of human health compromising pollutant components. Few places in the world have been so demanding regarding their environmental practices, and numbers are a clear reflection of these adaptation efforts. In their 2019 report, the EEA state that European emissions have globally declined, and have been declining since at least the year 2000. Moreover, and in contrast with China's case, the GDP does no seem to be connected to AP emissions. As can be seen in Figure 1.11, emissions are decoupled from economic growth, as there are now less emissions per GDP unit than before [16].

If one extends this analysis further, and separates emissions by using their origin, the trends are approximately the same: except for Ammonia (NH_3) (a side product of agricultural activities) a clear reduction is present in all sectors. These results can be seen in Figure 1.12 and were presented in [16].

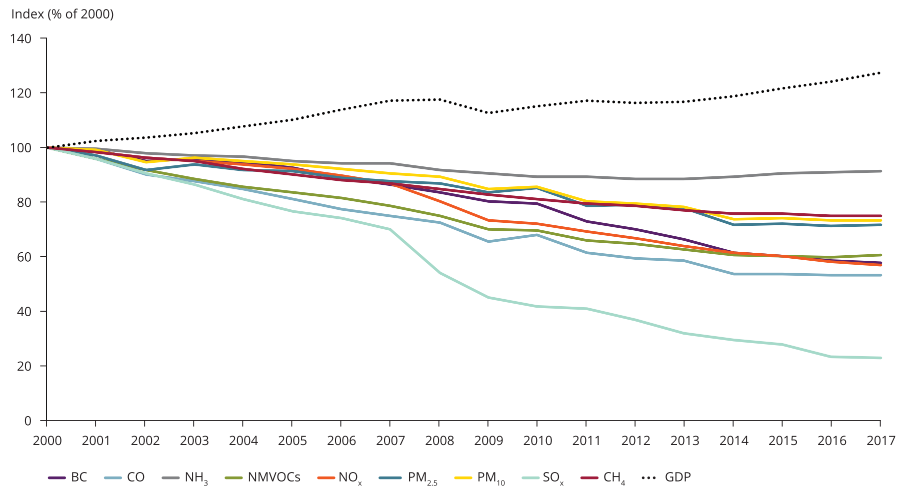

Figure 1.11: General trends for European emissions. Data presented in % emissions of year 2000. Note the downward global trend in pollutant emissions, and its decoupling with the European GDP [16].

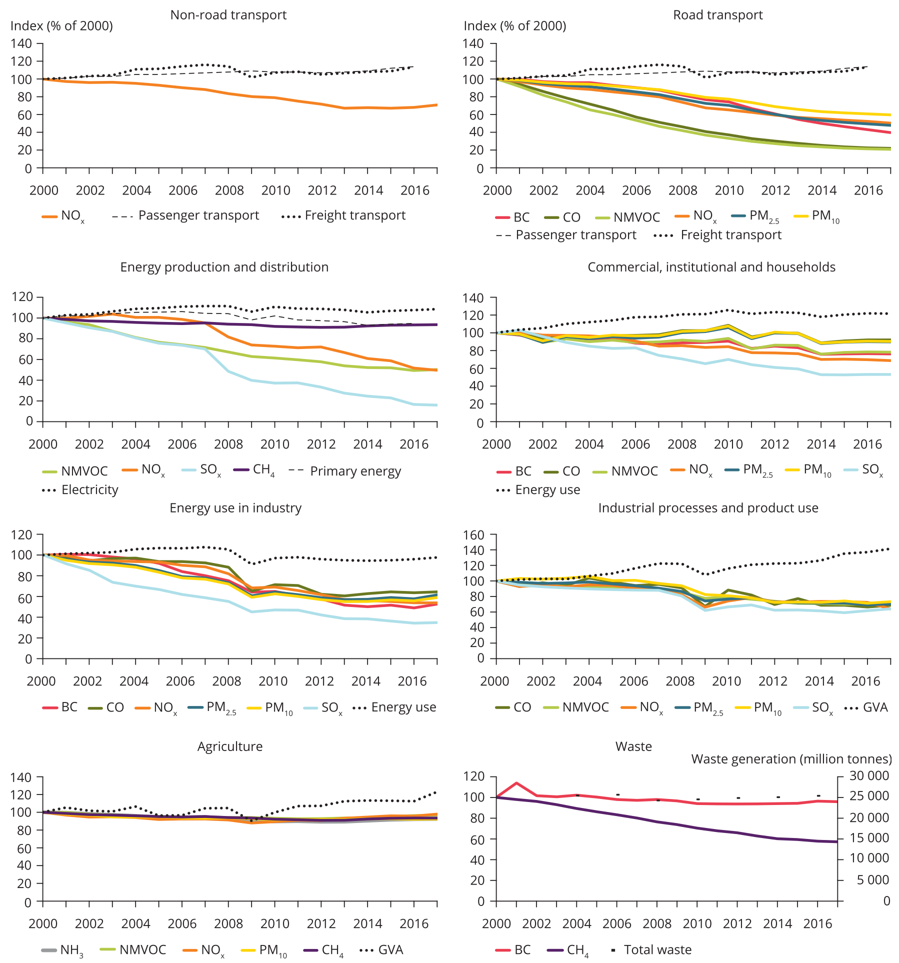

Figure 1.12: European emissions divided by activity sector. The global decreasing trend is confirmed, as industries all around are producing less and less AP with the passing years [16].

1.4 Air Pollution Monitoring Techniques

There is no doubt that AP is a global threat that affects everyone, both in personal terms (through the degradation of their health) and in societal terms, through the investments and limitations that we as a whole have to commit to in order to prevent larger, unmanageable problems. Reducing AP is a priority and a requirement for today's modern societies. This demands immediate and effective actions, which in turn imply that we have a solid and profound understanding of how pollutants are created, transported and transformed in the atmosphere. The scale on which these interventions must be conducted requires them to be made on a concerted and collaborative manner, and always leveraged by technological development [16]. Many of the air pollutants cannot be detected solely by our senses, or even if they can is at already dangerous concentrations. Technology is therefore a prerequisite to our fighting the problem of Air Pollution [38].

Pollution monitoring is itself based on the ability of a given measurement method to determine concentrations for trace gases, aerosols or radiation quantities. As with many other test techniques, in various fields, pollution monitoring techniques have three very important aspects to verify. The first of which is sensitivity, and also the most demanding. Important trace gases in atmospheric chemistry have sometimes vestigial concentrations, and the ability to correctly detect them is many times a technical challenge. The second most important is specificity, which is the ability of an atmospheric measurement to measure each compound independently, without a component influencing another component's measurement either positively or negatively. Finally, any usable monitoring technique must be sufficiently precise as to provide valid measurements.

Air Pollution monitoring techniques and devices are too many to address them all in this document. However, a small introduction to the topic is in order. A valid point of entry in this discussion would be a broad categorisation of monitoring techniques with regard to the proximity with which they are designed to interact with the target pollutant. As with the case of fire detecting systems, reported in [37], atmospheric pollution monitoring systems can be divided into three broad categories.

In-situ systems localised sensors that are influenced by gases in their immediate vicinity;

Large area (open path) systems able to evaluate the atmosphere around them (normally through somekind of optical measurement) up to a few km;

Remote systems placed in satellites, which were designed to perform a more global analysis of the atmosphere and identify larger-scale trends;

Sampling studies are still regarded as the gold standard for atmospheric pollution monitoring. They are fundamentally different from the other methods, because there is an important time gap between collection and analysis. Sampling methods cannot provide real time information on atmospheric composition. The gaseous analyte is moved into a collection medium before being transported to the laboratory, where a very powerful analytical method such as mass spectroscopy or chromatography is used to retrieve the chemical composition of the sample. The use of this kind of technique determines the importance of sampling methods in the study of the atmosphere's composition, but they also make them quite inconvenient for day to day use [38].

A much more convenient solution comes in the shape of electrochemical sensors. They were highly popularised in recent decades through their usage in the field of industrial hygiene [10]. The first generation of these sensors were called wet cells. The basic design for an O_2 sensor of this type is presented in Figure 1.13. When an electromagnetic force is applied to the cell, hydrogen appears at the cathode, and oxygen at the anode. Conversely, when the cathode is subject to an oxygen concentration and an appropriate electrolyte is used (for instance, KOH), an electronic charged develops through the oxidation of the anode into a hydroxide. If a load is presented to the system, the current flowing through it is proportional to the partial pressure of oxygen in the mixture [12, 10].

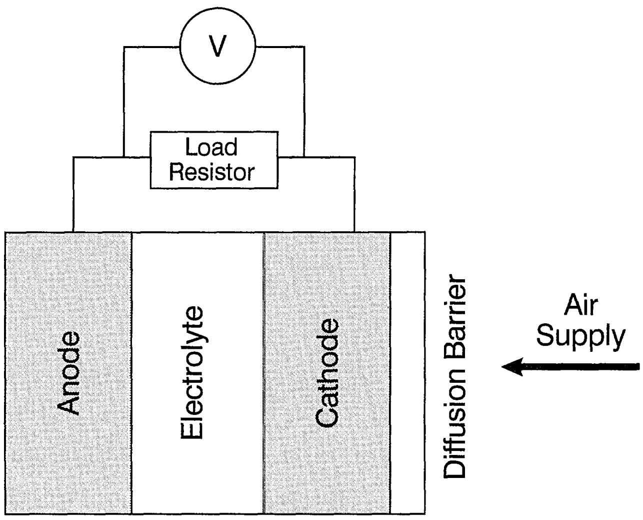

Figure 1.13: General schematic for an electrochemical sensor cell by City Technology [10].

A similarly applicable technology is the use of semiconductor sensors. These usually operate by the detection of a change in an electrical characteristic of the sensor's material. These sensors usually display sub-ppm detection limits, are easy to manufacture and to install and have simple high-level operating principles (although some of them are based on unknown phenomena [12]). They are also extremely cheap due to their needing minute quantities of sensing materials. The most common approach to the semiconductor sensors is the chemoresistive sensor. This sensor's resistance changes with the presence of the target gas. They are based in the work of Brattain and Bardeen [12, 6], in 1953. In spite of their many advantages, semiconductor sensors also have their limitations. For instance they are not as stable as most other measurement techniques. They are also quite limited in terms of their selectivity, and therefore should not be used in environments in which accuracy is a requirement. Besides, they suffer from the fact that they are only meant to detect what is directly in their vicinity, which means that they are easily influenced by local sources (think of a car's exhaust near to the sensor) which can mislead operators with regard to the atmosphere's composition.

Open path atmospheric monitoring techniques are completely different. Instead of relying in networks of small, local sensors, open-path measurement methods apply optical principles to assess the atmosphere's composition in a large area (up to a radius of a few km). Tunable Diode Laser (TDL) is one of such techniques, and one of the most popular. The measurement is focused on a single line of the absorption spectrum of a particular chemical species, to which *the* laser is tuned. TDL can be used to retrieve data from several gaseous pollutants at the same time. It is very user friendly, does not require any type of complex maintenance and it is reasonably easy to implement. However, since the laser is tuned to a particular wavelength, it has the important drawback of needing one laser per target component. Moreover, only a relatively limited set of components can be detected through this method, and PM and airborne objects are known to interfere with measurements from this technique [38, 24].

Differential Absorption LIDAR (DIAL) is another important open-path technique. It uses Light Detection and Ranging (LIDAR) in two different wavelengths and measures the difference in absorption between the two echos to determine the target gas concentration. By measuring response times, DIAL is also able to determine the spatial distribution of the gas that is being measured. With regards to drawbacks, there is a frequent problem with spectral artifacts that can introduce some bias towards high densities (real concentrations are smaller than they appear). Moreover, DIAL depends on the lasers that are used, so it can have a limited range of detected components [38].

Infrared radiation can also be used to measure atmospheric gas densities. The OP-FTIR method (general schematic presented in Figure 1.14) uses an interferometric measurement of infrared light to determine how much of a particular gas was in the analysed column. This is a very accurate method of obtaining average concentrations along a path. However, it can be quite expensive and is certainly the most complicated method described here. Moreover, strong infrared absorption by water in the atmosphere can lead to it not being useful in high-humidity environments. Raman spectroscopy can be used in these situations, but this method has a much lower resolution, due to the much lower intensity of the relevant signal [38].

One of the most important atmospheric monitoring techniques available is DOAS. As OP-FTIR and TDL, DOAS is based on Lambert-Beer's law, so it determines the quantity of a given gas in the atmosphere by how much light is absorbed on a certain light path and a certain wavelength (which with DOAS, can be a wavelength interval). The method, which is explained in more detail in Section **??** is able to simultaneously detect multiple trace gases with ppm level accuracy (depending on the assembly). A DOAS system is a very easy to operate system, since once it is assembled it requires no complicated maintenance.

The last atmospheric monitoring solution that I wish to delve on are satellite-based techniques. In the last decade, we have seen a global effort on behalf of governments (and transational entities) to invest in tools that can accurately monitor how atmospheric composition varies and evolves through time. The EU developed the Copernicus network, with several instruments already in orbit and Copernicus 5 scheduled for launch in 2023; South Korea has deployed its Geostationary Environment Monitoring

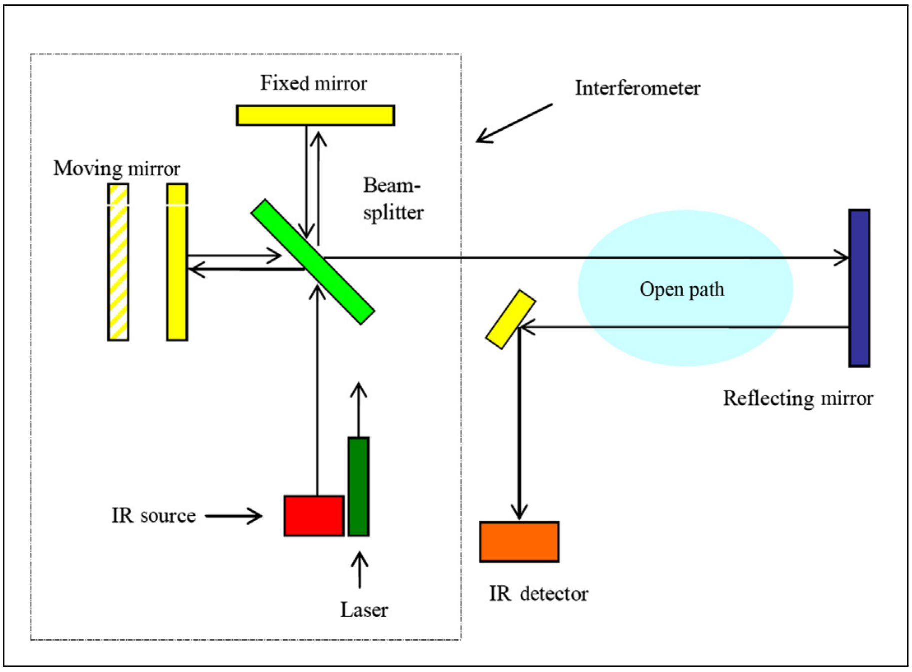

Figure 1.14: General schematic of a OP-FTIR instrument for atmospheric monitoring. Image adapted from [38].

Spectrometer in 2020, covering most of South-East Asia; and the USA are preparing to launch their Tropospheric Emissions: Monitoring of Pollution device in 2022. Together, this constellation of satellites will provide hourly data from the most important pollution sources in the world (example NO_2 map displayed in Figure 1.15). The amount and quality of data that will come from these initiatives is something unheard of until now, and has the potential to revolutionise how humans look at tropospheric emissions. However, these applications lack spatial and temporal resolution, as it is common for space-based terrestrial monitoring instruments. Moreover, in spite of its total availability (you can consult data on the internet), raw satellite data can be hard to interpret and most of the times requires special knowledge and tools.

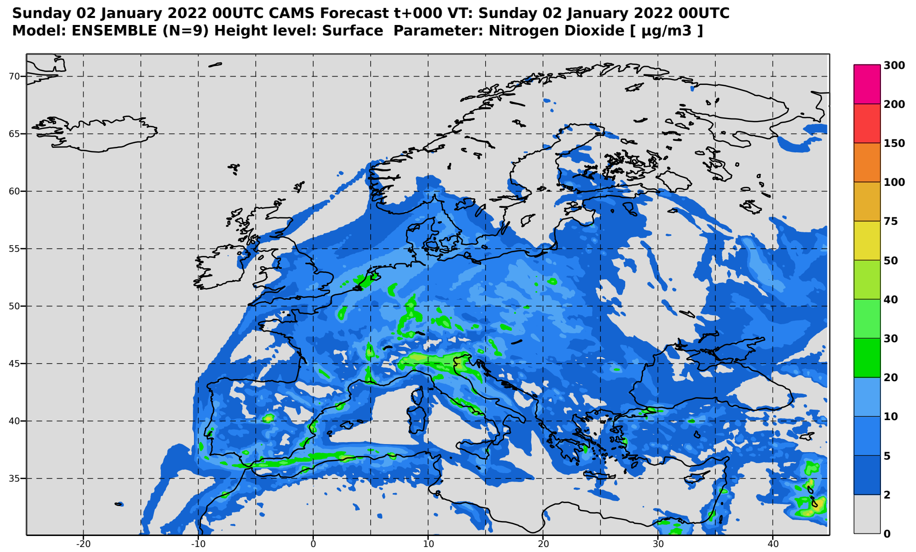

Figure 1.15: Satellite NO_2 measurements over Europe. Figure taken from Copernicus's website [15].

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