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# **Analysis of Pollution Control and Industrial Risks**

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## **Abstract**

Atmospheric pollution originating from industrial activities is widely acknowledged as a major factor influencing air quality. Liquefied natural gas (LNG) plants, in particular, represent a significant source of emissions, releasing considerable amounts of pollutants such as Methane (CH<sub>4</sub>), Sulfur dioxide (SO<sub>2</sub>), Nitrogen monoxide (NO), Nitrogen dioxide (NO<sub>2</sub>), and Carbon monoxide (CO). The Skikda LNG plant, the largest facility of its kind in Eastern Algeria, is a strategic contributor to the national economy, yet it also constitutes an important source of environmental risks.

This thesis aims to assess the concentrations of CH<sub>4</sub>, SO<sub>2</sub>, NO, NO<sub>2</sub>, and CO generated by the Skikda LNG plant (GLIK) across six different regions. Atmospheric pollutants were measured at each site and compared with the Algerian permissible limits. The findings reveal that the mean concentration of CH<sub>4</sub> at the plant reached 2775.88 µg/Nm<sup>3</sup>, far exceeding the national standard of 150 µg/Nm<sup>3</sup>. Similarly, the average CO concentration was 200.01 µg/Nm<sup>3</sup>, surpassing the permissible limit of 150 µg/Nm<sup>3</sup>. In contrast, the average levels of SO<sub>2</sub>, NO, and NO<sub>2</sub> remained within acceptable ranges in all monitored sites and complied with Algerian regulatory standards.

The thesis underscores that LNG plants represent a major source of atmospheric pollution, posing significant environmental risks and potential threats to public health. Therefore, it is essential for regulatory authorities to adopt stringent mitigation measures, including waste minimization, effective recycling strategies, and the deployment of continuous emission monitoring systems, in order to safeguard both the environment and human well-being from the adverse effects of industrial air pollution.

**Keywords:** Atmospheric pollution; LNG plant; Skikda; Algerian standards; Air quality; Environment impact; Emission monitoring; Methane (CH<sub>4</sub>); Sulfur dioxide (SO<sub>2</sub>); Nitrogen oxides (NO, NO<sub>2</sub>); Carbon monoxide (CO).

## Résumé

La pollution atmosphérique issue des activités industrielles est largement reconnue comme un facteur majeur influençant la qualité de l'air. Les usines de gaz naturel liquéfié (GNL), en particulier, représentent une source significative d'émissions, libérant d'importantes quantités de polluants tels que le méthane (CH<sub>4</sub>), le dioxyde de soufre (SO<sub>2</sub>), le monoxyde d'azote (NO), le dioxyde d'azote (NO<sub>2</sub>) et le monoxyde de carbone (CO). L'usine de GNL de Skikda, la plus grande installation de ce type dans l'Est de l'Algérie, contribue de manière stratégique à l'économie nationale, tout en constituant une source importante de risques environnementaux.

Cette thèse vise à évaluer les concentrations de CH<sub>4</sub>, SO<sub>2</sub>, NO, NO<sub>2</sub> et CO générées par l'usine de GNL de Skikda (GLIK) à travers six régions différentes. Les polluants atmosphériques ont été mesurés sur chaque site et comparés aux limites réglementaires algériennes. Les résultats révèlent que la concentration moyenne de CH<sub>4</sub> dans l'usine a atteint 2775,88 µg/Nm<sup>3</sup>, dépassant largement la norme nationale fixée à 150 µg/Nm<sup>3</sup>. De même, la concentration moyenne de CO, estimée à 200,01 µg/Nm<sup>3</sup>, a dépassé la limite autorisée de 150 µg/Nm<sup>3</sup>. En revanche, les niveaux moyens de SO<sub>2</sub>, NO et NO<sub>2</sub> sont restés dans des marges acceptables sur tous les sites surveillés et conformes aux standards algériens.

Cette thèse souligne que les usines de GNL représentent une source majeure de pollution atmosphérique, posant des risques environnementaux importants ainsi que des menaces potentielles pour la santé publique. Il est donc essentiel que les autorités mettent en œuvre des mesures d'atténuation strictes, notamment la réduction des déchets, le développement de stratégies efficaces de recyclage, ainsi que l'installation de systèmes de surveillance continue des émissions, afin de protéger l'environnement et le bien-être humain contre les effets néfastes de la pollution industrielle.

**Mots-clés :** Pollution atmosphérique ; Usine de GNL ; Skikda ; Normes Algériennes ; Qualité de l'air ; Impact environnemental ; Surveillance des émissions ; Méthane (CH<sub>4</sub>) ; Dioxyde de soufre (SO<sub>2</sub>) ; Oxydes d'azote (NO, NO<sub>2</sub>) ; Monoxyde de carbone (CO).

## ملخص:

إن التلوث الجوي الناتج عن الأنشطة الصناعية يُعدُّ على نطاق واسع عاملاً رئيسياً يؤثر على جودة الهواء. وتُعدُّ مصانع الغاز الطبيعي المسال (LNG) على وجه الخصوص من أهم مصادر الانبعاثات، حيث تُطلق كميات كبيرة من الملوثات مثل الميثان ( $CH_4$ )، وثاني أكسيد الكبريت ( $SO_2$ )، وأحادي أكسيد النيتروجين ( $NO$ )، وثاني أكسيد النيتروجين ( $NO_2$ )، وأحادي أكسيد الكربون ( $CO$ ). ويُعدُّ مصنع الغاز الطبيعي المسال في سكيكدة أكبر منشأة من نوعها في شرق الجزائر، مساهماً استراتيجياً في الاقتصاد الوطني، غير أنه في الوقت ذاته يشكل مصدراً مهماً للمخاطر البيئية.

تهدف هذه الأطروحة إلى تقييم تراكيز الغازات  $CH_4$  و  $SO_2$  و  $NO$  و  $NO_2$  و  $CO$  المنبعثة من مصنع الغاز الطبيعي المسال في سكيكدة (GLIK) عبر ست مناطق مختلفة. وقد تم قياس الملوثات الجوية في كل موقع ومقارنتها بالحدود المسموح بها وفقاً للمعايير الجزائرية. وأظهرت النتائج أن متوسط تركيز الميثان  $CH_4$  في المصنع بلغ 2775.83 ميكروغ/ن.م<sup>3</sup>، متجاوزاً بكثير المعيار الوطني المحدد عند 150 ميكروغ/ن.م<sup>3</sup>. وبالمثل، فإن متوسط تركيز أول أكسيد الكربون  $CO$  بلغ 200.01 ميكروغ/ن.م<sup>3</sup>، متخطياً الحد المسموح به البالغ 150 ميكروغ/ن.م<sup>3</sup>. في المقابل، بقيت المستويات المتوسطة لكل من  $SO_2$  و  $NO$  و  $NO_2$  ضمن الحدود المقبولة في جميع المواقع الخاضعة للمراقبة، ومتوافقة مع المعايير التنظيمية الجزائرية.

وتؤكد هذه الأطروحة أن مصانع الغاز الطبيعي المسال تُعدُّ مصدراً رئيسياً للتلوث الجوي، بما يترتب عليها من مخاطر بيئية كبيرة وتهديدات محتملة للصحة العامة. وعليه، فمن الضروري أن تعتمد السلطات التنظيمية تدابير صارمة للتخفيف من هذه الآثار، بما في ذلك تقليل النفايات، وتطوير استراتيجيات فعالة لإعادة التدوير، واعتماد أنظمة مراقبة مستمرة للانبعاثات، وذلك من أجل حماية البيئة والحفاظ على صحة الإنسان من التأثيرات الضارة للتلوث الصناعي.

**الكلمات المفتاحية:** التلوث الجوي؛ مصنع الغاز الطبيعي المسال؛ سكيكدة؛ المعايير الجزائرية؛ جودة الهواء؛ الأثر البيئي؛ مراقبة الانبعاثات؛ الميثان ( $CH_4$ )؛ ثاني أكسيد الكبريت ( $SO_2$ )؛ أكاسيد النيتروجين ( $NO$ ,  $NO_2$ )؛ أول أكسيد الكربون ( $CO$ ).

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## LISTE OF ABBREVIATIONS

- **ABL:** Atmospheric boundary layer
- **ANOVA:** Analysis of Variance
- **APCI:** Air Product and Chemicals Incorporation
- **CH<sub>4</sub>:** Methane
- **CLB:** Constant Level Balloon
- **CO:** Carbon monoxide
- **FGD:** Flue Gas Desulfurization
- **HC:** Hydrocarbons
- **HC:** Hierarchical clustering
- **HNO<sub>3</sub>:** Nitric acid
- **LNG:** Liquefied natural gas
- **LPG:** Liquefied petrol gas
- **MMO:** World Meteorological Organization
- **NG:** Natural gas
- **NO:** Nitrogen monoxide
- **NO<sub>2</sub>:** Nitrogen dioxide
- **PAHs:** Polycyclic aromatic hydrocarbons
- **PCA:** Principal Component Analysis
- **PM:** Particulate matter
- **SCR:** Selective Catalytic Reduction
- **SO<sub>2</sub>:** Sulfur dioxide
- **SP:** Suspended particulates
- **SPSS:** Statistical Package for Social Science

- **VOCs:** Volatile organic compounds

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***GENERAL  
INTRODUCTION***

## **General introduction**

Today, the air we breathe is facing increased and diverse pollution. Although natural sources contribute to this pollution, the primary concern arises from human activities. Worldwide, emissions from automobiles and industries, as well as those from biogenic sources and biomass combustion, are under scrutiny for their detrimental effects on air quality (**Martin et al, 2013; Butt et Bouchriti, 2016; Klimont et al, 2017; Wallace et al, 2018**).

The release of detrimental pollutants into the atmosphere, known as air pollution, can have negative effects not only on human health but also on the overall well-being of the planet. Consequently, persistent exposure to elevated levels of pollutants leads to significant issues, including respiratory problems, worsened cardiovascular conditions, and in some cases premature mortality (**Esposito et al, 2014; Ozcan et al, 2023**).

Air pollution is currently recognized as a significant public health and environmental issue, necessitating increased scientific attention. Starting from 2016, air pollution has emerged as the fourth leading cause of global mortality. Consequently, recent analysis through systematic reviews and meta-analyses focusing on the health effects of air pollution has revealed a significant increase in the generation of knowledge regarding the relationship between atmospheric pollution and human health (**Dominski et al, 2021; Cassidy et al, 2014**). The most significant substances of concern include carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), nitrogen monoxide (NO), nitrogen dioxide (NO<sub>2</sub>), and methane (CH<sub>4</sub>), particularly in densely populated, industrialized areas of countries involved in petrochemical activities such as petroleum refining and natural gas liquefaction (**Keawboonchu et al, 2023; Etemadfard et al, 2021**).

Natural gas plays a significant role as a highly versatile fuel in the global industrial sector. It serves as a crucial provider of fuel and energy services, catering to both heating and power needs. Additionally, it functions as a vital raw material in various industrial processes (**Mathur et al, 2022; Siddiqi, 2002**).

The atmospheric pollution issue in Skikda is related to the city's location **(Morawska- Horawska et al., 2003)**. However, there is a lack of detailed studies on the combination of meteorological factors and the differentiation of pollutant sources. Skikda city is situated in a complex interplay of microclimates due to its proximity to the Mediterranean Sea and varied topography. The unique morphology of the Skikda area contributes to heavy rainfall seasons and natural horizontal and vertical air ventilation **(Bokwa, 2019)**.

This thesis aims to assess the concentrations of CH<sub>4</sub>, SO<sub>2</sub>, NO, NO<sub>2</sub>, and CO generated by the Skikda LNG plant (GLIK) across six different regions. Atmospheric pollutants were measured at each site and compared with the Algerian permissible limits. The findings reveal that the mean concentration of CH<sub>4</sub> at the plant reached 2775.88 µg/Nm<sup>3</sup>, far exceeding the national standard of 150 µg/Nm<sup>3</sup>. Similarly, the average CO concentration was 200.01 µg/Nm<sup>3</sup>, surpassing the permissible limit of 150 µg/Nm<sup>3</sup>. In contrast, the average levels of SO<sub>2</sub>, NO, and NO<sub>2</sub> remained within acceptable ranges in all monitored sites and complied with Algerian regulatory standards.

The thesis underscores that LNG plants represent a major source of atmospheric pollution, posing significant environmental risks and potential threats to public health. Therefore, it is essential for regulatory authorities to adopt stringent mitigation measures, including waste minimization, effective recycling strategies, and the deployment of continuous emission monitoring systems, in order to safeguard both the environment and human well-being from the adverse effects of industrial air pollution.

Our work is structured around four interdependent chapters:

Chapter 1: The first chapter, fundamentals of air pollution, establishes the foundation by elucidating the core concepts of air pollution. It provides an in-depth overview of the origins, types, and sources of pollutants, offering a comprehensive understanding of the mechanisms behind air contamination.

Chapter 2: The second chapter, meteorological influence on air pollution, advances the discussion by examining how meteorological conditions affect air pollution. It investigates the interactions between temperature, wind, precipitation, and humidity with pollutants, influencing their concentration, dispersion and removal.

Chapter 3: The third chapter focuses on the study site, the sampling strategies, the materials, and the methodologies employed. It begins with an overview of the GL1K complex in Skikda, followed by a detailed exploration of natural gas properties, sampling procedures, and sample preparation techniques for analysis. Furthermore, it further provides a detailed presentation of the materials and analytical instruments used throughout this research. Given the importance of precision in evaluating atmospheric pollutants, careful consideration was given to the selection of sampling devices, gas-collection equipment, and analytical tools. Each material was chosen to ensure reliable sampling, accurate quantification of pollutant concentrations, and methodological consistency across all designated sampling locations. The following subsections describe the characteristics, operational principals, and scientific relevance of the key materials employed in the study, including Tedlar sampling bags, portable M25 multi-gas sensors, and the gas chromatography system. Together, these instruments form the technical foundation of the monitoring approach and support the validity and reproducibility of the results obtained.

Chapter 4: This chapter presents the results and discussion of air quality assessments around the Skikda LNG plant, analyzing concentrations of methane ( $\text{CH}_4$ ), carbon monoxide ( $\text{CO}$ ), nitrogen oxides ( $\text{NO}_x$ ), and sulfur dioxide ( $\text{SO}_2$ ) across six sampling sites. Statistical analyses, including one-way ANOVA and Principal Component Analysis (PCA), reveal significant spatial variations in pollutant levels, with  $\text{CH}_4$  and  $\text{CO}$  exceeding Algerian regulatory limits near the LNG facility. Hierarchical clustering and spatial distribution maps identify pollution hotspots and dispersion patterns influenced by wind and precipitation. The findings underscore the impact of industrial emissions and meteorological factors on local air quality, concluding with recommendations for emission control technologies and operational adjustments to mitigate environmental and health risks.

***Chapter I:  
General concepts of  
air pollution***

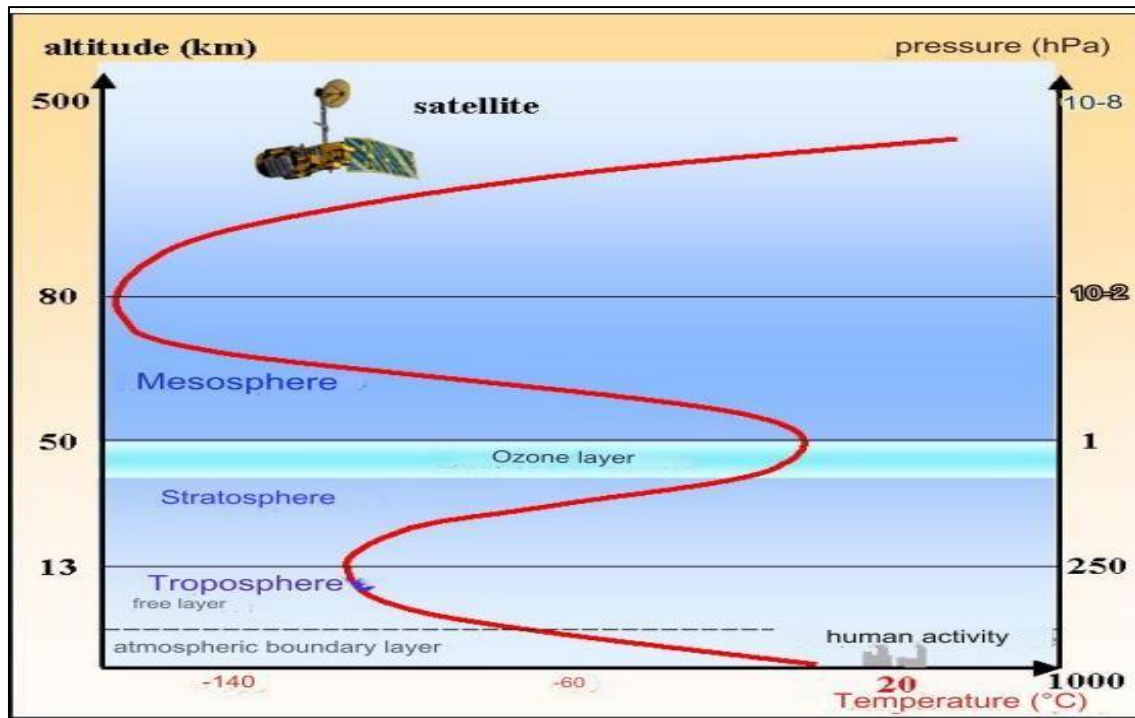
**Introduction**

Life is supported by the air we breathe, yet both natural and human-caused processes can introduce dangerous substances that endanger this essential resource. This chapter provides a thorough overview of air pollution, giving you the information you need to comprehend its effects and possible remedies. We'll start by defining the Earth's atmosphere, which is the backdrop for air pollution. After that, a precise definition of air pollution that distinguishes it from clean air will be developed. The chapter's main focus is on air pollution. We'll examine the various kinds of pollutants and classify their origins, which range from daily living to industrial operations. We'll also look at the harm that these pollutants do to the environment and human health. After that, the chapter explores the three main phases of the air pollution cycle: emission, transport, and deposition. It is essential to comprehend this cycle in order to create efficient control strategies. You will have a basic understanding of air pollution from this first chapter. By examining the factors that affect these contaminants' dispersal, the upcoming chapter will expand on this understanding.

**I.1. Vertical structure of the atmosphere**

The atmosphere is a thin layer of gas that surrounds our planet. This thin layer plays a vital role as a filter for solar radiation. The atmosphere is made up of 78.09% nitrogen, 20.95% oxygen, 0.93 % argon, and a variety of trace gases. As a result of various heating and cooling mechanisms, the temperature of the atmosphere changes with altitude (**UNG, 2003**).

The atmosphere is composed of various layers that are stacked on one another. The troposphere, stratosphere, mesosphere, and thermosphere are distinguished from the ground up. A typical profile of the various atmospheric layers is seen in Figure (I.1) (**Hufty,2001**).



**Figure (I.1):** The vertical profile of the Earth's atmosphere (Philippe, 2004).

The lowest layers of the atmosphere, which extend to less than 10 km in altitude, are made up of two sections (Figure I.1). The atmospheric boundary layer (ABL), which is the bottom part of the troposphere, has a height of about one kilometer. Above this lies the free layer, which forms the upper part of the troposphere. The arrangement of the atmosphere and the presence of contaminants play a major role in influencing climatic conditions (Philippe, 2004).

## I.2. Definition of air pollution

The 1996 Law on Air and the Rational Use of Energy defines air pollution as the presence of harmful substances (either gaseous or particulate) in the atmosphere, which negatively affect the environment and human health. These pollutants can originate from natural sources (such as volcanism, erosion, sea spray, oceans, and wildfires) or from human activities (including automobile emissions, industrial processes, energy production, combustion, and waste incineration). Recent studies have established a connection between the presence of these pollutants in the atmosphere and the deterioration of both environmental conditions and human health (AlBarakeh,2012).

**Table (I.1):** Composition of the Atmosphere (**Ramade, 2011**).

Constituents	Volume as a percentage
Nitrogen	78.01
Oxygen	20.95
Argon	0.93
Carbone dioxide	0.038
Neon	$1.8 \cdot 10^{-3}$
Helium	$5.24 \cdot 10^{-4}$
Methane	$1.7 \cdot 10^{-4}$
Krypton	$1.14 \cdot 10^{-4}$
Hydrogen	$5 \cdot 10^{-5}$
Carbone monoxide	$1 \cdot 10^{-5}$
Ozone	$10^{-6}$ to $4 \cdot 10^{-6}$
ammonia	$1 \cdot 10^{-6}$ to $3 \cdot 10^{-6}$
Nitrogen peroxide	$1 \cdot 10^{-7}$
Sulfur dioxide	$2 \cdot 10^{-6}$ to $1 \cdot 10^{-6}$

### I.2.1 The different scales of air pollution

Atmospheric pollution involves three main components: sources of emission, the environment (the atmosphere), and receptors (such as humans, animals, and plants). The study of this phenomenon is categorized into three spatiotemporal levels, which are determined by the movement and life span of chemical species, a factor influenced by the stability of pollutants (**UNG, 2003**).

#### I.2.1.1 Local scale (from 10 m to 10 km from pollution sources)

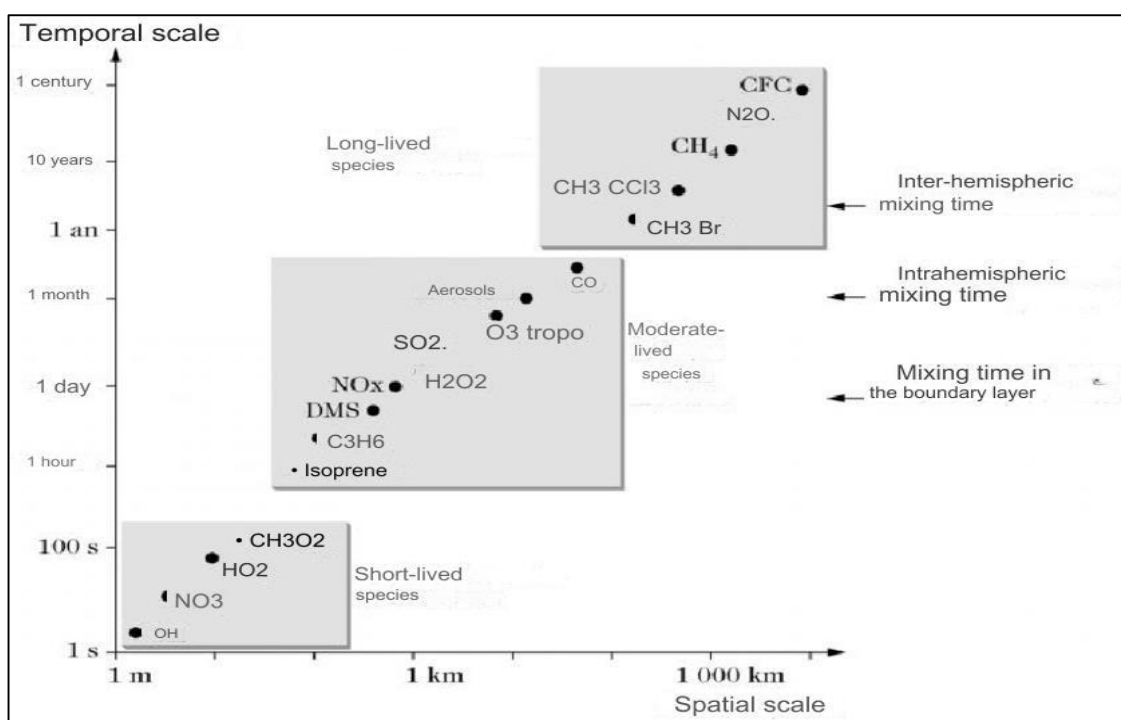
Pollutants at this scale arise from localized activities like heating, industrial operations, and vehicle emissions. These pollutants have direct impacts on human, animal health, vegetation, and materials (**Coman, 2008**).

### I.2.1.2 Regional scale (approximately 100 km from pollution sources)

At this scale, various complex physicochemical processes come into play. It covers areas where secondary effects are observed, such as acid rain, which significantly impacts forests and aquatic ecosystems, or the formation of ozone in the lower atmosphere. This type of pollution is heavily influenced by meteorological conditions (Coman, 2008).

### I.2.1.3 Global scale (around 1,000 km)

At the global level, studies examine vast regions where the effects of more chemically stable pollutants have a global reach, such as the depletion of the ozone layer at higher altitudes or the increase of ozone at lower altitudes.



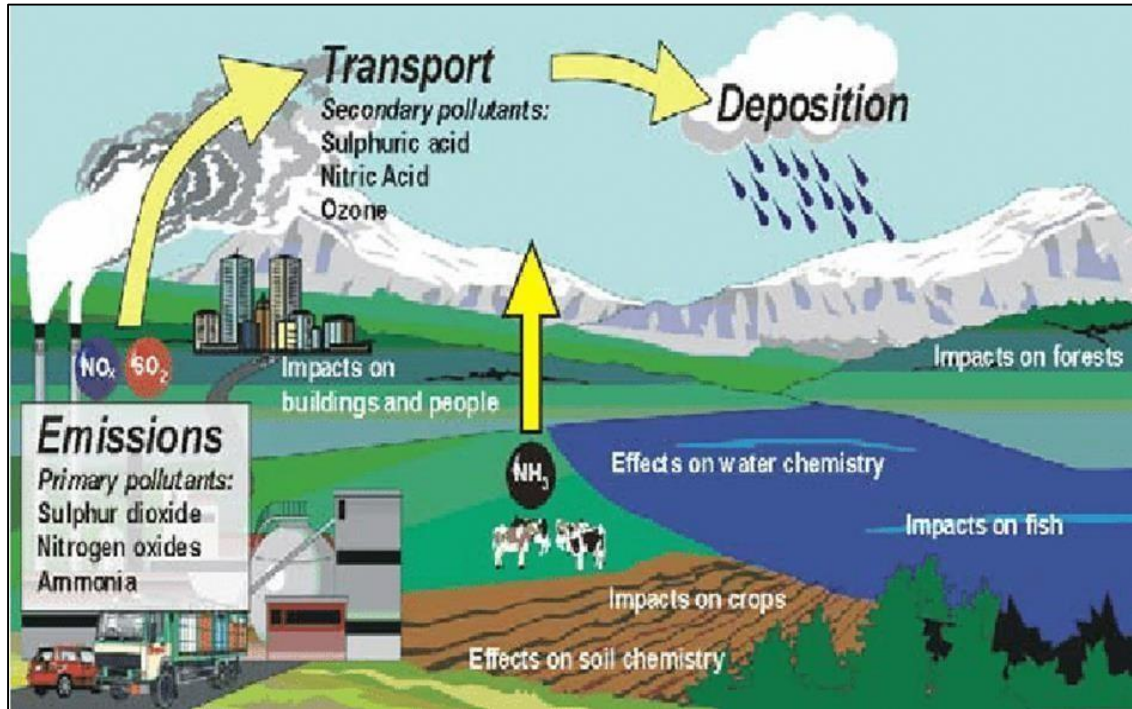
**Figure (I.2):** Spatio-temporal scales of air pollution (Coman, 2008).

According to CITEPA, pollution phenomena are classified into three-time scales: a global level for worldwide pollution, which spans a time scale of years; a regional level for long-range pollution, which occurs over a time scale of days; and a local level for localized pollution, with a time scale of hours.

### I.3. The pollution cycle

The atmospheric pollutant cycle consists of three main stages: emission, dispersion/transport, and deposition (Figure I.3). Factors related to the pollutant source

(such as discharge rate, source height, and temperature), as well as meteorological and climatic conditions (including solar radiation, temperature, turbulence, wind speed, and direction), and topographical features, are crucial in the transport and chemical transformation of pollutants (Coman, 2008).



**Figure (I.3) : Air pollutant cycle (Piot, 2011).**

### I.3.1. Emission of atmospheric pollutants

Once pollutants are released from various sources (whether natural or anthropogenic) in gaseous or particulate form, they are transported and/or transformed in the atmosphere. This process leads to the formation of other pollutants and allows them to travel thousands of kilometers from the original emission sources (Piot, 2011).

### I.3.2. Pollutant dispersion and transport

The dispersion of emitted pollutants is influenced by phenomena occurring primarily within the planetary boundary layer (0 to 3 km altitude). These pollutants often include heavier-than-air particles, which tend to settle quickly on the ground and in nearby residential areas. The atmospheric dispersion of pollutants is therefore largely dependent on various factors, such as wind, sunlight, local topography, temperature and rainfall.

### **I.3.3. Pollutant deposition**

Deposition refers to the process by which pollutants are removed from the atmosphere and deposited onto the ground, buildings, or vegetation. There are two types of deposition: wet and dry. Wet deposition occurs through processes such as precipitation (rain, snow, hail) or occult wet deposition, where cloud droplets impact a mountain or fog droplets settle. Dry deposition involves the transport of particles to surfaces, vegetation, soils, and surface waters in the absence of precipitation, through "dry" processes. Key dry deposition mechanisms include sedimentation, inertia impact, interception and diffusion (**Sportisse, 2008; Petroff, 2008**).

### **I.4. Main pollutants: sources and impacts**

An atmospheric pollutant is a substance of either anthropogenic or natural origin that is released into the atmosphere in gaseous or particulate form by various sources. Once emitted, the pollutant is transported and/or transformed within the atmosphere before being removed through dry or wet deposition (**Piot, 2011**). Atmospheric pollutants are classified into two main categories: Primary pollutants, which are directly emitted from sources (such as sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>), suspended particulates (SP), and carbon monoxide (CO)), and Secondary pollutants, which include ozone and secondary particulates, also known as photo-oxidants, formed through chemical or photochemical reactions from precursor pollutants (**Duché, 2013**).

#### **I.4.1. The various sources of air pollutants**

Atmospheric pollutants can originate from both natural and anthropogenic sources, which significantly affect their global distribution. Given the complex and dynamic nature of the atmosphere, global emission estimates can vary, making it challenging to accurately quantify the contributions of natural versus anthropogenic pollution. However, it is widely acknowledged that anthropogenic pollution is far more concentrated in densely populated and industrialized areas.

##### **I.4.1.1. Natural springs**

Natural sources of pollution include volcanic activity, which releases significant amounts of ash, carbon oxides (CO, CO<sub>2</sub>), and sulfur compounds (H<sub>2</sub>S, SO<sub>2</sub>) into the atmosphere. Each year, volcanoes emit around 30 million 0.3 to 1 μm,

are mostly formed when  $\text{SO}_2$  reacts with water vapor in the atmosphere. Lightning is another major natural source of nitrogen oxides ( $\text{NO}_x$ ), responsible for over a quarter of global  $\text{NO}_x$  emissions. Lightning can occur within a cloud or between a cloud and the ground, with the intensity of the discharge directly influencing  $\text{NO}_x$  production. Generally, the more intense the strike, the greater the  $\text{NO}_x$  output. Additionally, wind erosion contributes approximately 400 million tons of dust and aerosols to the atmosphere each year.

#### **I.4.1.2. Anthropogenic sources**

Atmospheric pollutants from human activity primarily consist of gases and particles released into the air through emissions from sources such as stoves and boilers (for both domestic and industrial heating), engines (from road, sea, and air traffic), thermal power plants, and industrial facilities (including chemical and pharmaceutical industries, paint and coating industries, and incineration plants). Additionally, pollutants are also associated with agricultural activities.

### **I.4.2. Different air pollutants**

#### **I.4.2.1. Methane ( $\text{CH}_4$ )**

Methane is a colorless, odorless gas with a wide distribution in nature. It is the principal component of natural gas, which is an abundant and inexpensive gas derived from various sources such as natural gas, biogas, oil extraction, coal mining, and anaerobic fermentation of biomass. This gas produces the second highest amount of greenhouse gas emissions.

##### **I.4.2.1.1. Impact of methane on the environment**

It participates directly in the phenomenon of increasing the greenhouse effect.

##### **I.4.2.1.2. Impact of methane on health**

It may catch fire and explode. It can cause cellular oxygen deficiency (acts like a gas asphyxiating by oxygen deprivation).

#### **I.4.2.2. Carbon monoxide ( $\text{CO}$ )**

Carbon monoxide ( $\text{CO}$ ) is a pollutant produced by the incomplete combustion of fossil fuels (such as gas, coal, fuel oil, or wood) in poorly regulated installations, with vehicle engines being a major source (AlBarakeh, 2012).  $\text{CO}$  is a colorless,

odorless gas commonly found in urban environments, particularly near traffic. Its levels are closely monitored due to its impact on air quality.

#### **I.4.2.2.1. Impact of Carbon monoxide (CO) on the environment**

Carbon monoxide participates in the mechanisms of ozone formation, transforms into carbon dioxide and contributes to the greenhouse effect responsible for changes in the global climate.

#### **I.4.2.2.2. Impact of Carbon monoxide (CO) on health**

CO binds instead of oxygen to the hemoglobin in the blood, leading to a lack of oxygenation of the nervous system and blood vessels. At very high concentrations, can cause chronic poisoning with headaches, dizziness, vomiting. In the case of very prolonged exposure, CO can be fatal.

#### **I.4.2.3. Sulfur dioxide (SO<sub>2</sub>)**

Sulfur dioxide (SO<sub>2</sub>) is a colorless, non-flammable gas released during the combustion of sulfur-containing fuels like coal, coke, and fuel oil, as well as from sources such as wood-fired boilers, blast furnaces, and combustion engines. SO<sub>2</sub> is often used as a tracer for industrial activities. Major industries contributing to SO<sub>2</sub> emissions include oil refineries, power generation, and metallurgy (Coman, 2008). Additionally, SO<sub>2</sub> is also produced naturally by volcanic eruptions ....

#### **I.4.2.3.1. Impact of Sulfur dioxide (SO<sub>2</sub>) on the environment**

In humid environments, sulfur dioxide contributes to the formation of acid sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) which is deposited on the ground and vegetation. This acid contributes, in association with other pollutants, acidification and impoverishment of natural environments and deterioration of materials used in the construction.

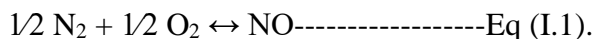
#### **I.4.2.3.2. Impact of Sulfur dioxide (SO<sub>2</sub>) on health**

SO<sub>2</sub> is a pungent gas. Thus, respiratory conditions can be caused (bronchitis...) which leads to irritation of the mucous membrane of the skin, and the upper respiratory tract (cough, difficulty breathing, asthmatic disorders, etc...).

#### **I.4.2.4. Nitrogen oxides (NO<sub>x</sub>)**

Nitrogen oxides (NO<sub>x</sub>) play a significant role in atmospheric pollution. These harmful gases are formed through the oxidation of molecular nitrogen (N<sub>2</sub>) with

molecular oxygen (O<sub>2</sub>) at high temperatures, such as during combustion processes (Equation I.1). This reaction primarily occurs in internal combustion engines and power plants (Arquès, 1998). Nitrogen oxides are considered indicators of urban pollution on a global scale, and more specifically, they serve as tracers of major combustion sources such as road traffic and urban combustion plants (AlBarakeh, 2012). The NO/NO<sub>2</sub> ratio can also be used to estimate the age of the air mass in which it is measured.



#### **I.4.2.4.1. Impact of Nitrogen oxides (NO and NO<sub>2</sub>) on the environment**

NO<sub>x</sub> plays a major role in the process of ozone formation in the lower atmosphere, they thus contribute to the phenomena of acidrain which threaten the soil and vegetation (concentration of nitrates in the soil) Indeed, nitric acid HNO<sub>3</sub> in solution gives H<sup>+</sup> ions responsible for the acidity of rain and nitrations).

#### **I.4.2.4.2. Impact of Nitrogen oxides (NO and NO<sub>2</sub>) on health**

NO<sub>2</sub> is an irritant gas that causes major respiratory problems, especially in children and the elderly. From 200 µg/m<sup>3</sup> NO<sub>2</sub> can penetrate into the finest ramifications of the pathways respiratory and causes an alteration of the respiratory function and hyper activity bronchial in asthmatics and children.

#### **I.4.2.5. Suspended particles (PM)**

Suspended particulate matter (PM) is classified based on its aerodynamic diameter into several categories:

- Coarse particles with an aerodynamic diameter greater than 10 micrometers.
- PM<sub>10</sub> Particles with a diameter of less than 10 µm, which include substances like bacteria and volatile dust.
- PM<sub>2.5</sub> Fine particles with an aerodynamic diameter of less than 2.5 µm.
- PM<sub>1</sub> Very fine particles with a diameter of less than 1 µm, typically formed from gas-to-particle conversion processes.

Particles in the atmosphere originate from both natural sources, such as volcanic eruptions and vegetation, as well as from anthropogenic activities, particularly industrial emissions. Suspended particulate matter is a complex mixture of organic and inorganic

substances, including chemical constituents like sulphates, nitrates, ammonium, inorganic ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Cl}^-$ , organic carbon and heavy metals. Particulate matter can be emitted directly into the air or formed through secondary reactions in the atmosphere from gaseous precursors, including sulfur dioxide, nitric oxide, ammonia, and non-methane volatile organic compounds.

#### **I.4.2.5.1. Impact of Suspended particles (PM) on the environment**

Dust absorbs and diffuses light, thus limiting visibility. They cause the formation of dirt by deposit and may have an odor unpleasant. Particles accentuate the effects of acidic pollutants, sulfur dioxide and notably sulfuric acid.

#### **I.4.2.5.2. Impact of Suspended particles (PM) on health**

The finest particles penetrate deep in the respiratory tract even at low concentrations and cause irritations and alterations of the respiratory function. These particles can be combined with toxic substances even carcinogenic like heavy metals and hydrocarbons.

#### **I.4.2.6. Volatile Organic Compounds (VOCs)**

Volatile organic compounds (VOCs) are hydrocarbons (HC) released from sources such as the evaporation of petroleum storage tanks and the filling of automobile tanks, as well as organic compounds emitted by industrial processes or the incomplete combustion of fuels. They can also come from solvents, agricultural activities, and natural environmental sources. In general, VOCs are classified into three main categories based on their boiling temperature: VOCs Compounds with a boiling temperature of less than 150-200°C. Semi-volatiles Compounds with a boiling temperature between 200°C and 500°C. Heavies Compounds with a boiling temperature greater than 500°C (Vincent, 2002).

#### **I.4.2.6.1. Impact of Volatile Organic Compounds (VOCs) on the environment**

They are involved in the process of formation of ozone in the bass atmosphere.

#### **I.4.2.6.2. Impact of Volatile Organic Compounds (VOCs) on health**

These pollutants have several effects on health including irritation and reduction of respiratory capacity as well as nuisances frequent olfactory.

### I.4.2.7. Ozone (O<sub>3</sub>)

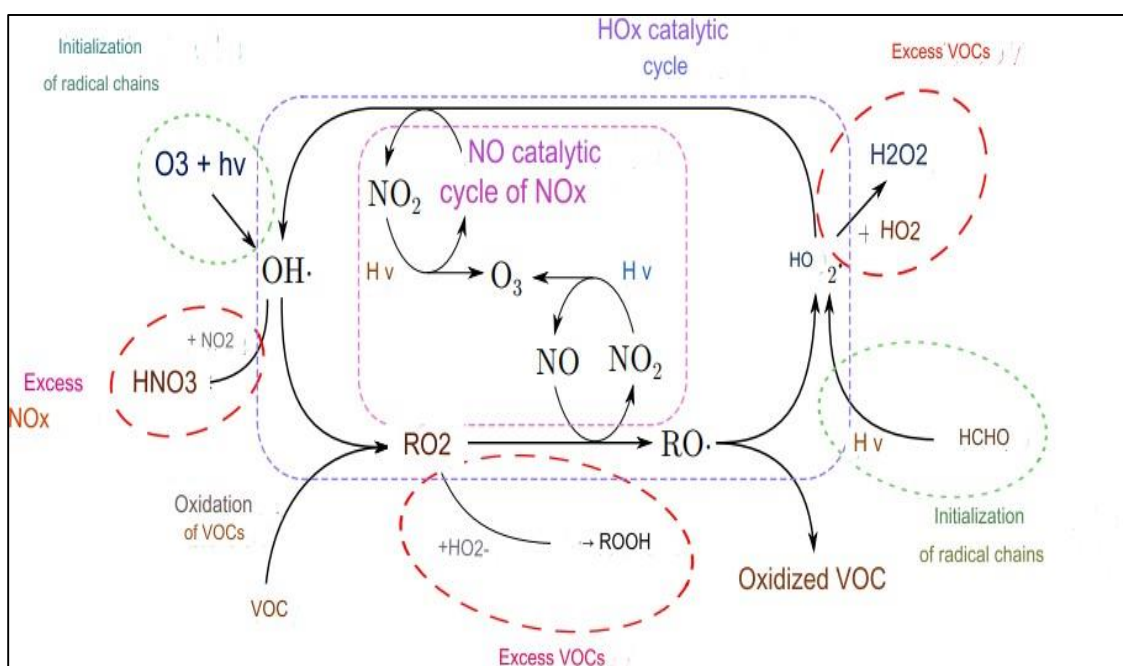
Ozone (O<sub>3</sub>) is a highly reactive and unstable form of oxygen. In the troposphere, ozone is primarily formed in two ways: about 20% comes from the descent of stratospheric ozone, while the remaining 80% is produced through photochemical reactions (Hache, 2014). These photochemical reactions require the presence of ozone precursors, which are primary pollutants such as nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO), methane (CH<sub>4</sub>), and volatile organic compounds (VOCs). Ozone is formed when ultraviolet (UV) light bombards stable oxygen molecules (O<sub>2</sub>), splitting them and allowing the formation of O<sub>3</sub>. The ozone formation cycle in the troposphere is illustrated in Figure (I.4).

#### I.4.2.7.1. Impact of Ozone (O<sub>3</sub>) on the environment

Very high concentrations of O<sub>3</sub> contribute to the acidification of the environment and subsequently a disturbance of the composition of the air, surface water and soil. Thus, this phenomenon leads to the disruption of photosynthesis which leads to a reduction in the performance of crops.

#### I.4.2.7.2. Impact of Ozone (O<sub>3</sub>) on health

O<sub>3</sub> is a very aggressive gas causing from a certain concentration (150 to 200 µg/m<sup>3</sup>) irritation to the eyes and skin throat, lung damage and migraines.



**Figure (I.4):** Tropospheric cycle of O<sub>3</sub> ozone formation (Sylvie Cassadou, 2002).

### **I.4.3. The effects of atmospheric pollutants**

Numerous epidemiological, toxicological, biological, and experimental studies have been conducted on the effects of air pollution since the 1990s. Notable examples include the European Psas-9 program (Programme de surveillance air et santé - 9 villes) (**Sylvie Cassadou, 2002**), APHENA (Air Pollution and Health—European and North American Approach) (Katsouyanni K & Committee, 2009), and the program of the Observatoire régional de santé d'Ile-de-France, Erpurs (**Karusisi, 2014**),

### **Conclusion**

This chapter has provided a thorough overview of air pollution, the invisible threat that resides within the very air we breathe. We began by examining the Earth's atmosphere, the stage where air pollution occurs. From there, we defined air pollution and explored its varying scales, highlighting the magnitude of this environmental issue. We then turned our focus to the pollutants themselves identifying their diverse sources, which range from industrial activities to natural processes. We also categorized the different types of pollutants, from harmful gases to particulate matter, and explored their harmful impacts on human health and the environment. This foundational understanding sets the stage for the next chapter, where we will explore the fascinating relationship between weather, geography, and how these factors influence the movement and dispersion of air pollutants.

***Chapter II:***  
***Influence of meteorological  
conditions on air pollution***

## Introduction

Air pollution remains a significant environmental challenge, impacting human health and ecological systems. While emission sources are often the primary focus, a crucial factor shaping their impact is frequently overlooked in meteorological conditions. This chapter delves into this intricate relationship. This study investigates how key meteorological parameters such as temperature, wind, precipitation, and humidity influence air quality by interacting with pollutants, affecting their concentration, movement, and removal of pollutants. By meticulously analyzing air quality data alongside meteorological information, this research aims to shed light on the intricate relationship between meteorological patterns and pollutant behavior. This knowledge is crucial for predicting air pollution events, developing effective mitigation strategies, and safeguarding the health of urban residents.

### II.1. Meteorology

Meteorology is an interdisciplinary scientific discipline that aims to understand atmospheric phenomena such as clouds, humidity, temperature, precipitation, or wind using physical, chemical, and mathematical parameters such as fluid mechanics or thermodynamics. To understand how they form and evolve. The word comes from the ancient Greek / meteoros (which is above the earth), which designates particles suspended in the atmosphere, and - / -logia, « speech » or « knowledge ».

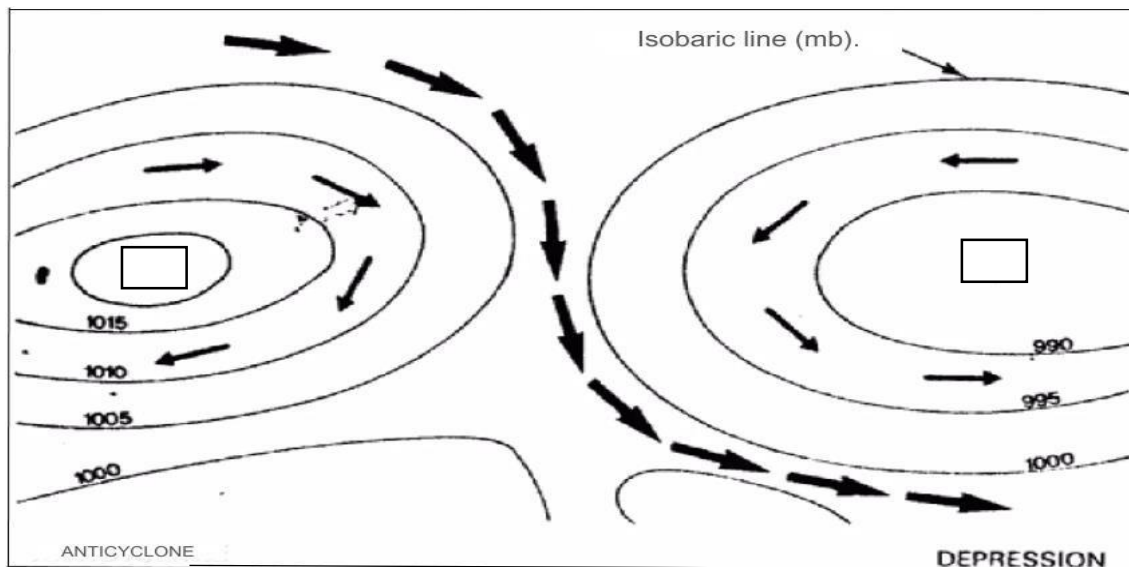
### II.2. The wind

#### II.2.1. Definition of wind

Winds are air movements born from pressure differences between two horizontal planes (Martin, 2014). Air flows from high-pressure zones (anticyclone) towards low-pressure zones (depression) (Boukhetta, 2011), that is to say from “source” regions towards “sink” regions (Koli Bi Zueli and Pauline Dibi, 2011). The flow is not rectilinear but it takes an “S” shape, because of the Coriolis force (Figure II.1) (Boukhetta, 2011).

An essential meteorological and climatic variable in the perception of time and human life, the wind, in association with other meteorological parameters, has a beneficial or harmful aspect concerning air quality. Indeed, depending on its strength and direction, the wind will disperse and transport pollutants according to flows more or less

affected by the topography (Carrega, 2008), atleast in the lower layers.



**Figure (II.1):** Movement of the area between the anticyclone (A) and the depression (D) (Poiton et al., 2014).

The ascent of air heated by the ground surface or by the condensation of water vapor causes local low pressure, while the descent of colder air causes high pressure. These depressions, or cyclones, and high-pressure systems, or anticyclones, are the driving forces behind winds (Poiton et al., 2014).

### II.2.3. The general mechanism

The wind is the result of atmospheric pressure gradients. (Godard and Tabeaud, 1998) define wind as "a displacement of air born from the differences in pressure existing on the same horizontal plane." If this displacement of air occurs from high to low pressure, the wind that materializes does not flow directly from anticyclones to depressions. Otherwise, it would be perpendicular to the pressure gradient (the case of rare gradient winds). However, the Coriolis force due to the Earth's rotation imposes an angle with the isobars on the wind flow in the troposphere, of about ten degrees over the oceans and about  $30^\circ$  over the continents. In the Northern Hemisphere, with your back to the wind, the wind leaves the anticyclones on the right and the depressions on the left, and vice versa in the Southern Hemisphere. Thus, the wind wraps around the anticyclones clockwise, and counter clockwise around the depressions (Agbo et al. 2021).

The wind increases from the ground to the base of the free atmosphere, as the friction forces decrease, while it becomes parallel to the isobars. At high altitudes, the winds

becoming parallel to the isobars are called geostrophic winds (**Beltrando and Chémery, 1995**) specify that "the wind speed is proportional to the pressure gradient, the air density, and the friction. Thus, the wind is all the faster as the isobars are closer together, the altitude is higher, and the ground offers few obstacles." On the scale of the general circulation.

#### **II.2.4. Measuring wind**

The wind is described by its speed and direction. The direction is expressed in cardinal points (south, west, etc.) or degrees through the angles of a circle. The measured value therefore does not lend itself to calculation. Indeed, the average of two north winds of  $359^\circ$  and  $1^\circ$  will give a wind of  $180^\circ$ , i.e. south. This problem is solved by the decomposition of the wind vectors (**Carrega, 2008**).

To measure wind at ground level, it is sufficient to place a cup anemometer to measure speed (m/s, km/h, or knots) and a wind vane, which is placed in the wind stream and gives the direction. The principle of measurement is therefore relatively simple. However, installing a mast several meters high is far from easy in the field. Admittedly, this type of device has certain drawbacks, particularly in terms of the accuracy of the measurements, but it has the advantage of providing information for a low investment.

To ensure that wind measurements are not disturbed by obstacles, there are a few recommendations that should be followed. First, the instrument should be placed at a height of at least 10 meters above the ground and in an open area. An open area is a surface where the distance between the anemometer and an obstacle is at least ten times, but preferably twenty times, the height of the obstacle (**Cadiou, 1997**).

In other words, it is not easy, and even rare, to find a truly open area, as defined by this definition, in the place where the information is sought. This is especially true since the equipment installed for several days must be secured if one wants to avoid damage, or even just to find it.

We will therefore try to get as close as possible to these observation conditions described by the World Meteorological Organization (**MMO, 2008**).

There are several methods of instrumentation for establishing vertical soundings. One of them is to take measurements using a captive (only possible in light winds: about 3 m/s maximum) or free balloon. Towers or large antennas can also be used to measure the wind at given altitudes up to a certain limit of about one hundred meters. However, it is still necessary to be able to access and climb them, so this is a limited technique.

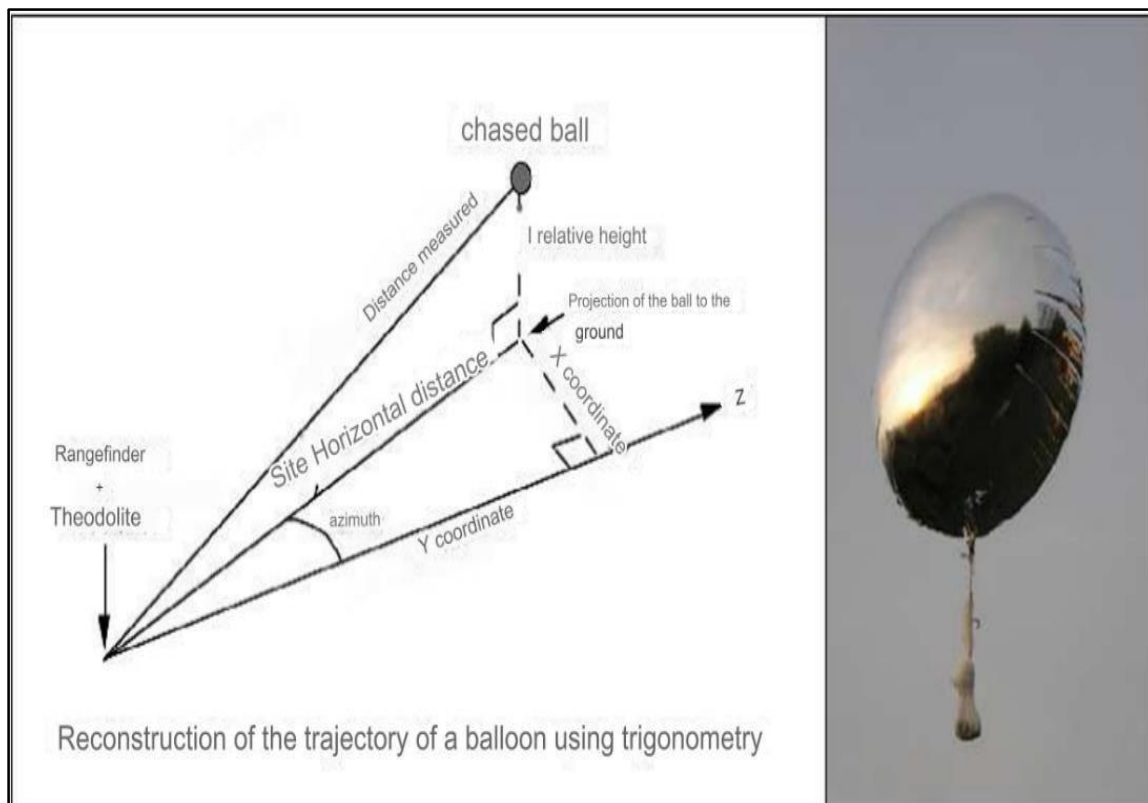
Other methods involve using lidars or profilers.

Even at altitude, but this time within the air mass, the objective here is to follow the movement of an air particle at low altitude (in the first few hundred meters above the ground) using a free balloon (made of mylar so that it does not deform; Figures II.2 and II.3) at a constant pressure level (called CLB for Constant Level Balloon). Unlike a vertical sound, the balloon will no longer pass through the air masses but will behave on the contrary like a bubble within the air mass, thus making it possible to trace the air flow that it materializes over a few kilometers. To achieve this, the balloon must float at the chosen pressure level by inflating it with a mixture of helium and air, and then balancing it with small pebbles or other objects generally found on site. At this point in the instrumentation, precision and above all experience are necessary. Indeed, a simple wooden twig can modify the flotation level by several meters.



**Figure (II.2):** CLB is ready to be released on 02/28/2012 around 12 p.m., at La Roquandte-sur- Siagne, at a place called PrésNeufs, view towards the northeast. In the foreground: on the left the theodolite, on the right the rangefinder.

The balloon is tracked by a telemeter to measure the distance and a theodolite to measure the azimuth angle (relative to the north) and the inclination (the site) relative to the horizontal (Figure II.3). These values can be measured at regular intervals, every 30 seconds for example. They allow us to reconstruct, finally thanks to trigonometry (Figure II.14), the behavior of the balloon either in section or in plan (Carrega, 2008; Carrega and al., 2010).



**Figure (II.3):** Diagram of calculating the trajectory of balanced balloons (Jones et al., 2010).

### II.2.5. Wind an agent of dispersion and advection of pollutants

Weak wind is partly responsible for the accumulation and elevation of pollutant concentrations. An observer looking at the spread of smoke easily sees that wind is the main factor in its dispersion. The stronger the wind, the greater and faster the dilution will be. This is because, in a given time interval, if the wind speed is doubled, the flow is spread over a dilution volume twice as large. On the other hand, the concentration of a pollutant downwind is inversely proportional to the wind speed (Forsdyke, undated). If the wind disperses and promotes better air quality near the emission, unless it is placed directly downwind, it also means that it carries, by its strength and direction, the pollutants in the air over more or less long distances depending on the general and local aerological situations.

Wind also promotes the resuspension of more or less coarse dust fractions (Jones et al., 2010). Topography also plays a major role since it generates flows that are decisive for the quality of air mixing. Indeed, if the emissions of primary pollutants are partly responsible for air pollution, it is the air flows which, predominantly in mountainous areas,

by their thickness, strength, and direction, control the concentrations of pollutants. At the mesoscale, if the Mistral, characterized by its strength and violence, normally leads to a cleaning of the air in the Rhone Valley and the Marseille region, caused by the advection of cold and clean air from the north, it is nevertheless capable, in summer, of contributing to air pollution by the long-distance transport of pollutants, including ozone precursors from the Paris region (**Corsmeier and al, 2005**). On the other hand, the Mistral, depending on its strength, can also more or less oppose the sea breeze front, which carries pollutants from the Marseille urban and industrial area to the north. At regional and local scales, the relationship between breezes and air pollution has been specified and demonstrated. (**Simpson, 1994; Nester, 1995; Carrega, 2006; Dahech and al, 2006; Dudouit and al, 2006; Carrega and al, 2010; Bastin and al, 2005**). Sea breezes can convect pollutants far inland, and even incorporate them into long-distance transport, particularly in the Durance Valley.

In addition, if the life of pollutants is subject only to the back-and-forth process of breezes, then their dilution is limited since they are recycled. And if the general meteorological conditions remain stable, then one can expect a local progressive increase in pollutant levels in the air (**Millan et al, 1997**) established, in the western part of the Mediterranean Basin, that polluted air convected during the day over land was brought back to the sea at night, similarly in the Sfax region of Tunisia (**Dahech et al, 2005**). In Chile, (**Romero et al, 1999**) demonstrated the role of local winds on pollution levels in the Santiago basin. On the other side of the Andes, in Argentina, (**Arkouli et al, 2010**) worked on the same subject in the Buenos Aires urban area. The alternation of valley-mountain breezes also influence the circulation of pollutants and their recycling. For example, in winter, the city of Freiburg (Germany) sees its pollutants transported to the Black Forest during the day and return to the city at night when the mountain breeze blows from this forest (**Baumbach and Vogt, 1999**).

On a finer geographical scale, in the same study area, (**Fiedler, 2003**) revealed that slope winds advected pollutants to the summit areas of the Schauinsland massif. Still, at the local scale, studies and measurements of air flow at low altitudes above the Paillon basin (Paillon de Contes and Paillon de l'Escarène) in the Alpes-Maritimes, indicate that these valleys are poorly ventilated (therefore the air is poorly renewed) and that the thermal breeze regime is by far the most frequent (**Carrega, 2000, 2009**). In this breeze regime, the air is channeled by the Paillon valley towards the downstream (agglomeration and city of Nice) at night and in the early morning, both in winter and in summer, over a thickness

of about 300 meters (Carrega., 2009).

The direction of this flow reverses during the day, towards the upstream, but over a greater thickness, which allows for better dilution. There is therefore an alternation of the directions of the breezes, and therefore of the advection of pollutants. In addition, at night and especially in winter, a lake of cold air settles at the bottom of the valley, which is not favorable for the dispersion of pollutants. With the presence of industrial emissions and road traffic, high concentrations of particles are thus observed in the Paillon valleys. Still in the department, as a supplement and illustration, the following photos taken a few tens of minutes apart show smoke from green waste burning (Figure II.4). They show, on a winter morning, the alternation of the directions of the breezes and the advection of pollutants downstream towards the Cannes coast, then upstream according to the wind direction on the Grasse conurbation.



**Figure (II.4):** Alternating directions of breezes and smoke plumes over the Grasse conurbation on 02/03/2011. Top: around 10:00 a.m, land-sea breeze interference. Below: around 10:30 a.m, widespread sea breeze. The transport of pollutants takes place in one direction and then the other depending on the direction of the flow. View to the southeast. The direction of the arrows is indicative (Jones et al., 2010).

In addition, the smoke near the coast (Figure II.4, top) testifies to the interweaving of thermal flows. The colder, denser, and therefore heavier air slides under the relatively warmer and therefore lighter air (Figure II.4, top). Also, these smokes mark the

beginnings of the sea breeze which will win the entire air mass a few moments later (Figure II.6, below). The pollutants emitted within the urban area are therefore dispersed in an air mass that is gradually warming up, becoming more unstable under the effect of convection and turbulence. They are jointly transported northwards under the effect of the sea breeze. Thus, part of the pollutants probably reached the Grasse Prealps massif by mid-day.

Wind can therefore be beneficial or harmful to air quality, especially if you are downwind of an emitter, as shown in the photo below (Figure II.5).



**Figure (II.5):** Smoke emitted above a thermal inversion (90 m above sea level) and dispersed downstream under the effect of the land breeze. Auribeau-sur-Siagne, view towards the northeast, on 01/30/2011 around 8 a.m (Bouchlaghem et al,2007).

Similarly, (Bouchlaghem et al,2007) proved this for the Sousse region (Tunisia) where ozone and sulfur dioxide concentrations could be multiplied by three when the sea breeze was combined with a synoptic maritime flow advecting the emissions of a power plant on the city. Finally, while it is certain that a weak wind is not favorable to good dispersion of pollutants, it is nevertheless noted through the literature that no established principle would mean that, when the wind blows, except to be very strong or stormy, it is necessarily synonymous with good air quality. Indeed, we have just seen that a synoptic wind could transport gaseous substances over long distances or combine with a thermal breeze to carry pollutants. Just as in the mountains, we are not sure to breathe always

"pure" air, in the absolute, because of the valley and slope breeze capable of advecting pollutants on the massifs as specified by (Dalstein-Richier et al, 2005) as well as (Carrega et al,2010) using air mass tracers. Finally, if the general aerological conditions give the trend, it is observed that the local variations of ventilation show infinitely varied nuances in the spatiotemporal distribution of air pollution (Irchad et al, 2020).

### II.2.6. Impact of wind on air pollution

Its impact can be positive or negative.

- Wind is favorable to the dispersion of pollutants. It intervenes by its direction to direct the plumes of smoke or by its speed to move the pollutants.
- In a simplified way, the wind, depending on its direction and intensity, can disperse the pollutants or concentrate them on a reduced geographical area.
- The wind can carry particles over very long distances (sand clouds, pollens...) (Meersens,2021).

## II.3. Precipitation

### II.3.1. Definition of precipitation

Precipitation is any liquid or frozen water that forms in the atmosphere and falls back to the earth. It comes in many forms, like rain, sleet, and snow. Along with evaporation and condensation, precipitation is one of the three major parts of the global water cycle.

Liquid Precipitation:

- Rain: Droplet diameter  $> 0.5$  mm.
- Drizzle: Droplet diameter  $< 0.5$  mm.
- Fog: Suspended water droplets.
- Freezing rain or drizzle: Causes "meteorological glaze". Supercooled water is common includes up to  $\sim -10^{\circ}\text{C}$  (even possible beyond).

➤ Solid Precipitation:

- Snow.
- Hail.

### II.3.2. The process of precipitation

Precipitation forms in the clouds when water vapor condenses into bigger and bigger droplets of water. When the drops are heavy enough, they fall to the earth. If a

cloud is colder, like it would be at higher altitudes, the water droplets may freeze to form ice. These ice crystals then fall to the earth as snow, hail, or rain, depending on the temperature within the cloud and at Earth's surface. Most rain actually begins as snow high in the clouds. As the snowflakes fall through warmer air, they become raindrops.

Particles of dust or smoke in the atmosphere are essential for precipitation. These particles, called "condensation nuclei," provide a surface for water vapor to condense upon. This helps water droplets gather together and become large enough to fall to the earth.

### **II.3.3. Impact of precipitations on air pollution**

- Rain also has a positive influence on air quality. It allows a good dispersion of atmospheric pollution.
- Heavy precipitation carries the heaviest pollutants to the ground and can sometimes accelerate the dissolution of certain pollutants.
- Overall, pollutant concentrations in the atmosphere decrease significantly during rainy weather, particularly for dust and soluble elements such as suspended particles, sulphur dioxide and nitrogen dioxide (Meersens,2021).

## **II.4. Temperature**

### **II.4.1. Definition of temperature**

Temperature is a key parameter in the study and characterization of climates given its predominant role in radiation and energy balance, hence its capital importance in studies that closely or remotely touch the field of climate change. Temperature is therefore a limiting factor given its implication in the control of all metabolic phenomena and by this fact the total conditioning of the distribution of all living beings (Ramade, 1984). Temperature is considered as a physical quantity linked to the immediate notion of hot and cold. Temperature is the manifestation, at the macroscopic scale, of the movement of atoms and molecules. The thermal regime of a medium is the variation of temperatures recorded in this medium. The annual thermal amplitude is the difference in temperature between the hottest and coldest months during a year. Temperature varies with the seasons, altitude, latitude, and proximity to the sea (Vincent., 2013).

### **II.4.1. Impact of temperature on air pollution**

- Temperatures whether too high or too low are unfavorable to air quality.
- Temperature affects the chemistry of pollutants as well as their emissions.

- Cold temperatures reduce the volatility of certain gases but increase automobile emissions due to less efficient combustion.
- Indirectly, cold weather can generate peaks of fine particles; in cold weather, operating chimneys will be a source of fine particles.
- Heat as well as sunshine favour the photochemical formation of ozone (Meersens,2021).

## II.5. Humidity

### II.5.1. Definition of humidity

The degree of humidity in the air depends on the quantity of water present there. The oceans are the main source of water vapor in the air, as they cover three-quarters of the surface of the planet. Other sources are rivers, lakes and streams, soil, and vegetation (DOUCET, 2006).

### II.5.2. Health impacts of compound risk of humidity and air pollution

Three out of 33 studies had significant findings on the compound risk of humidity and air pollution on human health (Machin et al, 2019; Pande et al, 2002; Lepeule et al, 2018). Yet, the compound effects of all three variables were not the central research of any of these papers. All three papers were observational (two retrospective cohorts and one prospective cohort (Lepeule et al, 2018) studies and focused on urban populations in the following cities: Delhi, India (Pande et al, 2002), Cuiabá, Brazil (Machin et al, 2019), and Boston, USA (Lepeule et al, 2018) (Machin et al, 2019) focused specifically on people over the age of 60 while (Pande et al, 2002) did not limit population by age. (Lepeule et al, 2018) studied males aged 21–80. Both (Pande et al, 2002 and Machin et al, 2019) focused on medical care utilization (hospital or out-patient visits) for respiratory conditions, with (Pande et al, 2002) also studying cardiovascular conditions. Both studies found that there was an inverse relationship between air pollution and humidity variables. Although both studies primarily focused on air pollution impacts, Machin found that hospitalizations of patients over 60 for respiratory conditions were highest when temperature, relative humidity, and rainfall were low. This correlated with a high proportion of wildfires and increased pollution (Machin et al, 2019). Further, (Pande et al,2002) found that Sulphur dioxide (SO<sub>2</sub>), Carbon monoxide (CO), and Nitrogen oxide (NO<sub>x</sub>) were not significant predictors of cardio-respiratory events when

temperature and humidity were included in the model.

### II.5.3. Impact of humidity on air pollution

Humidity influences the transformation of primary pollutants emitted. It plays a key role in the formation and elimination of “acid fog”, which includes:

- sulfuric acid ( $\text{H}_2\text{SO}_4$ ) (formed from sulfur dioxide –  $\text{SO}_2$ )
- nitric acid ( $\text{HNO}_3$ ) (in connection with nitrogen oxides –  $\text{NO}_x$ ) (Meersens,2021).

### Conclusion

The air we breathe is a complex mixture, influenced not only by the pollutants is contingent upon the complex interplay of meteorological factors. While human activities like factories and vehicles undoubtedly contribute pollutants to the atmosphere, their ultimate fate hinges on the interplay between wind, rain, humidity, and temperature. Strong winds act as nature's air freshener, dispersing pollutants across vast distances. Calm conditions, however, allow them to accumulate, leading to hazy skies and poor air quality. Rain serves as a cleansing force, washing away water- soluble pollutants and trapping others within falling raindrops. Humidity plays a more nuanced role, sometimes aiding in the formation of certain pollutants like smog. Heat, too, can exacerbate problems, particularly by contributing to the creation of ozone, a lung irritant.

***Chapter III:***  
***Study site, sampling,***  
***materials and methods***

## Introduction

The work's methodological approach is explained in this chapter. To accurately portray the environmental implications of our study site, we will first describe the study site, followed by the sample, materials, and techniques.

### III.1. Study site

#### III.1.1. Presentation of the GL1K complex

As part of the strategic objective of exploiting natural gas resources mainly from the HASSI R'MEL deposit, LNG plants have been built in the north of the country, the main purpose of which is to export LNG to Europe and the USA by LNG carriers.

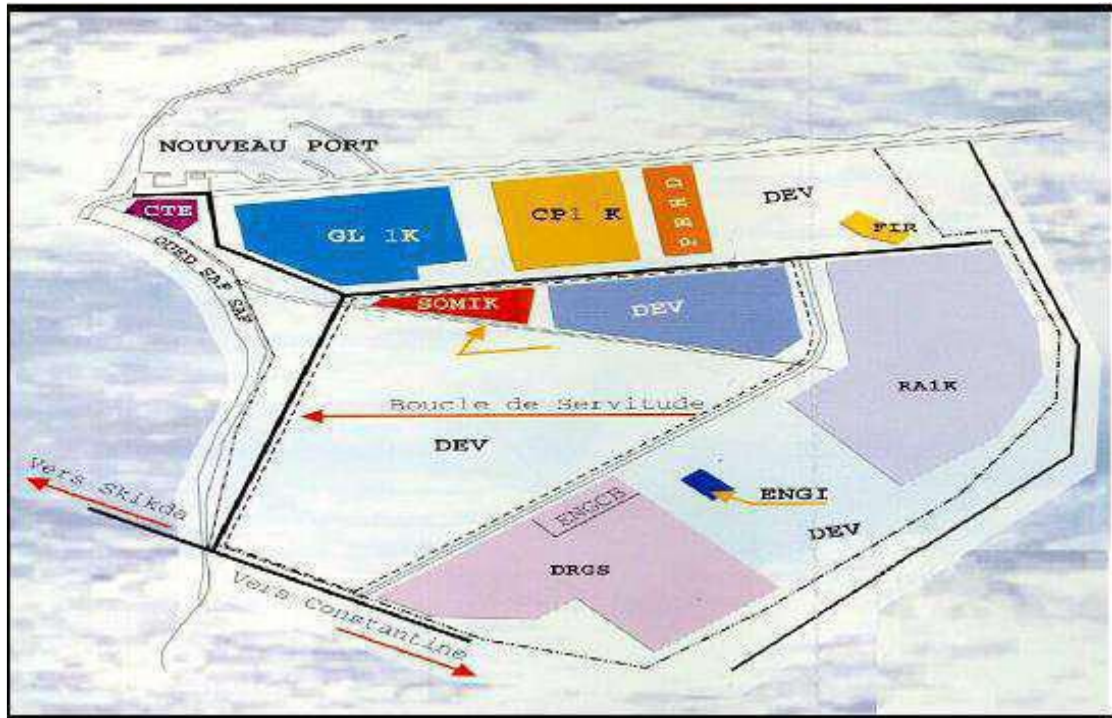
These include the GL1/K complex in Skikda, which began construction in March 1969 and production in November 1972. This complex covers an area of 90 hectares and receives by gas pipeline a length of 580 km and 40 inches in diameter GN from the HASSI R'MEL deposit. Its annual production capacity is 6.7 million m<sup>3</sup> of LNG and a storage capacity of 196,000 m<sup>3</sup> of LNG. It employs 1200 permanent workers (Amiour.I, 2018).



Figure (III.1): GL1K complex.

##### III.1.1.1. Geographical location of the GL1K complex

The plant is located 3 km east of the city of Skikda, it currently covers about 92 hectares.



**Figure (III.2):** Geographical location of the GNL1K complex in the industrial area of Skikda.

### III.1.1.2 Description of the GNL complex facilities

The complex mainly comprises:

- The New LNG Train: the mega train uses the APCI (Air Product and Chemicals Incorporation) process to liquefy NG.
- Unit 10 and Units 5P/6P: for NG liquefaction.
- The LPG unit: for processing and storing propane and butane.
- LNG, LPG, and gasoline storage and shipping facilities.
- Utilities
- The fire protection network:
  - Protect hydrocarbon stocks against fire to mitigate the fire and limit its spread.
  - Control and extinguish the fire, thereby minimizing a potential hazard and limiting its possible spread to other areas of the plant.

**III.1.1.3. Description of GL1K units****a. Counting unit**

Role: Measure and account for all NG entering existing units and the New LNG Train. It includes:

- Three totalizers.
- Three motorized isolation valves.
- A chromatograph to analyze gas composition and density in order to calculate the mass flow rate of incoming NG.
- An online CO analyzer.

**b. Compression unit**

At the outlet of the metering system (42 bar and 25°C), the NG is compressed to 66 bar to facilitate liquefaction. This reduces the energy required for liquefaction, thus increasing the plant's efficiency. This energy is supplied by the gas turbines that drive the refrigeration compressors.

**c. Processing units**

The processing units are:

- The decarbonization unit.
- The dehydration unit.
- The demercurization unit.
- The liquefaction unit.
- The fractionation unit.
- The storage unit.

**III.1.1.4. Process control methods of GL1K**

Automation of an industrial system is to equip it with an industrial control computer system, intended for control for adjustment, and in a more general way for the conduct and automation of the industrial process. In its simplest form, an industrial computer system can be regarded as a control system that is designed at the hardware and software level so that the commanded system evolves in accordance with the criteria and instructions provided by the operator. An industrial process control system consists of software and hardware components. The main components are:

- The sensors used in the GL1K complex:

These are the technological components that provide the measurement interface between the control system and the industrial process, they are of very different types and use the most varied physical phenomena to measure the physical parameters of the process by transforming them into exploitable electrical sizes. There are two families of sensors operated at the complex, either to detect the presence of gas or fire. Detection is carried out according to the environment and the risk involved; it is necessary to define the appropriate detection means to be put in place at the strategic points. At the level of the GL1K complex, gas detection is carried out according to two types of detection:

- Gas either through point gas sensors GG or linear (infrared barriers) GR.
- Cold by GT temperature sensors, for liquefied gas leaks at the level of LNG storage tanks.
- Fire detection is also performed by two types of detection:
  - Smoke from the GS smoke detectors.
  - Flame from the GF flame detector.

### **III.1.2. Natural gas**

#### **III.1.2.1. Definition of natural gas**

Natural gas (NG) is a gas mixture containing mainly hydrocarbon gases. It is colorless and odorless in its pure form. It is the cleanest fossil fuel with the lowest carbon dioxide emissions. NG is also used as an important base material for fertilizers and petrochemicals.

NG was first discovered in Algeria in 1956 in the Hassi R'mel and Ain Amenas fields in the south of the country. This NG produced by the Hassi R'mel field is transported to the complex via a 580 km, 40-inch-diameter pipeline, arriving from the field at a pressure of 42 bar and a temperature of 25°C.

#### **III.1.2.2. Natural gas distribution**

##### **New LNG Train:**

- 36" main supply line.
- 6" line from 1<sup>er</sup> turbo alternator start-up.
- 10" GN make-up line for the following needs:
  - Vacuum protection for LNG, butane, propane and gasoline storage tanks.

- Sweeping of flare manifolds.
- Torch and burner pilots.
- Pressurization/vaporization of the liquid at the Blow down.
- Burner assistance gas.

**Existing units (GL1K):**

- 20" line to unit 10.
- 24" line to 5P/6P units.
- 6" line to fuel network.
- 3" line to pole 2 (torch, LPG, HELISON).

**Production capacity:**

The GL1K Skikda NG liquefaction complex produces:

- LNG production: 4.5 million tones/year.
- Ethane production: 164,700 tones/year.
- Propane production: 207,600 tones/year.
- Butane production: 171,400 tones/year.
- Naphtha production: 108,700 tones/year.
- Helium-rich feed gas production: 163 million Nm<sup>3</sup>/year.

**III.1.2.3. NG treatment and liquefaction processes**

Before liquefaction, the natural gas must undergo several treatments to be freed of elements harmful to the operation of the installation (**Boudjine.M, 2015**).

- Carbon dioxide (CO<sub>2</sub>).
- Water (H<sub>2</sub>O).
- Mercury (Hg).

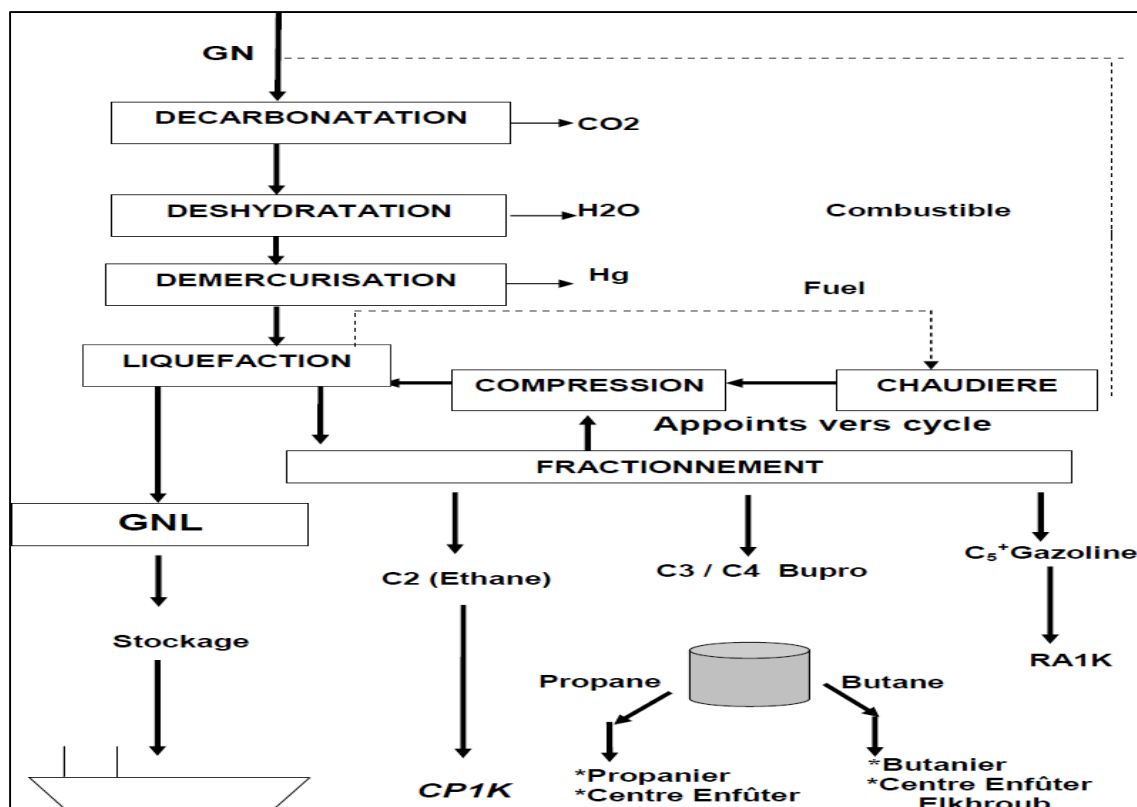


Figure (III.3): GL1K treatment and liquefaction process.

#### III.1.2.4. Liquefaction process

##### III.1.2.4.1. Description of liquefaction process

Natural gas is first transported by pipeline from the source where it was extracted to a liquefaction plant with a seafront and port facilities (Connaissance des énergies, 2025).

In the liquefaction unit, natural gas undergoes several successive treatments:

- **Scrubbing:** involves removing carbon dioxide ( $\text{CO}_2$ ) from natural gas as it can damage liquefaction units by solidifying, as well as hydrogen sulphide ( $\text{H}_2\text{S}$ ) and other sulphur compounds.
- **Dehydration:** water ( $\text{H}_2\text{O}$ ) is removed from the gas to prevent the formation of methane hydrates which can block cryogenic exchangers. Once “dry”, natural gas is almost pure methane. It is also cleaned of all traces of mercury ( $\text{Hg}$ ), a toxic element that can corrode the alloys used in the process.
- **Precooling:** the natural gas is first cooled to a temperature close to  $-30^\circ\text{C}$ . A series of distillations (in the purification columns) allows to isolate heavier hydrocarbons as well as LPG (liquefied petroleum gas: propane and butane). These can be sold as feedstock

in petrochemicals or as fuel.

- Liquefaction: the gas is compressed, cooled to constant pressure and then released. This operation is repeated two or three times in refrigerating columns (heat pumps) from which the gas exits between - 161°C and - 163°C, fully liquid at atmospheric pressure.

The liquefaction process consumes a significant amount of energy: on average, the liquefaction plant uses almost 10% of the gas supplied for its own operation, in particular to supply its heat pumps.

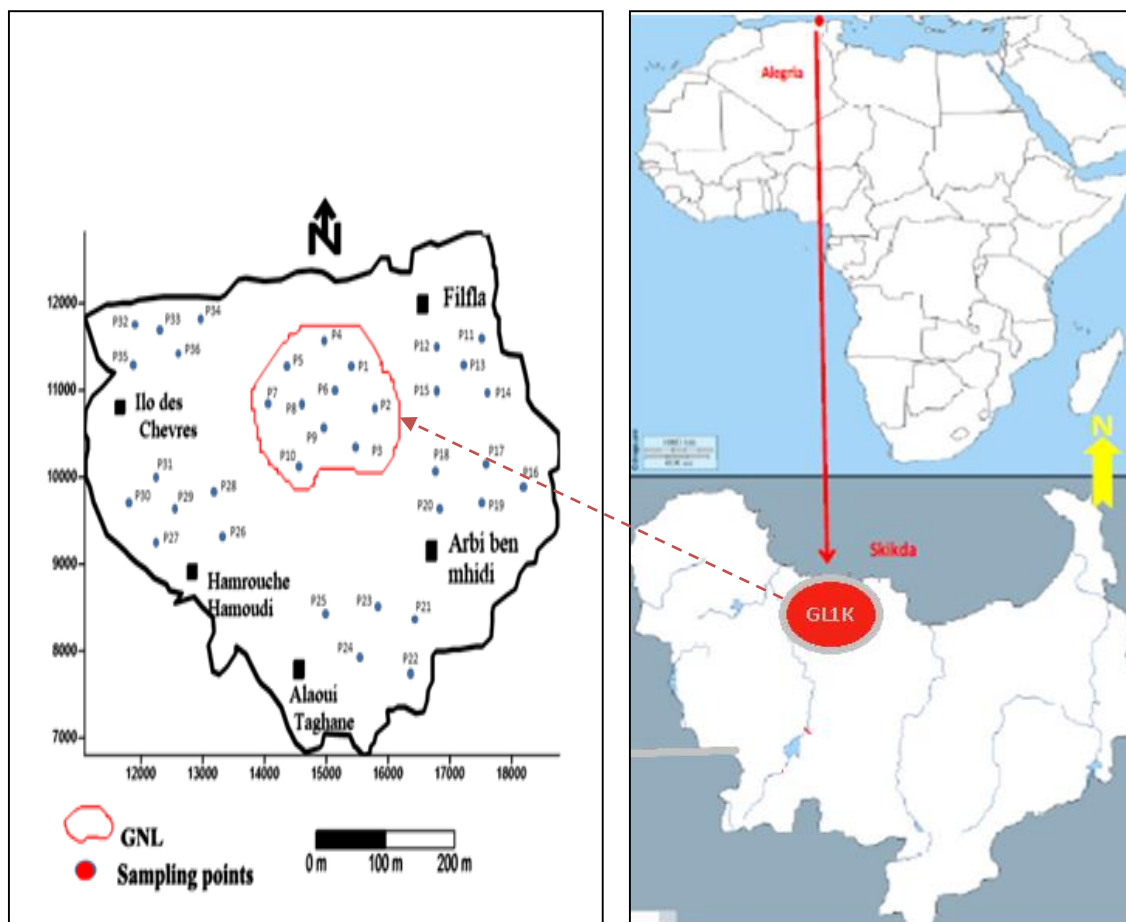
#### **III.1.2.4.2. Liquefaction objectives**

- Liquefaction reduces the volume of natural gas, making it easier and more cost-effective to store and move to consumers.
- Easier importing and exporting for global trade
- Liquefaction allows for rural and offshore locations to have a reliable avenue for accessing natural gas.
- LNG provides an excellent backup for intermittent renewable energy sources like solar and wind power. **(Progas LLC, 2023).**

### **III.2. Sampling**

#### **III.2.1 Description of liquefaction natural gas LNG plant**

The petrochemical complex LNG is a natural gas liquefaction plant and it is situated to about four kilometers to the east of Skikda. It is implanted in the Industrial zone of Skikda located in the Gulf of Stora. The LNG complex is supplied with natural gas from the Hassi R'Mel deposit by a pipeline with a length of 580 km and 40 inches in diameter throughout five compressor stations along the pipeline **(Sonatrach, 2010).**



**Figure (III.4):** Location map of the study area.

Sampling was conducted from June 2019 to May 2020 on 36 sampling sites, including 360 air samples. In Skikda, the air quality is checked via fixed and mobile stations. The stations possess equipment that vary between measuring instruments and analyzers of the pollutants such as Methane ( $\text{CH}_4$ ), Sulfur dioxide ( $\text{SO}_2$ ), Nitrogen oxides ( $\text{NO}_x$ ), and Carbon monoxide ( $\text{CO}$ ). They also contain devices for meteorological measurements. The cloud concentrations have been measured by three portable sensors of type BM25, which cloud has allowed us to calculate the concentration of cloud dispersion that is composed of many partial gases by itself. As a matter of a fact this system operates coherently with the ability to read the air quality daily in the areas most affected by this phenomenon, like the big cities and industrial zones.



Figure (III.5): Sampling sites.

**Table (III.1):** Detailed location of sampling stations.

Sites	Stations	Location
Site 4	P1-P10	LNG plant
Site 5	P26-P31	Hamrouche Hamoudi
Site 3	P16-P20	Arbi Ben M'hidi
Site 1	P11-P15	Filfila
Site 2	P21-P25	Alaoua Taghane
Site 6	P32-P36	L'ilot des chèvres

**Figure (III.6):** Map shows location of study area and sampling points.

### III.3. Materials and methods

#### III.3.1. Description of Tedlar Bag

The Tedlar bag is useful for industrial and research gas sampling. These bags are a simple, cost-effective, and easy way to perform sampling. It can collect gas samples for part-per-billion (ppb) to part-per-million (ppm) levels of inert gasses, organic solvent gases, permanent gasses, and volatile organic compounds (VOCs). It helps in ambient air, indoor air, and stationary source emission testing (**Techinstro, 2017**).



**Figure (III.7):** Tedlar Bag (Techinstro, 2017).

### III.3.2. Description of portable sensor

The BM 25 is a portable gas sensor that can be used in explosive gas atmospheres according to directive ATEX 94/9/EC and the IECEx international certification system. It provides simultaneous detection of up to 5 gases present in the air by means of sensors specific to each risk to be evaluated (under-oxygenation, explosive or toxic gases) (**BM 25 Gas sensor Manual, 2021**).



**Figure (III.8):** BM25 multi-gas sensor (BM 25 Gas sensor Manual, 2021).

### III.3.3. Gas chromatography (GC)

#### III.3.3.1. Definition of gas chromatography

Gas chromatography (GC) is an analytical technique used to separate and detect the chemical components of a sample mixture to determine their presence or absence and/or quantities. These chemical components are usually organic molecules or gases. For GC to be successful in their analysis, these components need to be volatile, usually with a molecular weight below 1250 Da, and thermally stable so they don't degrade in the GC system. GC is a widely used technique across most industries (Technology Networks, 2020).

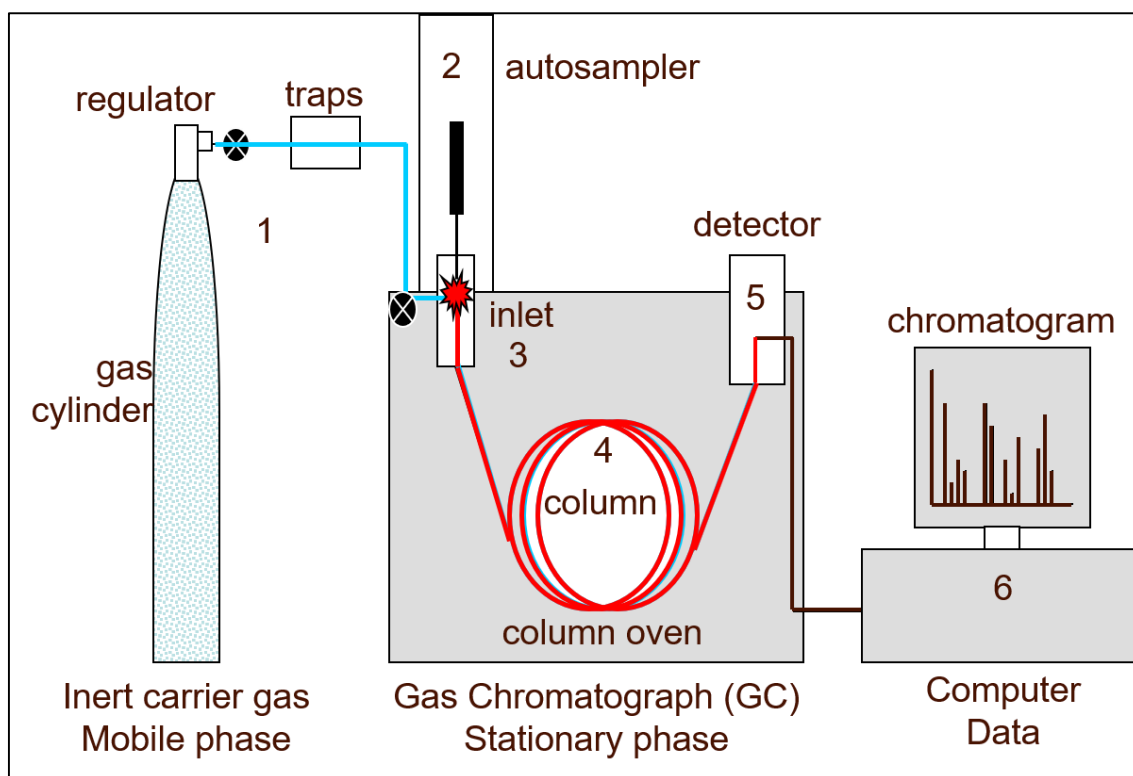
#### III.3.3.2. Mechanism of gas chromatography

GC uses a carrier gas in the separation; this plays the part of the mobile phase (Fig III.9). The carrier gas transports the sample molecules through the GC system, ideally without reacting with the sample or damaging the instrument components.

- The sample is first introduced into the gas chromatograph (GC), either with a syringe or transferred from an autosampler that may also extract the chemical components from solid or liquid sample matrices. The sample is injected into the GC inlet through

a septum which enables the injection of the sample mixture without losing the mobile phase.

- Connected to the inlet is the analytical column, a long (10 – 150 m), narrow (0.1 – 0.53 mm internal diameter) fused silica or metal tube which contains the stationary phase coated on the inside walls.
- The analytical column is held in the column oven which is heated during the analysis to elute the less volatile components.
- The outlet of the column is inserted into the detector which responds to the chemical components eluting from the column to produce a signal.
- The signal is recorded by the acquisition software on a computer to produce a chromatogram.



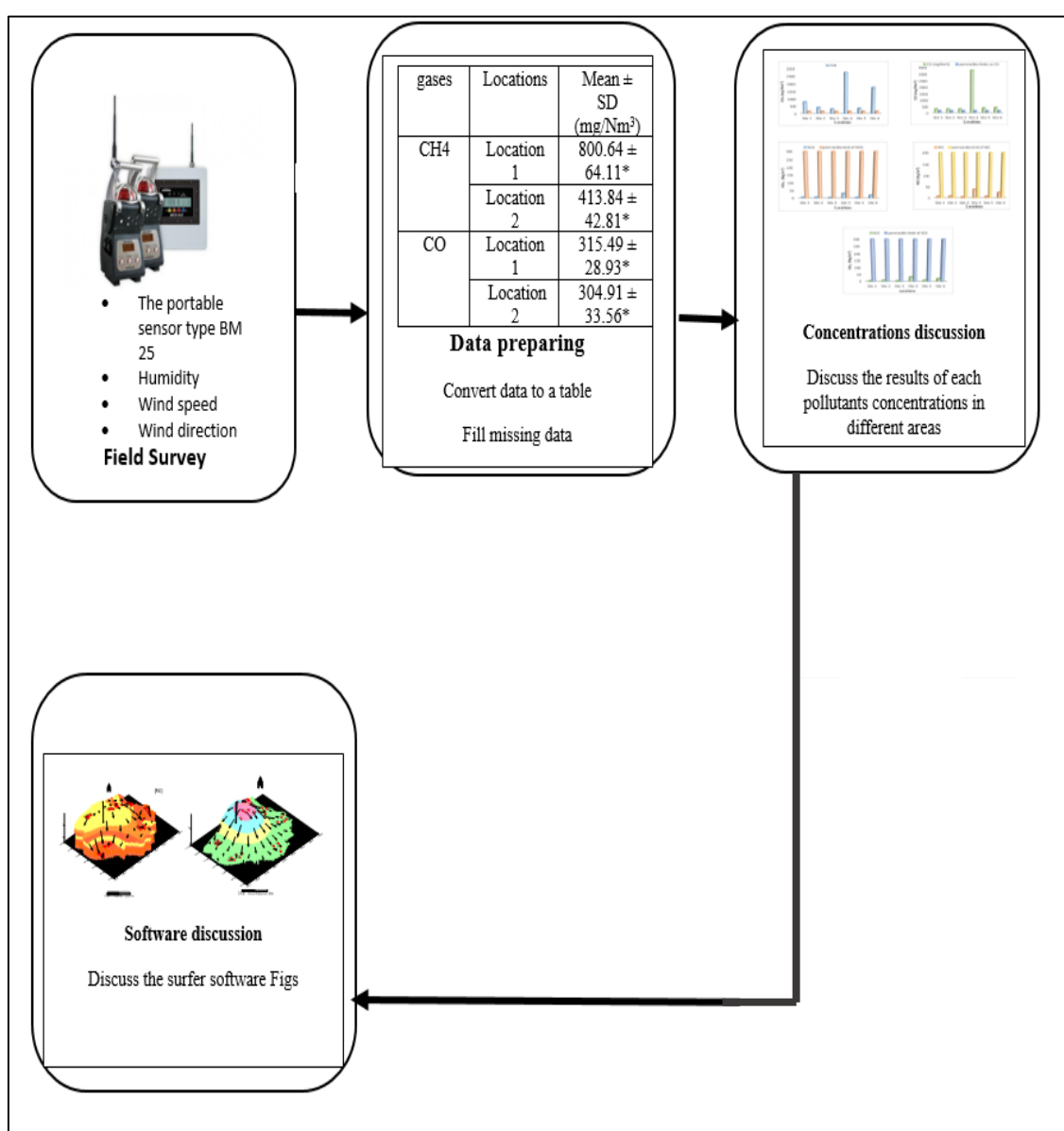
**Figure (III.9):** A simplified diagram of a gas chromatograph (Douabul et al, 2013).

#### III.4. Statistical analysis

Based on the 360 observations, the mean, minimum and maximum values and standard deviations were computed and recorded. Statistical Package for Social Science (SPSS) version 21 was used for computing all statistical analyses. One-Way Analysis of

Variance (ANOVA) was used to test the differences of atmospheric pollutants concentrations between areas. The difference by regions was considered to be significant when at a probability threshold ( $p$ ) is less than 5% ( $p < 0.05$ ). The tests were used to compare means of concentrations of different atmospheric pollutants with Algerian permissible limits.

Principal component analysis (PCA) is a multivariate analysis used in environmental research. PCA has been applied to represent the association between different gases in different areas, and to identify different pollutant sources. Hierarchical Clustering (HC) is a traditional method of dimension reduction (Douabul et al, 2013).



**Figure (III.10):** Proposed method.

### III.5. Statistical of emissions data

Skikda monitors air quality using a network of fixed and mobile stations equipped with various instruments. These include analyzers for pollutants such as methane (CH<sub>4</sub>), sulfur dioxide (SO<sub>2</sub>), nitrogen oxides (NO<sub>2</sub>), and carbon monoxide (CO), as well as devices for collecting meteorological data. Additionally, three portable BM25 sensors measure cloud concentrations. This data allows for calculating the concentration of cloud dispersion, which is composed of various gases. Ultimately, this system provides daily air quality readings in locations most affected by air pollution, such as major cities and industrial zones.

To further explore the data, Principal Component Analysis (PCA) was used to reveal associations between different pollutants across locations and identify potential sources of pollution. Additionally, hierarchical clustering (HC) serves as a traditional dimension reduction technique, providing further insights into the data structure.

### Conclusion

This chapter outlines the methodological framework used to assess air quality around the Skikda LNG plant. It includes an overview of the GLIK complex, sampling strategies, and analytical methods. A total of 360 air samples were collected over 12 months, using Tedlar bags and BM25 detectors for field measurements. Laboratory analysis with gas chromatography quantified pollutants (CH<sub>4</sub>, CO, NO<sub>x</sub>, SO<sub>2</sub>), while multivariate statistical techniques identified patterns and emission sources. The rigorous approach ensures reliable findings and offers a replicable model for environmental assessments in industrial settings.

***Chapter IV:***  
***Results and discussion***

## Introduction

Skikda's air quality is likely influenced by its location, but more research is needed. This should explore how weather patterns interact with various pollution sources. Interestingly, Skikda's environment offers potential advantages. The city benefits from natural ventilation due to its proximity to the Mediterranean Sea, and highlights the presence of diverse microclimates and periods of heavy rainfall, which could help disperse pollutants (Bokwa, 2019).

This study aims to assess air quality and how specific pollutants (methane, carbon monoxide, nitric oxide, nitrogen dioxide, and sulfur dioxide) emitted from the nearby Skikda LNG plant behave in surrounding areas. We will also consider how wind, rain, temperature, and humidity affect these pollutants.

### IV.1. Results and discussion

The measured concentration of atmospheric pollutants in the six sites revealed the presence of atmospheric pollutants, represented in boxplot form in Fig (IV.1). The statistical description of all atmospheric pollutants, including CH<sub>4</sub>, NO, NO<sub>2</sub>, SO<sub>2</sub> and CO and the analysis of variance by one-way ANOVA are given in Table (IV.1).

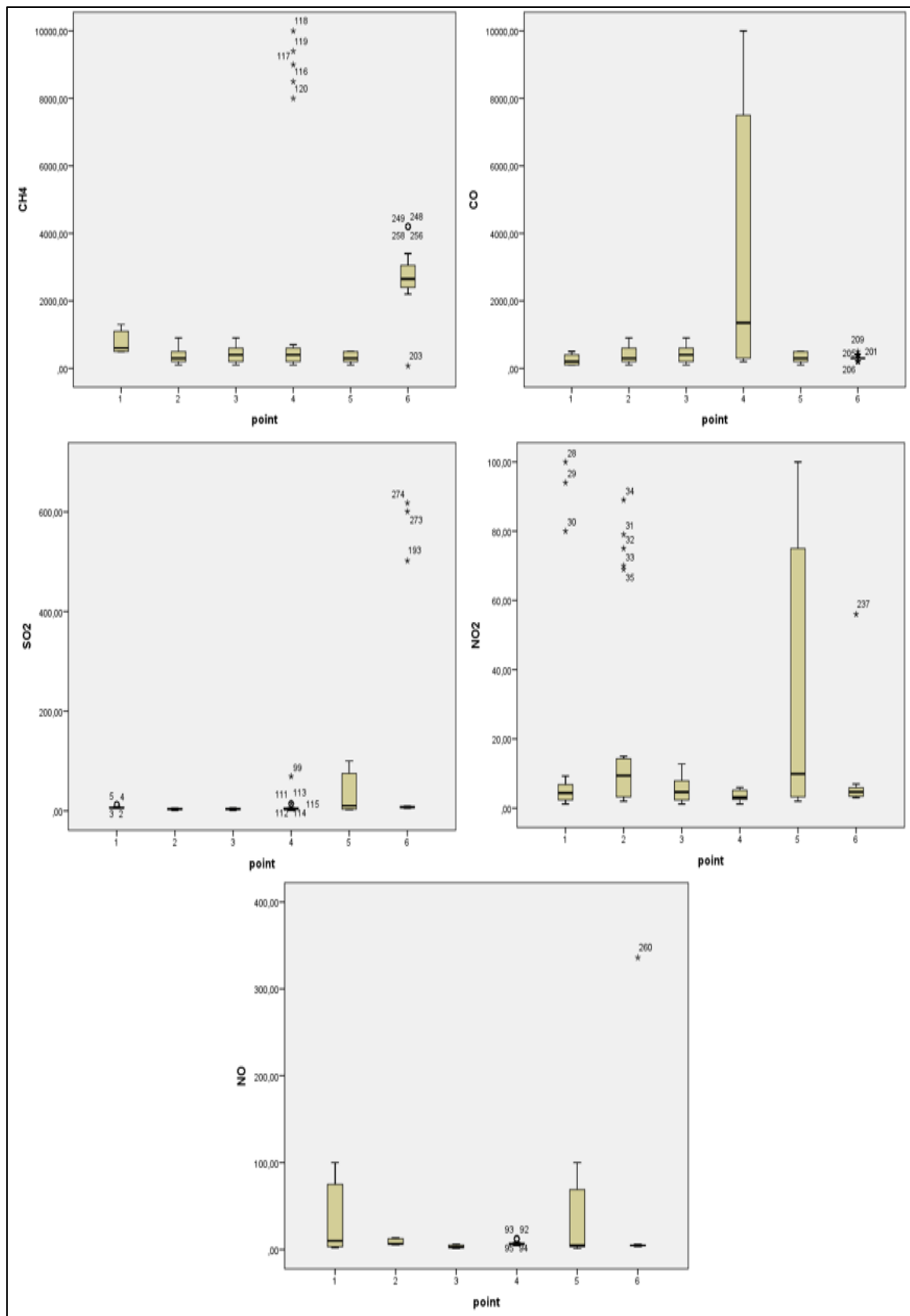


Figure (IV.1): Box plots of hazardous gas concentration ( $\mu\text{g}/\text{Nm}^3$ ) for air in study area.

**Table (IV.1):** Comparison of atmospheric pollutant concentration ( $\mu\text{g}/\text{Nm}^3$ ) in the air around the LNG plant in Skikda.

Gases	Site	Mean $\pm$ SD ( $\mu\text{g}/\text{Nm}^3$ )	Min ( $\mu\text{g}/\text{Nm}^3$ )	Max ( $\mu\text{g}/\text{Nm}^3$ )	LMP ** ( $\mu\text{g}/\text{Nm}^3$ )	One way ANOVA	
						F	P
CH <sub>4</sub>	Site 1	800.64 $\pm$ 64.11*	500.70	1300.48	150	55.15	0.0001
	Site 2	413.84 $\pm$ 42.81*	110.17	900.25			
	Site 3	310.52 $\pm$ 29.3*	98.91	499.76			
	Site 4	2775.88 $\pm$ 49.65*	74	4200.98			
	Site 5	367.21 $\pm$ 42.97*	111.03	925.43			
	Site 6	1780.41 $\pm$ 600.93*	100.20	10000			
CO	Site 1	315.49 $\pm$ 28.93*	99.20	500.94	150	33.80	0.0001
	Site 2	304.91 $\pm$ 33.56*	100.20	500.94			
	Site 3	301.60 $\pm$ 4.26*	200.11	500.01			
	Site 4	3313.64 $\pm$ 683.1*	250.01	10000			
	Site 5	380.55 $\pm$ 44.30*	100.26	900.25			
	Site 6	414.02 $\pm$ 43.01*	100.20	906.23			
NO <sub>2</sub>	Site 1	5.06 $\pm$ 0.37*	3.01	56	300	15.21	0.0001
	Site 2	5.68 $\pm$ 0.66*	1.2	12.75			
	Site 3	3.60 $\pm$ 0.3*	1.20	5.94			
	Site 4	31.38 $\pm$ 2.56*	1.98	98.85			
	Site 5	4.20 $\pm$ 0.49 *	1.20	9.25			
	Site 6	19.17 $\pm$ 4.86*	2.01	89			
NO	Site 1	7.08 $\pm$ 0.46*	4.58	12.75	200	7.23	0.0001
	Site 2	8.44 $\pm$ 0.58*	5.40	13.50			
	Site 3	3.24 $\pm$ 0.30*	1.20	5.94			
	Site 4	39.28 $\pm$ 8.33*	2.50	100			
	Site 5	6.88 $\pm$ 2.3*	3.16	336			
	Site 6	24.59 $\pm$ 6.51*	1.20	100			
SO <sub>2</sub>	Site 1	3.37 $\pm$ 0.29*	1.20	5.94	300	1.32	0.26
	Site 2	7.64 $\pm$ 2.25*	1.20	69			
	Site 3	3.21 $\pm$ 0.29*	1.20	5.69			

	Site 4	31.94 ± 6.84*	2.01	100			
	Site 5	7.67 ± 0.55 *	5.59	12.75			
	Site 6	19.17 ± 6.79*	5.01	618			

Table (IV.1) shows that there were significant differences between CO levels in the six areas.

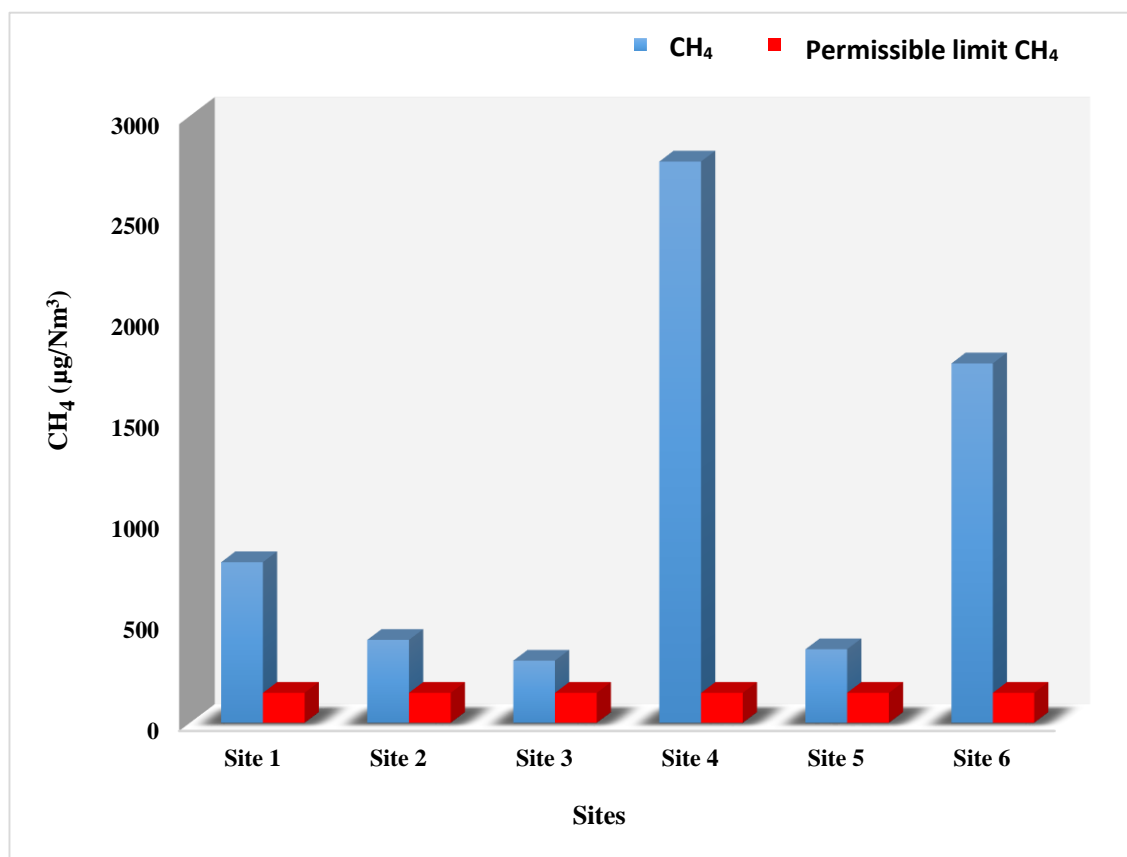
**SD:** refer to Standard Deviation of gases concentration

**F:** refer to Friedman values of one way ANOVA

**p:** refer to significant of ANOVA

**\***: Significant differences from Algerian permissible limits ( $P < 0.05$  of t-Student test) are marked with asterisks

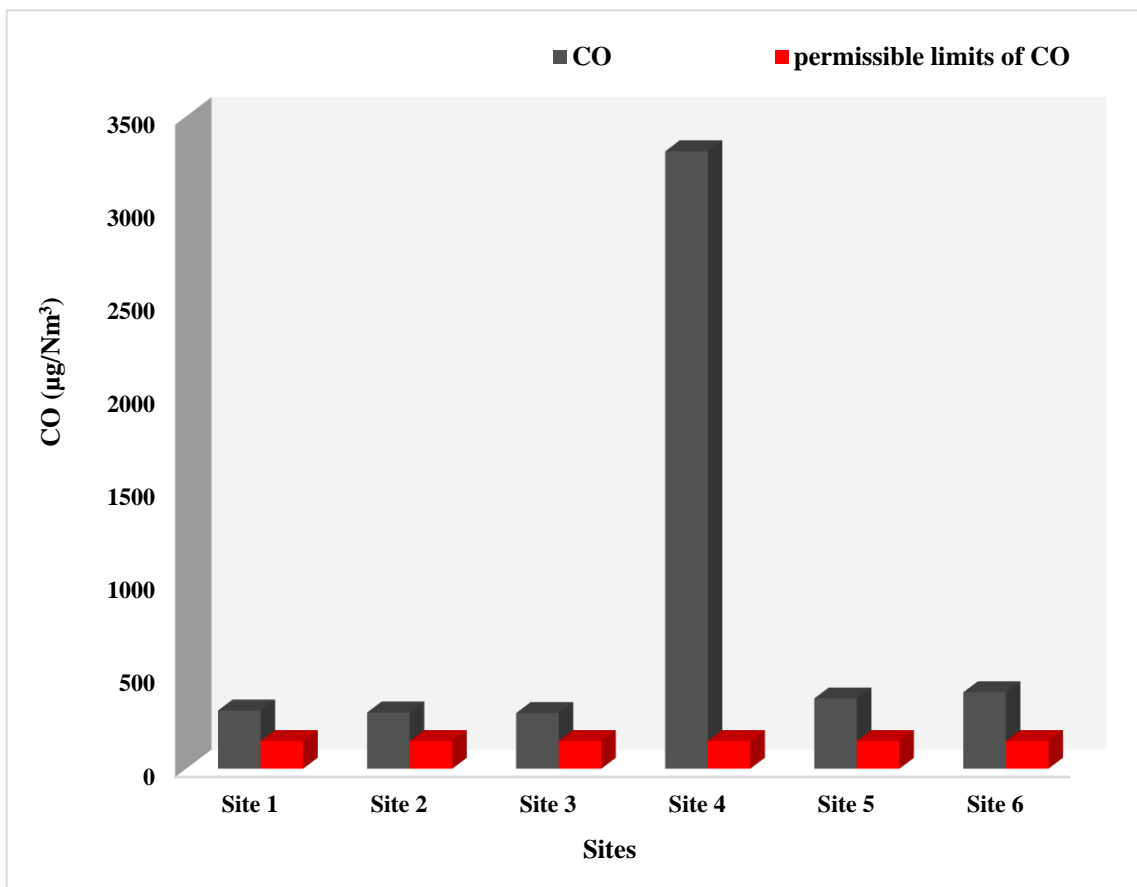
**\*\*LMP:** The Official Journal of the Algerian Republic, dated July 2003, (No. 03 of 10), published on 19 July 2003 (**Official Journal of the Algerian Republic, 2003**).



**Figure (IV.2):** Concentration of CH<sub>4</sub> (µg/Nm<sup>3</sup>).

Fig (IV.2) shows the mean concentration levels of CH<sub>4</sub> in the six sites of Skikda, with a total sample population of 360. The maximum concentration of CH<sub>4</sub> found in S4

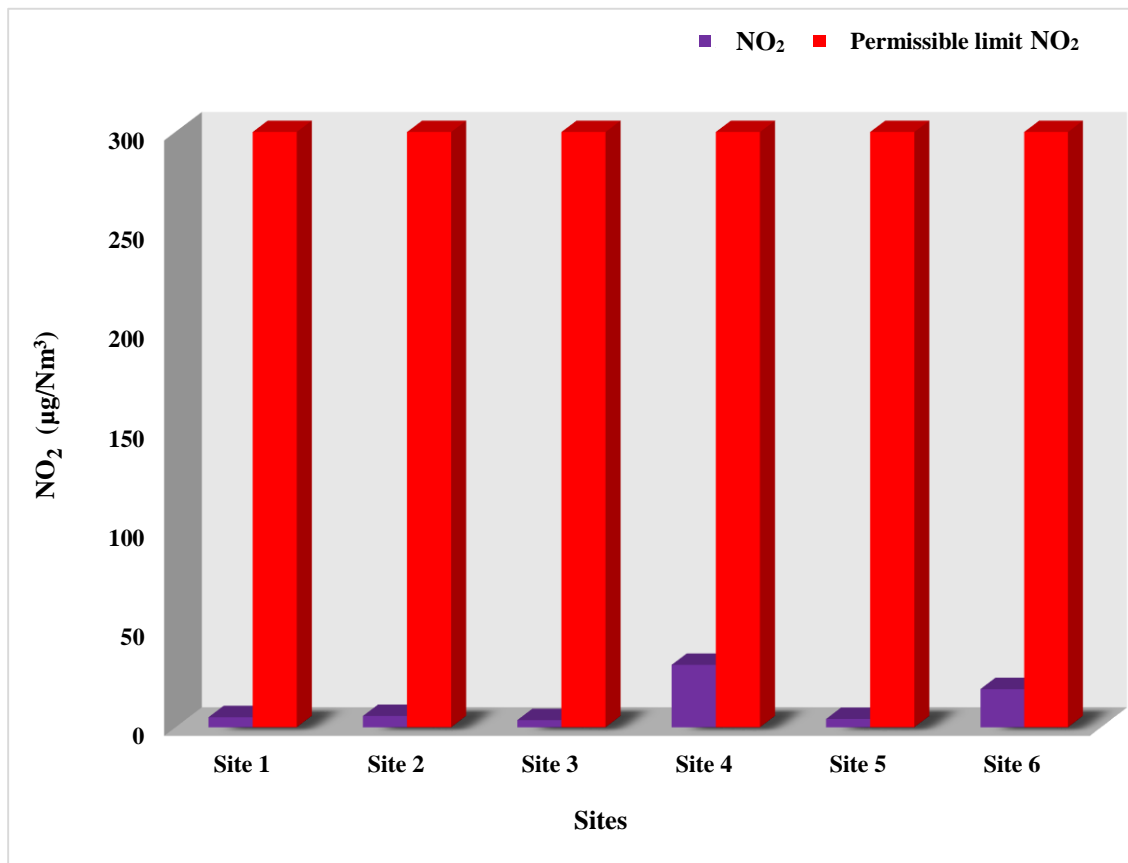
(LNG plant) ranged from  $74 \mu\text{g}/\text{Nm}^3$  to  $4200.98 \mu\text{g}/\text{Nm}^3$  with a mean of  $2775.88 \mu\text{g}/\text{Nm}^3$  and a standard deviation of  $49.65 \mu\text{g}/\text{Nm}^3$ . On the other hand, the lowest concentration of  $\text{CH}_4$  was detected in S3 compared to other sites. The level of  $\text{CH}_4$  in the six sites was significantly different and higher than the permissible limit of  $150 \mu\text{g}/\text{Nm}^3$ . However, the one-way ANOVA analysis revealed a significant difference in  $\text{CH}_4$  concentration among the different sites (ANOVA,  $F=55.15$ ,  $p<0.05$ ) because of the activities related to natural gas liquefaction and refining of petroleum.



**Figure (IV.3):** Concentration of CO ( $\mu\text{g}/\text{Nm}^3$ ).

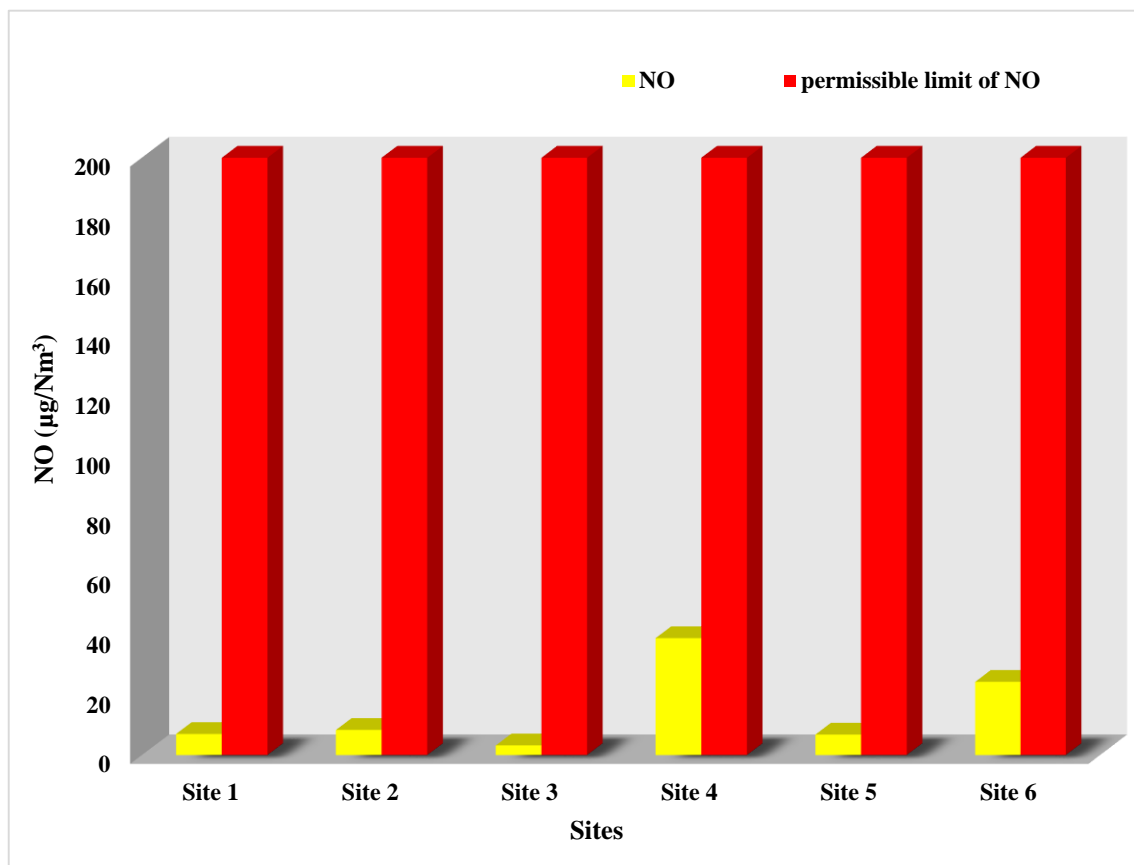
Fig (IV.3) shows the mean concentration of CO in the six studied sites. The highest mean concentration of CO was detected in S4, representing the LNG plant ( $3313.64 \mu\text{g}/\text{Nm}^3$ ). CO atmospheric pollution is the outcome of the activities related to flue gases following petroleum refining activities, natural gas liquefaction, and automobile escape gases. The lowest mean concentration of CO was found in S6 with  $301.60 \mu\text{g}/\text{Nm}^3$ . As shown in Table (IV.1), the test of CO demonstrated that the mean

concentrations in the studied sites were remarkably different and high compared to the limit threshold value. A comparison of CO concentrations between the studied areas showed significant differences (Fig IV.3) (ANOVA,  $F=33.80$ ,  $p<0.05$ ).



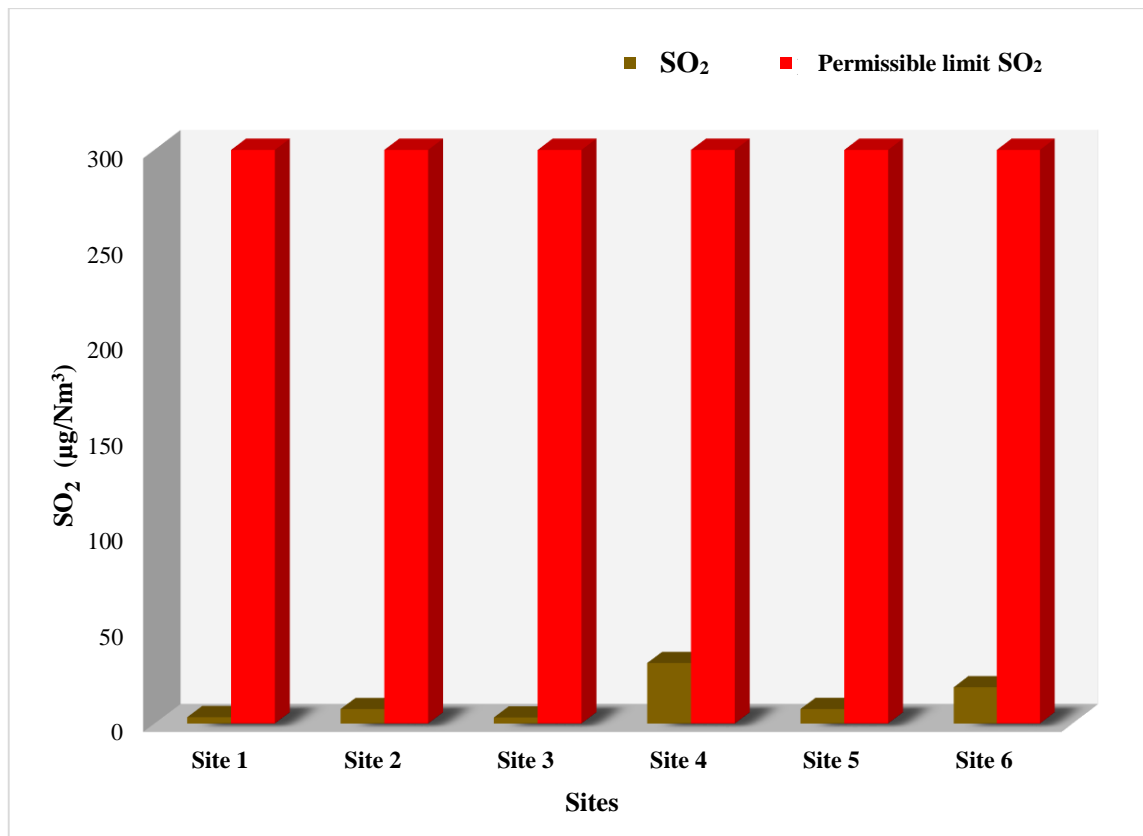
**Figure (IV.4):** Concentration of NO<sub>2</sub> (µg/Nm<sup>3</sup>).

Fig (IV.4) presents the variation of the mean concentration of NO<sub>2</sub> between sites. The mean maximum and minimum concentrations of NO<sub>2</sub> were 31.38 µg/Nm<sup>3</sup> and 3.60 in S4 and S3, respectively. The NO<sub>2</sub> levels in the six studied areas were lower than the permissible limits, and the ANOVA test revealed significant differences between the studied areas (ANOVA,  $F=15.21$ ,  $p<0.05$ ).



**Figure (IV.5):** Concentration of NO ( $\mu\text{g}/\text{Nm}^3$ ).

The measured concentrations of NO in atmospheric samples of the studied sites are shown in Fig (IV.5). The maximum and minimum mean concentrations were  $39.28 \mu\text{g}/\text{Nm}^3$  and  $3.24 \mu\text{g}/\text{Nm}^3$ , respectively, detected in S4 and S3. The one-way ANOVA analysis revealed a significant difference in NO concentration among the different sites (ANOVA,  $F=7.23$ ,  $p<0.05$ ).



**Figure (IV.6):** Concentration of SO<sub>2</sub> (µg/Nm<sup>3</sup>).

Fig (IV.6) shows the concentration level of SO<sub>2</sub> in the six study areas in Skikda, with a sample population of 60. The maximum mean concentration of SO<sub>2</sub> was 31.94 µg/Nm<sup>3</sup> found in S4 (LNG plant). However, the lowest mean concentration was found in S3 with 3.21 µg/Nm<sup>3</sup> compared to other sites. As shown in Table (IV.1), the mean concentrations in the regions studied do not exceed the limits allowed for SO<sub>2</sub>. For these reasons, there were no differences between the means of SO<sub>2</sub> (ANOVA, F=1.32, p>0.05) in the six areas.

This study also shows that the mean concentrations of gas for the six sites types S1, S2, S3, S4, S5, and S6 follow the order Classification by site:

- S1: CH<sub>4</sub>>CO >NO>NO<sub>2</sub>>SO<sub>2</sub>.
- S2: CH<sub>4</sub>>CO>NO>SO<sub>2</sub>>NO<sub>2</sub>.
- S3: CH<sub>4</sub>>CO>NO<sub>2</sub>>NO>SO<sub>2</sub>.
- S4: CH<sub>4</sub>>CO>NO>SO<sub>2</sub>>NO<sub>2</sub>.
- S5: CO>CH<sub>4</sub>>SO<sub>2</sub>>NO>NO<sub>2</sub>.
- S6: CO>CH<sub>4</sub>>SO<sub>2</sub>>NO>NO<sub>2</sub>.

Trends in gas concentrations in the different sites were in the following order:

- CH<sub>4</sub>: S<sub>4</sub>>S<sub>6</sub>>S<sub>1</sub>>S<sub>2</sub>>S<sub>5</sub>>S<sub>3</sub>.
- CO: S<sub>4</sub>>S<sub>6</sub>>S<sub>5</sub>>S<sub>1</sub>>S<sub>2</sub>>S<sub>3</sub>.
- NO<sub>2</sub>: S<sub>4</sub>>S<sub>6</sub>>S<sub>2</sub>>S<sub>1</sub>>S<sub>5</sub>>S<sub>3</sub>.
- NO: S<sub>4</sub>>S<sub>6</sub>>S<sub>2</sub>>S<sub>1</sub>>S<sub>5</sub>>S<sub>3</sub>.
- SO<sub>2</sub>: S<sub>4</sub>>S<sub>6</sub>>S<sub>5</sub>>S<sub>2</sub>>S<sub>1</sub>>S<sub>3</sub>.

Table (IV.1) shows that the air collected behind the LNG plant contains the following air pollutants: CH<sub>4</sub>, CO, NO, NO<sub>2</sub> and SO<sub>2</sub>. However, differences in atmospheric pollutant levels among the sites can be attributed to various petroleum plant activities. Moreover, results revealed that the samples contained hazardous levels of atmospheric pollutants, especially the constituents of natural gas, which include CH<sub>4</sub>. The composition of natural gas can explain the presence of CH<sub>4</sub>. As a result, CH<sub>4</sub> contributes to global warming potential concerning the previous estimate. It absorbs radiation at a shorter wavelength in the lower atmosphere. CH<sub>4</sub> is a greenhouse gas that contributes to Climate Change (**Etminan et al ,2016; Jackson et al, 2020**).

This study is similar to those of (**Ghasemzade et al, 2017**) The study found that CH<sub>4</sub> is a substantial problem, particularly in highly urbanized, industrialized regions of nations with petrochemical activity like petroleum refining and natural gas liquefaction (**Likus-Cieřlik et al, 2020**).

Whereas the presence of the pollutants, CO, can be explained by emissions from industrial petrochemical activities due to flare releases and gas leaks at the natural gas liquefaction complex, emissions from fossil-fuel-powered engines and Produced gas in landfills (**Ghasemzade et al, 2017**).Carbon monoxide (CO) is a pollutant that can adversely affect human health as it can reduce the delivery of oxygen to the body's organs and tissues (**Jalali et al, 2019**).

On the other hand, the lowest values are found far away from roads and in proximity to residential areas and green spaces. Furthermore, results pointed out that the samples contained hazardous levels of SO<sub>2</sub>, especially near the LNG plant of Skikda. The presence of SO<sub>2</sub> can be explained by the pretreatment of natural gas petroleum fuels, which consists of desulfurization as flared gases and a significant role in energy production, especially crude oil production (**Salmabadi et al, 2019**).

According to the results obtained and compared to the Algerian standard, the NO<sub>2</sub>

and NO concentrations do not exceed Algerian limits. NO<sub>2</sub> is produced from anthropogenic emissions, industrial burning of fossil fuels: oil, gas, and coal; vehicle exhaust, electricity and natural sources (soils through the decomposition process of nitrates and lightning).

In addition, results suggest that the natural gas liquefaction activities at the Skikda LNG plant could harm the health of sensitive individuals working in the plant's operational areas and those living nearby. Several studies conducted that NO<sub>x</sub> can cause human health impacts (Afghan et al, 2020).

Based on the concentration of atmospheric pollutants in all of this study's samples, the trends gases concentrations in the different sites were in the following order: CH<sub>4</sub>> CO > NO > NO<sub>2</sub>> SO<sub>2</sub>, which is in accordance with the overall trend in the literature of Liquefied natural gas (LNG) plants. Overall, all measurements show cased the necessity to take action to reduce the emission of pollutants and gases emitted from LNG plants.

Subsequently, people living near roads or industrial areas are endangered on a daily basis to several harmful emissions that may affect their health. Thus, a proper strategy should be applied to reduce air pollution in this area.

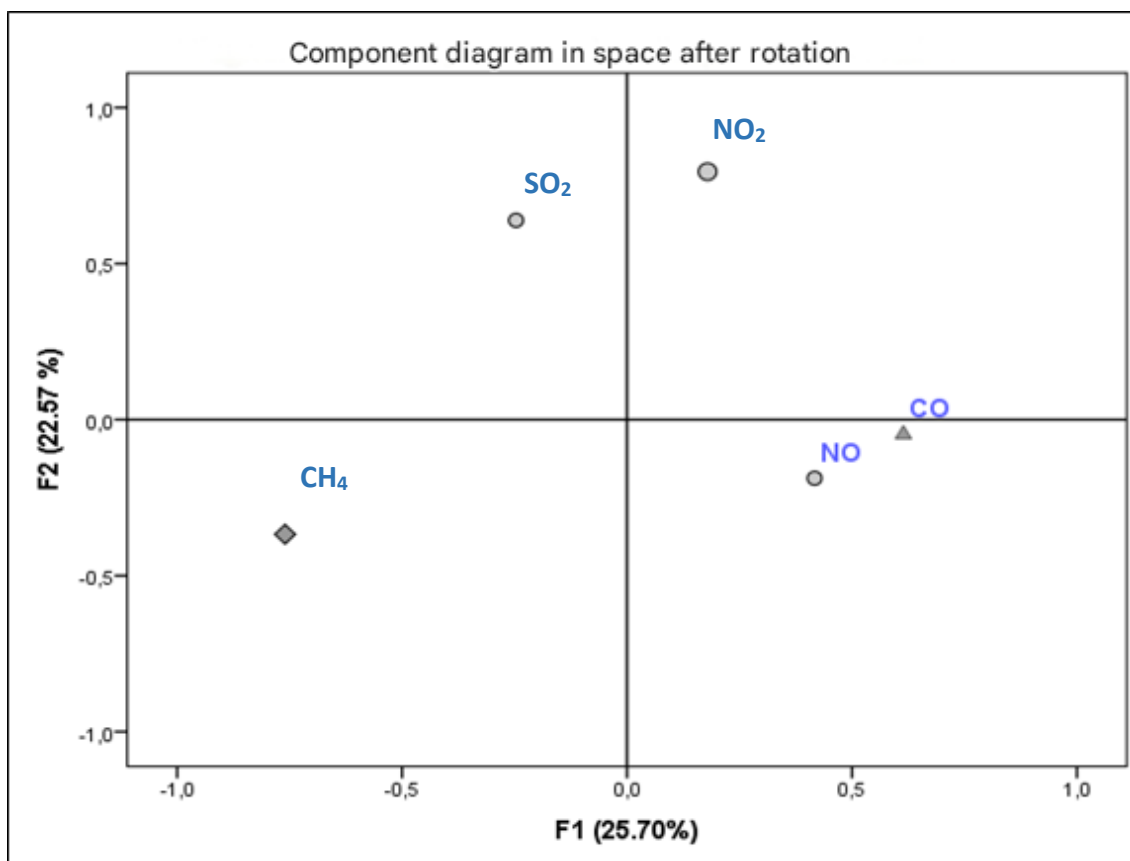
#### **IV.2. Application of principal component analysis (PCA) to atmospheric pollutants correlation study**

Multivariate statistical methods such as principal component analysis and cluster analysis were widely applied to study differences and correlations between atmospheric pollutants concentrations to find the distributions of pollutants in explored areas. They are efficient in representing air pollutants.

The correlation matrix is helpful because it can point out associations between variables that can show the overall coherence of the dataset and identify the influence factors, which help identify the sources of different elements. Table (IV.2) presents the correlation matrix of the five gas variables in the atmosphere. Only those with correlation values greater than 0.50 are taken into account. However, the gas correlation matrices show that different gas pollutants do not have positive correlations.

**Table (IV.2):** Correlation matrix calculated using Pearson coefficients between pollutants.

	CO	NO	NO <sub>2</sub>	SO <sub>2</sub>	CH <sub>4</sub>
CO	1,000	-0,006	-0,023	-0,011	-0,171
NO	-0,006	1,000	-0,036	-0,023	-0,102
NO <sub>2</sub>	-0,023	-0,036	1,000	0,138	-0,214
SO <sub>2</sub>	-0,011	-0,023	0,138	1,000	0,014
CH <sub>4</sub>	-0,171	-0,102	-0,214	0,014	1,000



**Figure (IV.7 (a)):** Loading plot of variables.

Principal Component Analysis (PCA) has been implemented to study differences and correlations between the air gas concentrations to find the distribution of the atmospheric pollutants in explored areas. According to the results, waste gas

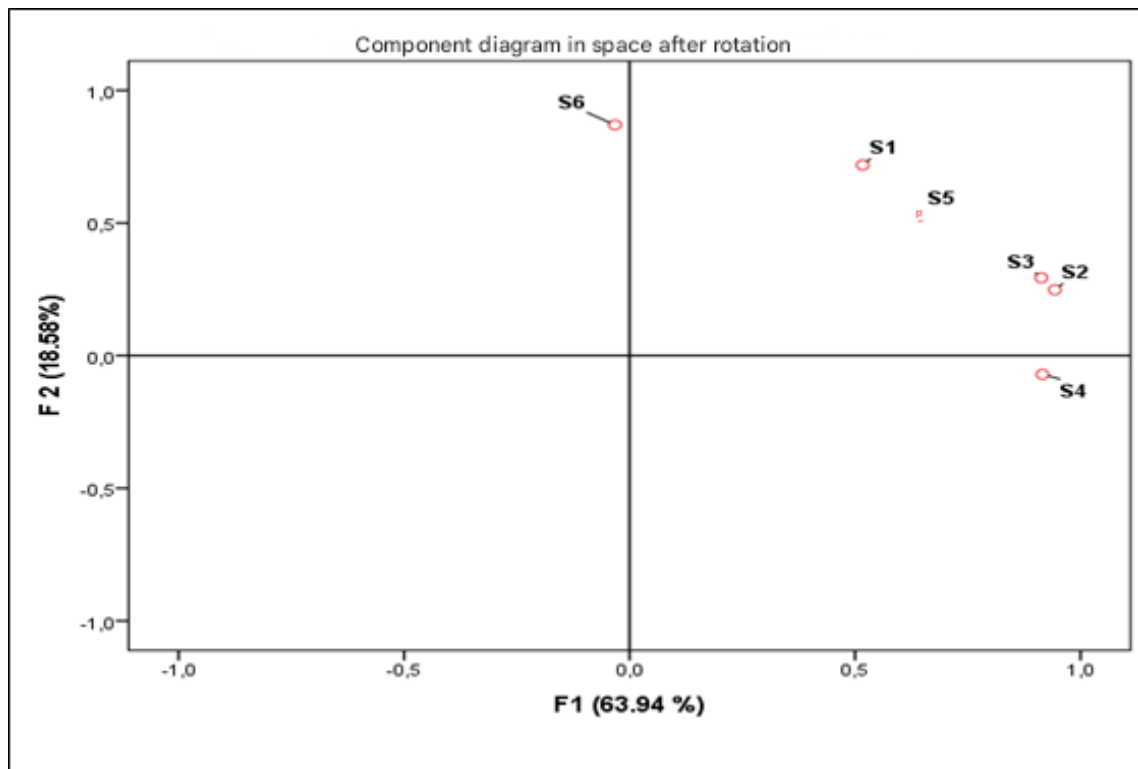
concentrations in different regions can be arranged into two principal components, described as 25.70 % and 22.57% of the variability observed in gas levels produced in various study areas. It can be observed from Fig (IV.7 (a)) that the correlation between CO and NO was significant. These results imply that CO, CH<sub>4</sub> and NO may originate from a similar pollution source: the LNG plant. These results could prove that the complexity of natural gas liquefaction is a significant source of NO, CO and CH<sub>4</sub> pollution.

In addition, the principal component analysis and factor analysis were performed for sites on 365 observation points. PCA better explains the possible groups/sources that influence air systems (Table IV.3, Fig IV.7 (b)).

**Table (IV.3):** Correlation matrix calculated using Pearson coefficients between sites.

	S1	S2	S3	S4	S5	S6
S1	1,000	0,639	0,671	0,320	0,732	0,422
S2	0,639	1,000	0,956	0,841	0,669	0,229
S3	0,761	0,956	1,000	0,780	0,660	0,251
S4	0,321	0,841	0,780	1,000	0,479	0,065
S5	0,732	0,669	0,660	0,479	1,000	0,279
S6	0,422	0,229	0,251	0,065	0,279	1,000

From table (IV.3), the site correlation matrices show that different preferment sites pairs have strong positive correlations between S2 and all other sites, including S2-S4 ( $r = 0,841$ ), S2- S5 ( $r = 0,669$ ), S3-S4( $r = 0,780$ ), S3-S5 ( $r = 0,660$ ), S1-S5( $r = 0,732$ ), S1-S2 ( $r = 0,639$ ) and S1-S3( $r = 0,671$ ). S2 is strongly and positively correlated with S3 ( $r = 0,956$ ). The results obtained show that gas in the atmosphere have a common source.



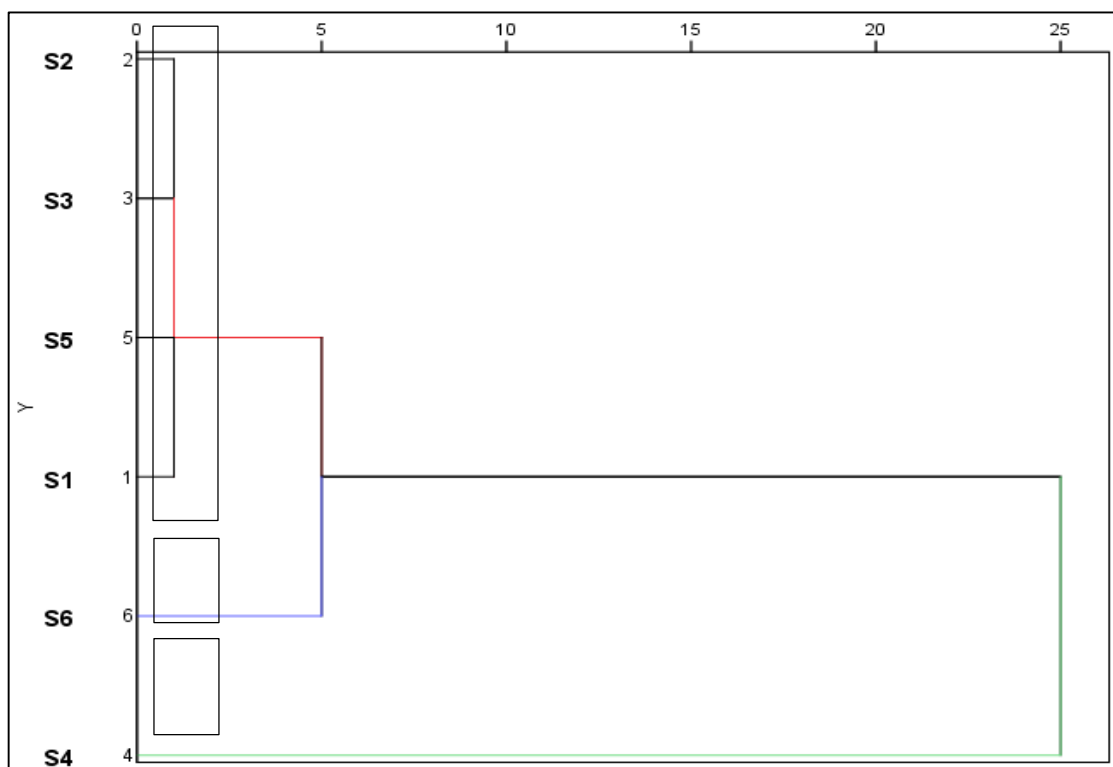
**Figure (IV.7 (b)):** Score plot of samples sites.

From the loading plot in Fig (IV.7 (b)), it was observed that the concentration of waste gas in S4 can be correlated more easily. The F1 axis described 63.94 % is linked to S4, representing the LNG Skikda plant, the most polluted site. The F1 axis is related to S4, S2, and S3 on the right side. While the F2 axis described 18.58 % and is associated with S6, S1 and S5.

Comparing between the two plots in Fig (IV.7) assisted to identify the variations between sites and their different atmospheric pollutants. Looking at the two plots in Fig (IV.7(a)), a distinctive variety among regions was observed, and the various pollutants introduced in them were also seen.

#### IV.2.1. Hierarchical cluster analysis

The cluster analysis has successfully classified hazardous and contaminated sites by identifying the spatial similarity between the studied sites according to atmospheric pollutants. It identifies polluted areas. This study used cluster analysis to visualize air pollutant clustering. Fig (IV.8) shows the results. The Dendrogram of 6 sampling sites for atmospheric pollutants is divided into three major clusters in Fig (IV.8).



**Figure (IV.8):** Dendrogram of Hierarchical Cluster Analysis of sampling stations from area.

Cluster 1 has four sites: S1, S2, S3 and S5. These sites are the regions around the petrochemical complex where atmospheric pollution spreads; even inhabitants in the Hamrouche Hamoudi sites constitute a risk for the population. Whereas cluster 2 consists of site 6, close to the industrial area, generating significant pollution. However, cluster 3 consists only of S4. This point of Natural gas liquefaction complex LNG plant is the primary source of air pollution. These findings show that the spatial groupings produced from the multivariate analysis are the same.

#### **IV.2.2. Spatial distribution of pollutant's concentrations**

The distribution maps of CH<sub>4</sub>, CO, NO, NO<sub>2</sub>, and SO<sub>2</sub> (Figs IV.9 to IV.18) were generated using the "Kriging" method in Surfer software (version 10.1.561, March 1, 2011). The specific procedure for generating these maps is outlined below:

In the process of creating detailed visual representations of pollutant distributions, the transition from data compilation to final map production in Surfer involves several critical steps. Initially, a table capturing pollutant concentrations alongside X and Y

coordinates (and optionally Z for 3D modeling) is prepared. Subsequently, this data is imported into Surfer, where the coordinate system is defined to ensure spatial accuracy. Employing the Kriging interpolation method with carefully chosen parameters and cell sizes facilitates the generation of a precise gridded representation. From this gridded data, contour maps are then created, which are further enhanced through customization with a color palette tailored to highlight concentration gradients effectively. Optionally, integrating a base map provides additional contextual information. Finally, leveraging Surfer's suite of analytical tools allows for in-depth exploration of spatial patterns, facilitating the extraction of meaningful insights regarding pollutant distribution and environmental impact.

Note: The red line in each distribution map marks the study area, complex GL1K, in the City of Skikda (Algeria).

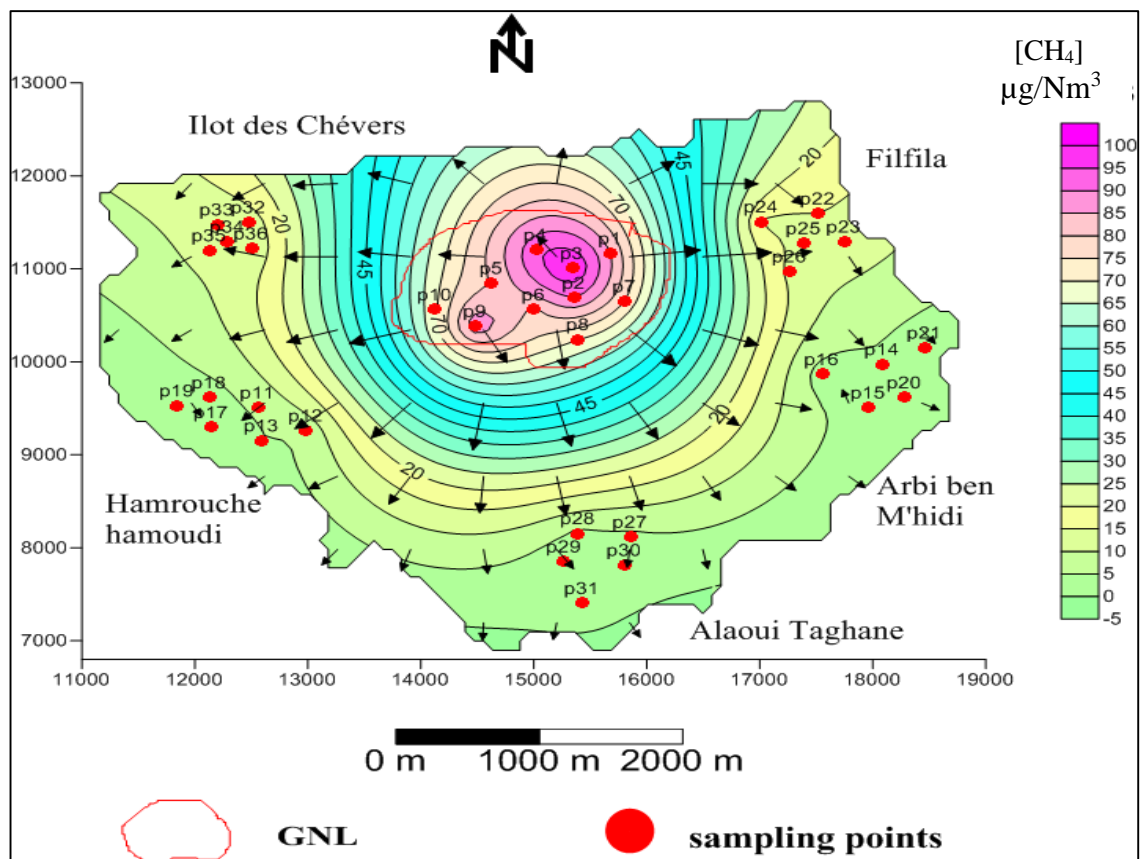
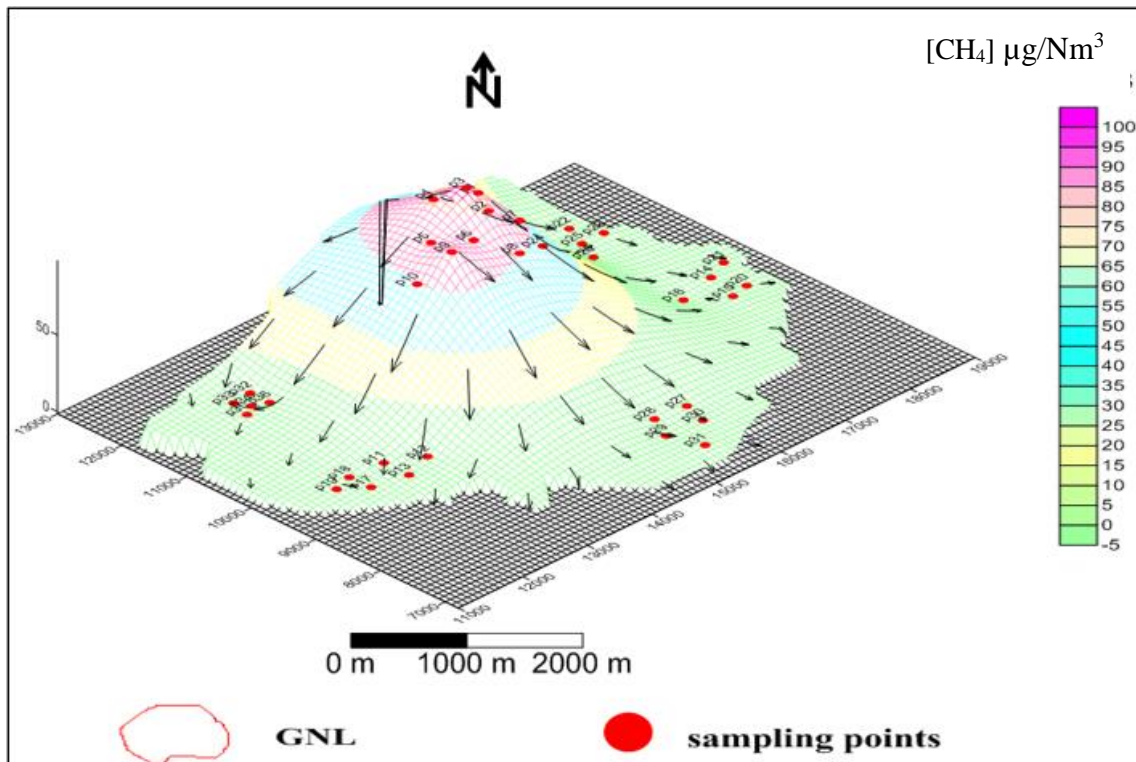


Figure (IV.9): Spatial distribution map of CH<sub>4</sub> in Skikda.



**Figure (IV.10):** 3D Spatial distribution map of CH<sub>4</sub> in Skikda.

Figs (IV.9 and IV.10) shows the spatial distribution pattern of CH<sub>4</sub>. It is evident that concentrations are significantly elevated at ten specific locations (P1 to P10) within the GL1K study site, surpassing the standard threshold:  $[\text{CH}_4]_{\text{mean}} = 2775.88 \mu\text{g}/\text{Nm}^3 > [\text{CH}_4]_{\text{standard}} = 150 \mu\text{g}/\text{Nm}^3$ . Therefore, the site is classified within the unacceptable zone (polluted zone).

Analysis of maximum and minimum methane (CH<sub>4</sub>) concentrations in neighboring areas surrounding the GL1K study site reveals the following:

- Site 1 (Filfila):  $[\text{CH}_4]_{\text{max}} = 1300.48 \mu\text{g}/\text{Nm}^3$ ,  $[\text{CH}_4]_{\text{min}} = 500.70 \mu\text{g}/\text{Nm}^3$ .
- Site 2 (Alaoui Taghane):  $[\text{CH}_4]_{\text{max}} = 900.25 \mu\text{g}/\text{Nm}^3$ ,  $[\text{CH}_4]_{\text{min}} = 110.17 \mu\text{g}/\text{Nm}^3$ .
- Site 3 (Arbi Ben M'hidi):  $[\text{CH}_4]_{\text{max}} = 499.76 \mu\text{g}/\text{Nm}^3$ ,  $[\text{CH}_4]_{\text{min}} = 98.91 \mu\text{g}/\text{Nm}^3$ .
- Site 5 (Hamrouche Hamoudi):  $[\text{CH}_4]_{\text{max}} = 925.43 \mu\text{g}/\text{Nm}^3$ ,  $[\text{CH}_4]_{\text{min}} = 111.03 \mu\text{g}/\text{Nm}^3$ .
- Site 6 (Ilot des Chèvres):  $[\text{CH}_4]_{\text{max}} = 10000 \mu\text{g}/\text{Nm}^3$ ,  $[\text{CH}_4]_{\text{min}} = 100.20 \mu\text{g}/\text{Nm}^3$ .

These observations indicate very high methane concentrations, likely exacerbated by wind convection (Skikda experiences predominant afternoon winds), there by placing these areas in the unacceptable red zone. The substantial presence of methane

(CH<sub>4</sub>) in the air around the GL1K study site is thought to stem from gas leaks, posing significant health risks to individuals in the region.

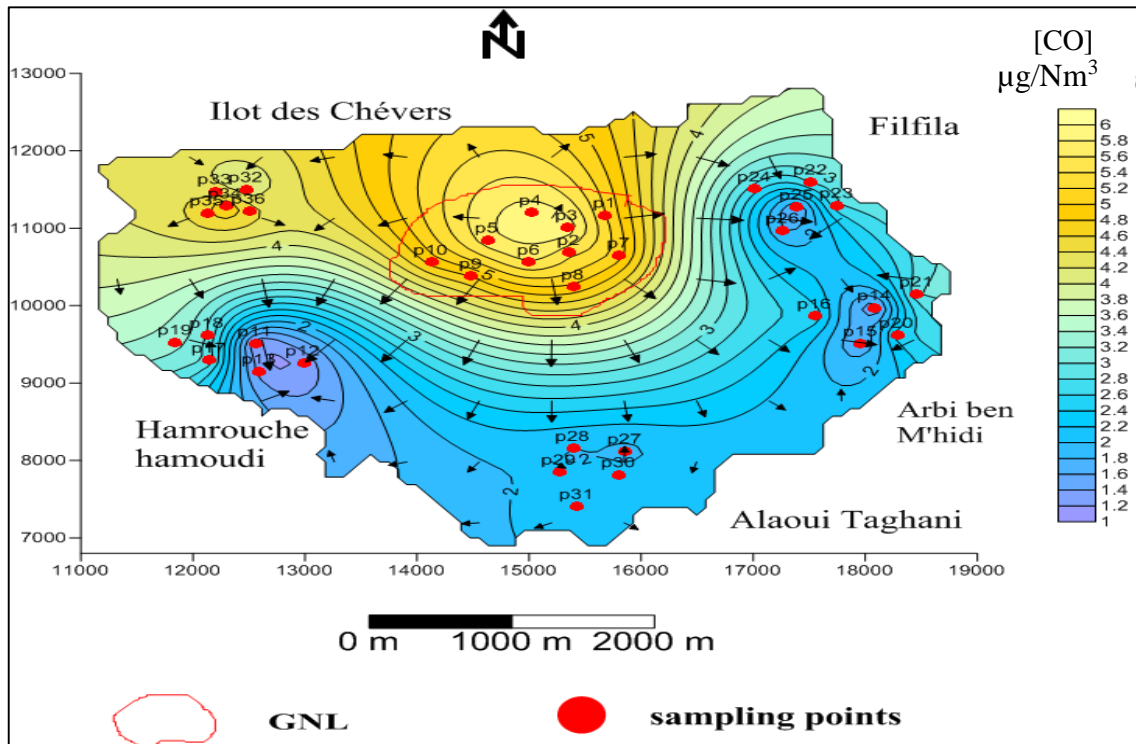


Figure (IV.12): 3D Spatial distribution map of CO in Skikda.

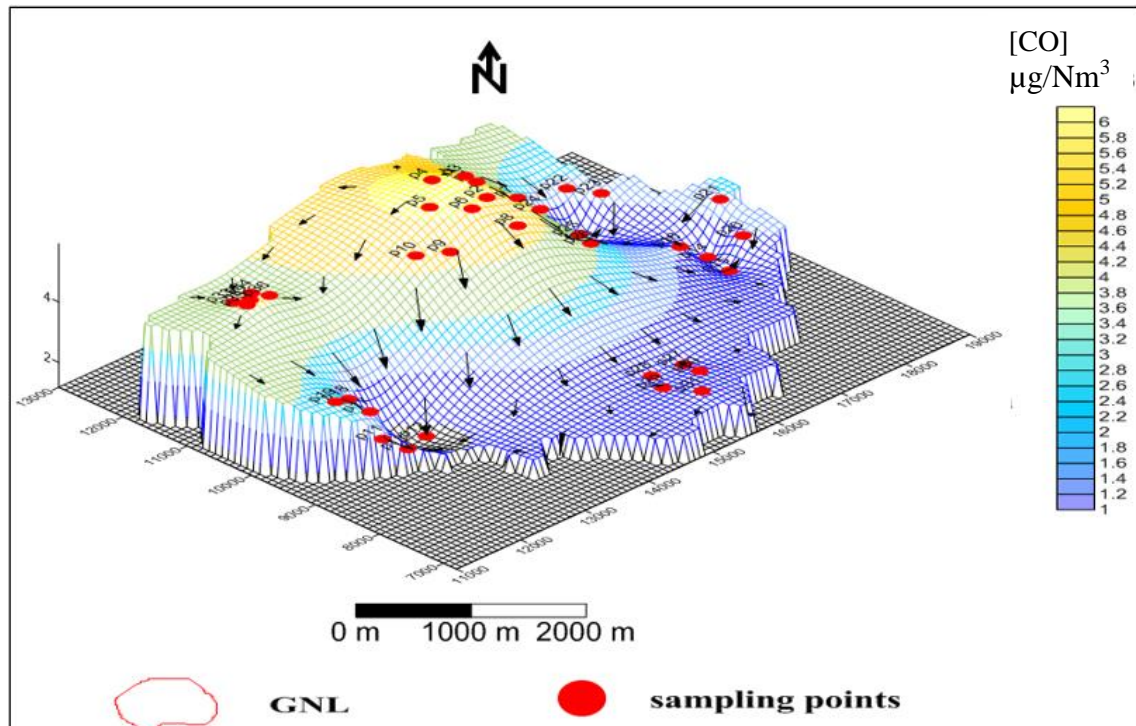


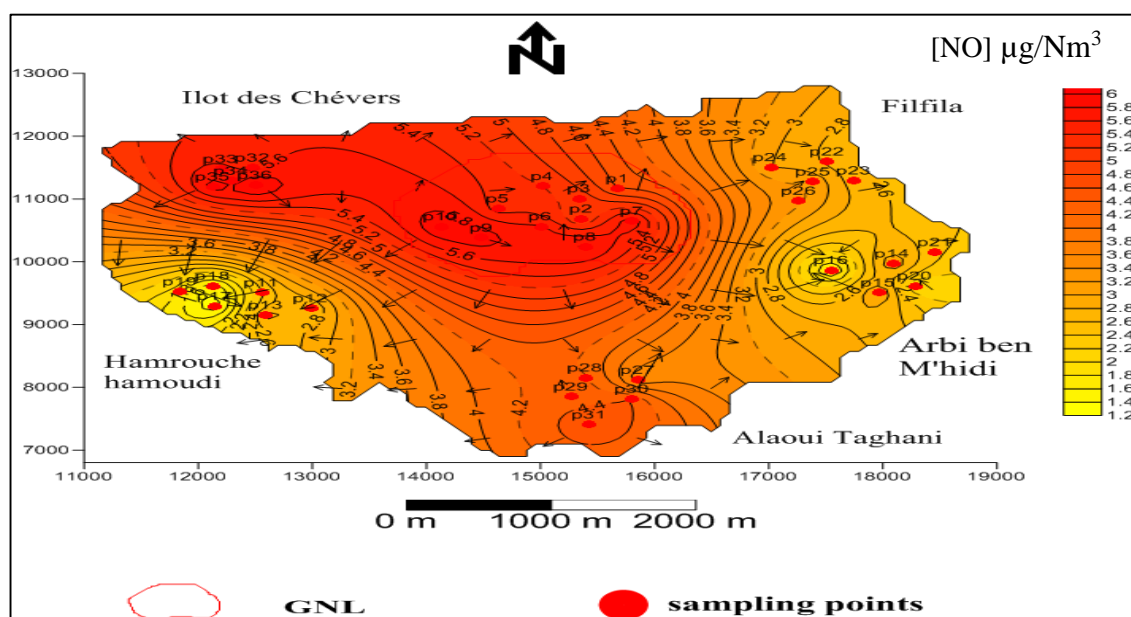
Figure (IV.11): Spatial distribution map of CO in Skikda.

Based on the findings from Figs (IV.11 and IV.12), Surfer's modeling reveals elevated atmospheric carbon monoxide (CO) pollution levels in Skikda. Concentrations at ten locations within the GL1K study site exceed the standard threshold:  $[CO]_{\text{mean}} = 3313.64 \mu\text{g}/\text{Nm}^3 > [CO]_{\text{standard}} = 150 \mu\text{g}/\text{Nm}^3$ , categorizing the study site as being in the unacceptable (polluted) zone.

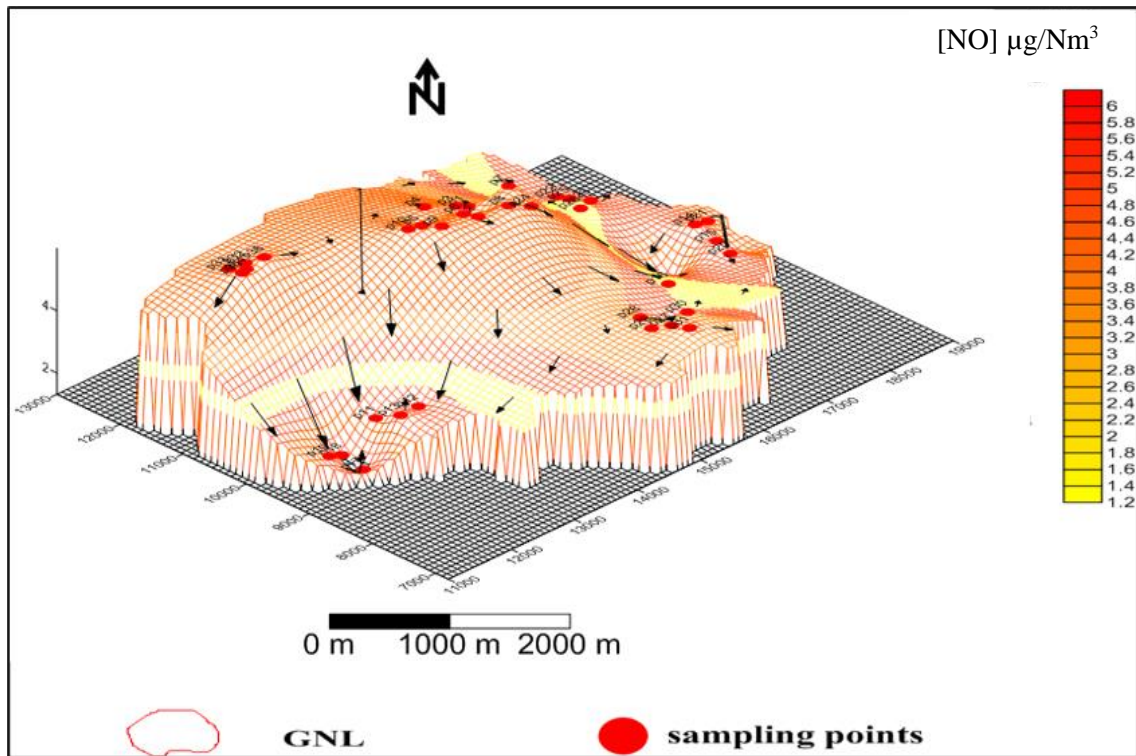
Examining maximum and minimum carbon monoxide (CO) concentrations in surrounding areas near the GL1K study site yields the following results:

- Site 1 (Filfila):  $[CO]_{\text{max}} = 500.94 \mu\text{g}/\text{Nm}^3$ ,  $[CO]_{\text{min}} = 99.20 \mu\text{g}/\text{Nm}^3$
- Site 2 (Alaoui Taghane):  $[CO]_{\text{max}} = 500.94 \mu\text{g}/\text{Nm}^3$ ,  $[CO]_{\text{min}} = 100.20 \mu\text{g}/\text{Nm}^3$
- Site 3 (Arbi Ben M'hidi):  $[CO]_{\text{max}} = 500.01 \mu\text{g}/\text{Nm}^3$ ,  $[CO]_{\text{min}} = 200.11 \mu\text{g}/\text{Nm}^3$
- Site 5 (Hamrouche Hamoudi):  $[CO]_{\text{max}} = 3900.25 \mu\text{g}/\text{Nm}^3$ ,  $[CO]_{\text{min}} = 100.26 \mu\text{g}/\text{Nm}^3$
- Site 6 (Ilot des Chèvres):  $[CO]_{\text{max}} = 906.23 \mu\text{g}/\text{Nm}^3$ ,  $[CO]_{\text{min}} = 100.20 \mu\text{g}/\text{Nm}^3$

While concentrations are comparatively lower than those at GL1K, they consistently fall within the unacceptable red zone due to influencing meteorological factors such as wind convection. The elevated levels of carbon monoxide (CO) detected in the air surrounding the GL1K study area are attributed to combustion sources, including vehicular emissions.



**Figure (IV.13):** Spatial distribution map of NO in Skikda.



**Figure (IV.14):** 3D Spatial distribution map of NO in Skikda.

Based on the findings from Figs (IV.13 and IV.14), it has been determined that the levels of nitrogen monoxide (NO) component comply with the established standard:

$$[\text{NO}]_{\text{mean}} = 39.28 \mu\text{g}/\text{Nm}^3 < [\text{NO}]_{\text{standard}} = 200 \mu\text{g}/\text{Nm}^3.$$

Therefore, the GL1K study site is classified as being in an acceptable zone (non-polluted).

Further examination of maximum and minimum concentrations in areas near the GL1K study site reveals the following results:

- Site 1 (Filfila):  $[\text{NO}]_{\text{max}} = 12.75 \mu\text{g}/\text{Nm}^3$ ,  $[\text{NO}]_{\text{min}} = 4.58 \mu\text{g}/\text{Nm}^3$
- Site 2 (Alaoui Taghane):  $[\text{NO}]_{\text{max}} = 13.50 \mu\text{g}/\text{Nm}^3$ ,  $[\text{NO}]_{\text{min}} = 5.40 \mu\text{g}/\text{Nm}^3$
- Site 3 (Arbi Ben M'hidi):  $[\text{NO}]_{\text{max}} = 5.94 \mu\text{g}/\text{Nm}^3$ ,  $[\text{NO}]_{\text{min}} = 1.20 \mu\text{g}/\text{Nm}^3$
- Site 5 (Hamrouche Hamoudi):  $[\text{NO}]_{\text{max}} = 336 \mu\text{g}/\text{Nm}^3$ ,  $[\text{NO}]_{\text{min}} = 3.16 \mu\text{g}/\text{Nm}^3$
- Site 6 (Ilot des Chèvres):  $[\text{NO}]_{\text{max}} = 100 \mu\text{g}/\text{Nm}^3$ ,  $[\text{NO}]_{\text{min}} = 1.20 \mu\text{g}/\text{Nm}^3$ .

These concentrations are within compliance with the standard, confirming their classification in the acceptable zone.

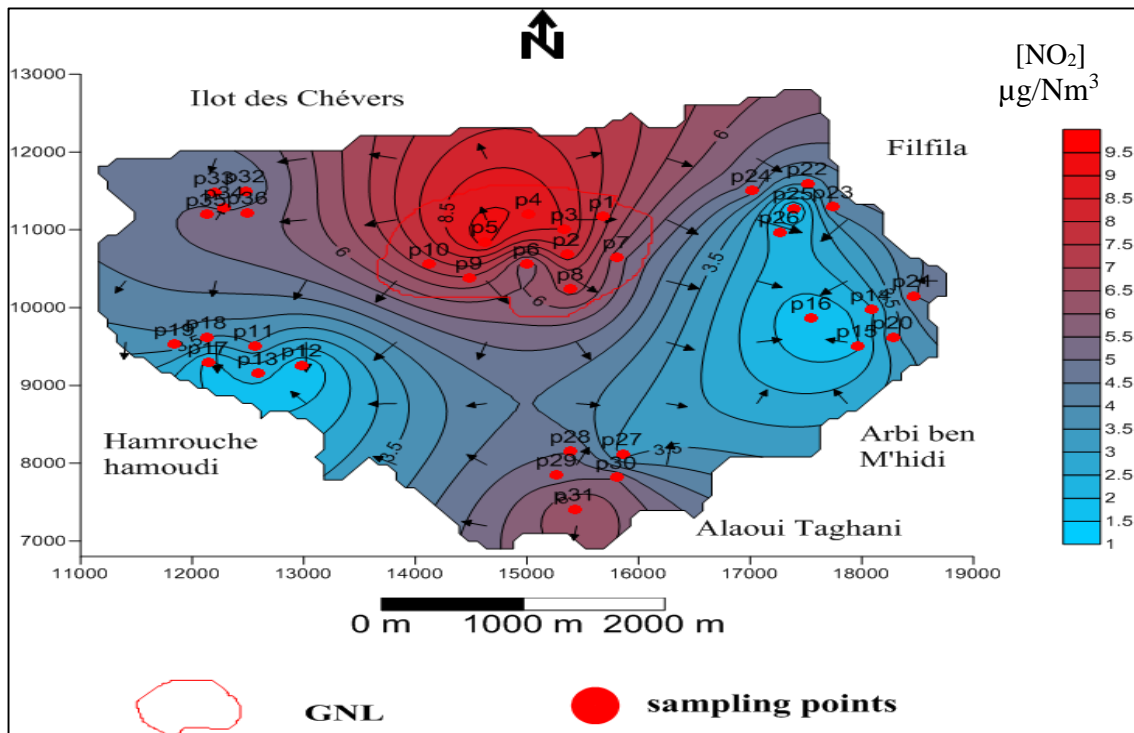


Figure (IV.15): Spatial distribution map of NO<sub>2</sub> in Skikda.

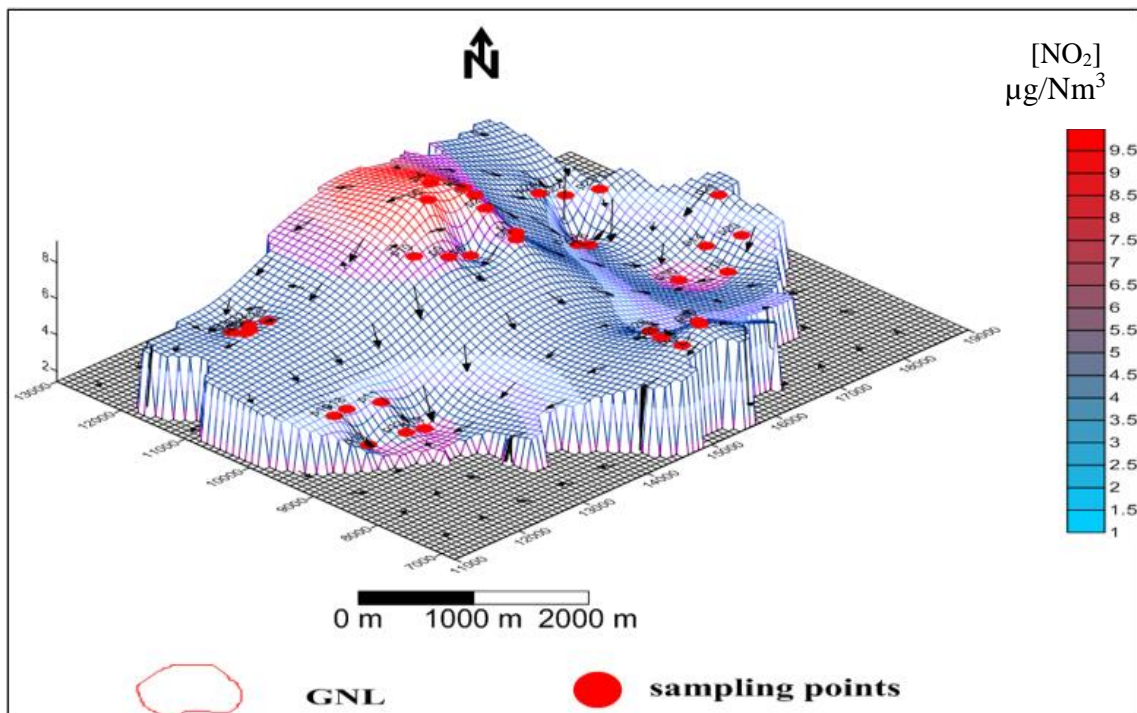


Figure (IV.16): 3D Spatial distribution map of NO<sub>2</sub> in Skikda.

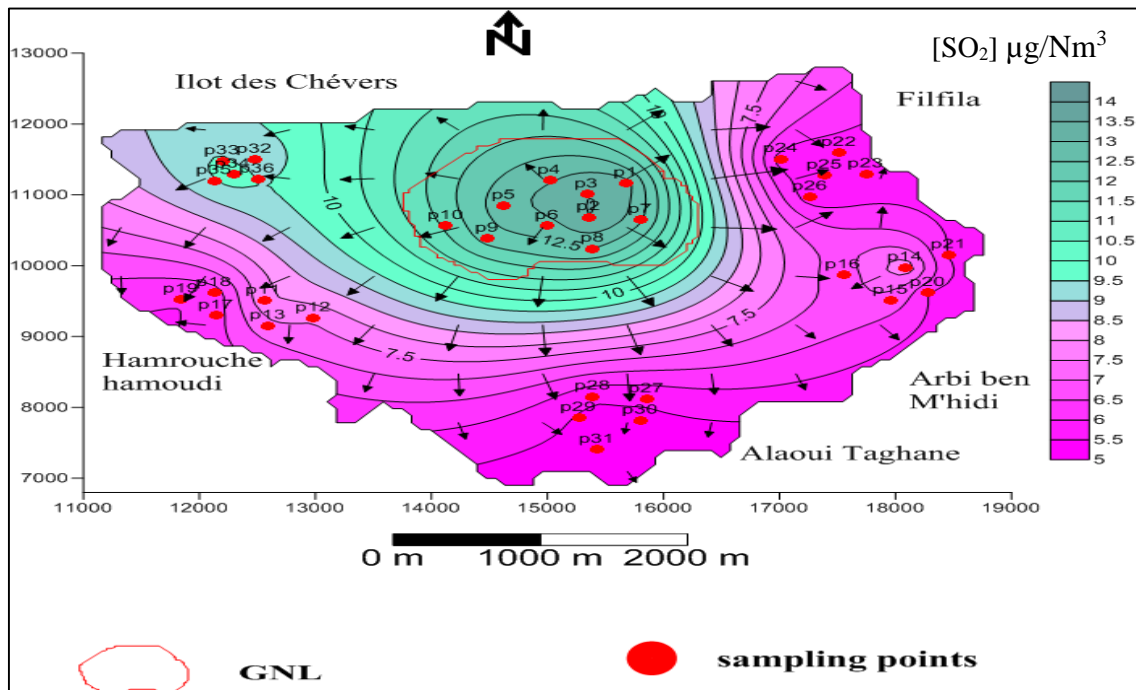
Based on the results depicted in Figs (IV.15 and IV.16), the concentrations of nitrogen dioxide ( $\text{NO}_2$ ) pollutant at the GL1K site are well within the standard limits, with a mean  $[\text{NO}_2]$  concentration of  $31.38 \mu\text{g}/\text{Nm}^3$ , notably below the standard  $[\text{NO}_2]$  concentration of  $300 \mu\text{g}/\text{Nm}^3$ . Therefore, this zone is classified as acceptable in terms of  $\text{NO}_2$  pollution levels.

Further analysis of sampling points near the GL1K area provides the following maximum and minimum concentrations:

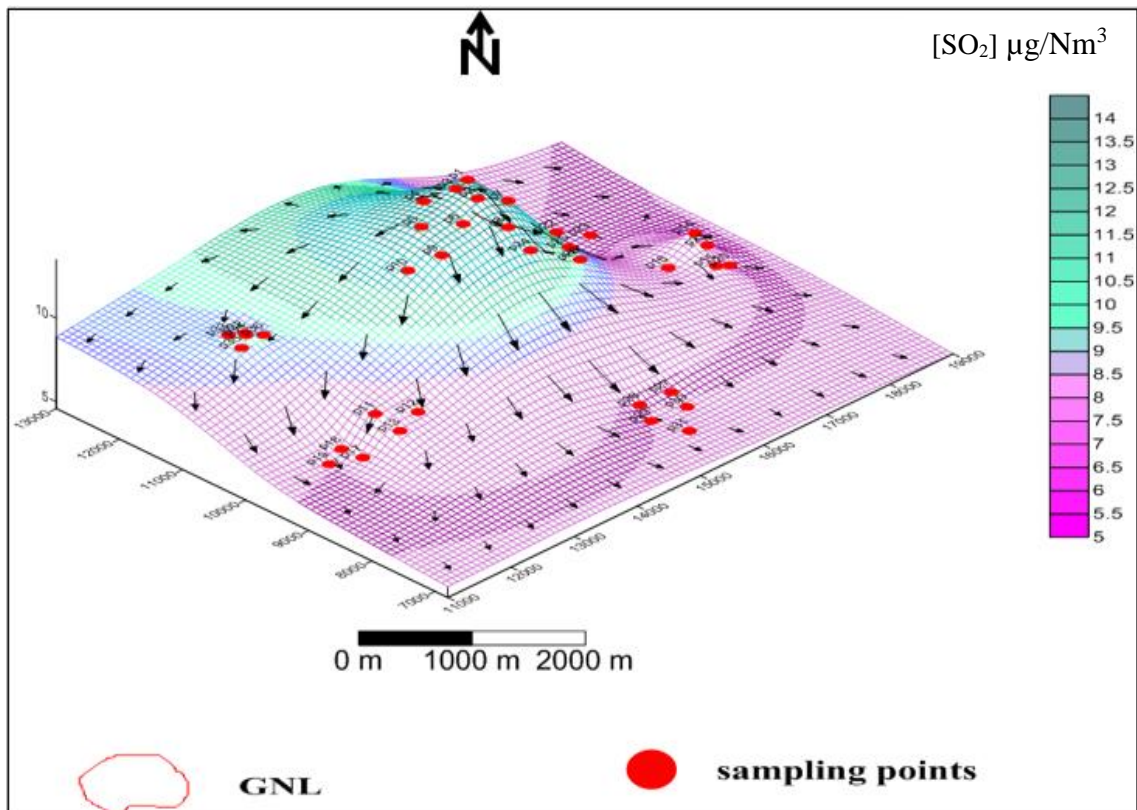
- Site 1 (Filfila):  $[\text{NO}_2]_{\text{max}} = 56 \mu\text{g}/\text{Nm}^3$ ,  $[\text{NO}_2]_{\text{min}} = 3.01 \mu\text{g}/\text{Nm}^3$
- Site 2 (Alaoui Taghane):  $[\text{NO}_2]_{\text{max}} = 12.75 \mu\text{g}/\text{Nm}^3$ ,  $[\text{NO}_2]_{\text{min}} = 1.2 \mu\text{g}/\text{Nm}^3$
- Site 3 (Arbi Ben M'hidi):  $[\text{NO}_2]_{\text{max}} = 5.94 \mu\text{g}/\text{Nm}^3$ ,  $[\text{NO}_2]_{\text{min}} = 1.2 \mu\text{g}/\text{Nm}^3$
- Site 5 (Hamrouche Hamoudi):  $[\text{NO}_2]_{\text{max}} = 9.25 \mu\text{g}/\text{Nm}^3$ ,  $[\text{NO}_2]_{\text{min}} = 1.2 \mu\text{g}/\text{Nm}^3$
- Site 6 (Ilot des Chèvres):  $[\text{NO}_2]_{\text{max}} = 89 \mu\text{g}/\text{Nm}^3$ ,  $[\text{NO}_2]_{\text{min}} = 2.01 \mu\text{g}/\text{Nm}^3$

These concentrations are in accordance with the standard levels, confirming their classification within an acceptable range. Despite the presence of various pollution sources, such as combustion activities at the GL1K study site, no pollution is detected.

Our conclusion is that atmospheric processes like wind and precipitation washout have significantly contributed to diluting air pollutants, maintaining favorable environmental conditions regarding nitrogen dioxide ( $\text{NO}_2$ ) in the GL1K study area.



**Figure (IV.17):** Spatial distribution map of  $\text{SO}_2$  in Skikda.



**Figure (IV.18):** 3D Spatial distribution map of SO<sub>2</sub> in Skikda.

Based on the observations from Figs (IV.17 and IV.18), the concentration of Sulfur dioxide (SO<sub>2</sub>) at the GL1K location complies with the standard, with a mean [SO<sub>2</sub>] concentration of 31.94 µg/Nm<sup>3</sup>, which is below the standard threshold of 300 µg/Nm<sup>3</sup>. Therefore, this zone is classified as being within the acceptable range for SO<sub>2</sub> pollution levels.

Further examination of nearby points near the GL1K area reveals the following maximum and minimum concentrations:

- Site 1 (Filfila): [SO<sub>2</sub>]<sub>max</sub> = 5.94 µg/Nm<sup>3</sup>, [SO<sub>2</sub>]<sub>min</sub> = 1.2 µg/Nm<sup>3</sup>
- Site 2 (Alaoui Taghane): [SO<sub>2</sub>]<sub>max</sub> = 69 µg/Nm<sup>3</sup>, [SO<sub>2</sub>]<sub>min</sub> = 1.2 µg/Nm<sup>3</sup>
- Site 3 (Arbi Ben M'hidi): [SO<sub>2</sub>]<sub>max</sub> = 5.69 µg/Nm<sup>3</sup>, [SO<sub>2</sub>]<sub>min</sub> = 1.2 µg/Nm<sup>3</sup>
- Site 5 (Hamrouche Hamoudi): [SO<sub>2</sub>]<sub>max</sub> = 12.75 µg/Nm<sup>3</sup>, [SO<sub>2</sub>]<sub>min</sub> = 5.59 µg/Nm<sup>3</sup>
- Site 6 (Ilot des Chèvres): [SO<sub>2</sub>]<sub>max</sub> = 618 µg/Nm<sup>3</sup>, [SO<sub>2</sub>]<sub>min</sub> = 5.01 µg/Nm<sup>3</sup>

Despite significant emissions originating from the GL1K area, these concentrations consistently fall within the acceptable range for sulfur dioxide (SO<sub>2</sub>) levels. This classification is maintained even with variations observed due to meteorological influences such as precipitation and wind convection.

## Conclusion

This study investigates the interplay between emissions of methane (CH<sub>4</sub>), carbon monoxide (CO), nitrogen dioxide (NO<sub>2</sub>), nitrogen monoxide (NO), and sulfur dioxide (SO<sub>2</sub>) measured across various locations near an LNG plant, considering factors such as wind convection, precipitation, temperature, and humidity. Using spatial mapping, the study reveals distinct concentration patterns of these pollutants, underscoring the significant influence of meteorological conditions on air quality dynamics and pollution dispersion.

Overall, while the LNG plant emerges as a primary emission source, elevated methane concentrations exceeding Algerian regulatory standards are observed due to dispersion. To address this, the study recommends implementing seasonal adjustments and operational modifications, such as regulating gas flow rates based on seasonal meteorological variations. Additionally, integrating technologies like Flue Gas Desulfurization (FGD) to reduce sulfur oxides (SO<sub>x</sub>) emissions and Selective Catalytic Reduction (SCR) to mitigate nitrogen oxides (NO<sub>x</sub>) can enhance emission control measures.

Furthermore, optimizing stack heights can facilitate better pollutant dispersion by releasing emissions at higher altitudes, where they can disperse and dilute more effectively before reaching ground level. These strategies collectively aim to mitigate environmental impact and improve air quality around the LNG plant and its neighboring areas.

# ***GENERAL CONCLUSION***

## **General conclusion**

The assessment of atmospheric pollution in the industrial and urban areas surrounding the GL1K Liquefied Natural Gas (LNG) plant in Skikda demonstrates the complex interactions between industrial emissions, meteorological conditions, and overall air quality. By analyzing key pollutants such as methane (CH<sub>4</sub>), carbon monoxide (CO), nitrogen oxides (NO and NO<sub>2</sub>), and sulfur dioxide (SO<sub>2</sub>), the study provides a comprehensive understanding of the spatial and temporal distribution of contaminants in a region characterized by intensive petrochemical activity.

Results obtained from field measurements, statistical analysis using SPSS, and spatial modeling with Surfer software tool enables the tracing of spatial maps showing concentrations of pollutants, revealing distribution patterns. It confirms the significant impact of previous conditions on air quality by managing the propagation of pollutants and exacerbating air pollution. Despite the LNG plant being the main source of pollutants, concentrations of CH<sub>4</sub> exceed Algerian permissible standards in other areas due to dispersion.

The study also highlights the crucial role of meteorological parameters in influencing the dispersion, accumulation, or dilution of airborne pollutants. For instance, thermal inversions can trap pollutants near the surface, thereby heightening the risk of exposure for populations residing near the industrial zone.

These findings align with global scientific literature demonstrating that prolonged exposure to elevated pollutant concentrations presents a serious health risk, contributing to respiratory diseases, cardiovascular complications, and, in severe cases, premature mortality. This underscores the urgent need for effective mitigation strategies aimed at protecting both environmental quality and public health.

In conclusion, the recommendations proposed to effectively deal with this problem include seasonal adjustments and adapting operational parameters based on seasonal variations in meteorological conditions. Implementing systems like flue gas desulfurization (FGD) to remove sulfur oxides (SO<sub>x</sub>) from flue gas before release and

using selective catalytic reduction (SCR) to reduce nitrogen oxides (NO<sub>x</sub>) emissions are essential. Optimized and taller stacks allow better dispersion of plumes by wind, releasing pollutants higher in the atmosphere where they can be diluted before reaching lower levels.

# ***REFERENCES***

## REFERENCES

- Afghan, F. R., et al. (2020). Health impacts assessment due to PM<sub>2.5</sub>, PM<sub>10</sub> and NO<sub>2</sub> exposure in National Capital Territory (NCT) Delhi. *Pollution*, 6(1), 115-126.
- Albarakeh, Z. (2012). Air pollution monitoring by multi-sensor system: Mixed method of classification and determination of a pollution index [Thèse de doctorat, École Nationale Supérieure des Mines de Saint-Étienne].
- Amiour, I. (2018). GL1K. Scribd document.
- Arkouli, M., et al. (2010). Distribution and temporal behavior of particulate matter over the urban area of Buenos Aires. *Atmospheric Pollution Research*, 1(1), 1-8.
- Arquès, P. (1998). Atmospheric pollution. In *Air Pollution* (pp. 369-382).
- Bastin, S., et al. (2005). Impact of the Rhône and Durance valleys on sea-breeze circulation in the Marseille area. *Atmospheric Research*, 74(1-4), 303-328.
- Baumbach, G., et al. (1999). Experimental determination of the effect of mountain-valley breeze circulation on air pollution in the vicinity of Fribourg. *Atmospheric Environment*, 33(24-25), 4019-4027.
- Beltrando, G., et al. (1995). *Dictionnaire du climat*. Larousse.
- BM 25 Gas Detector Manual. (2021). Portable gas detection: BM 25. Gas Detect.
- Bokwa, A. (2019). Rozwoj badań nad klimatem lokalnym Krakowa. *Acta Geographica Lodziensia*, 108, 7–20.
- Bouchlaghem, K., et al. (2007). Impact of a sea breeze event on air pollution at the eastern Tunisian coast. *Atmospheric Research*, 86(2), 162-172.
- Bouketta, S. (2011). L'effet de la géométrie urbaine sur l'écoulement du vent et la ventilation naturelle extérieure [Mémoire de Magister, Université de Constantine].
- Cadiou, H. (1997). La mesure du vent : Sa perturbation par les obstacles (Note technique n°33). Météo-France.
- Carrega, P. (2000). Contes (Alpes-Maritimes Françaises) : Une vallée continentale et mal ventilée bien que proche de la mer. *Publications de l'AIC*, 12, 34-42.
- Carrega, P. (2008). Le vent : Importance, mesures, modélisation et tribulations. *Bulletin de la Société Géographique de Liège*, 51, 17-29.
- Carrega, P. (2009). Écoulements d'air à faible altitude au-dessus du bassin du Paillon (Rapport n° 2). Université de Nice, Équipe GVE, UMR 6012 ESPACE/CNRS.

- Carrega, P., et al. (2010). Ozone et flux d'air dans l'arrière-pays niçois : Mesures et modélisation à fine échelle spatiale durant un épisode estival. *Pollution Atmosphérique*, 207, 297-313.
- Cassadou, S., et al. (2002). Programme de surveillance air et santé : 9 villes (PSAS-9). Institut de Veille Sanitaire.
- Coman, A. (2008). Spatio-temporal modeling of urban air pollution from an air quality monitoring network [Thèse de doctorat].
- Connaissance des Énergies. (2025). Gaz naturel liquéfié (GNL). <https://www.google.com/search?q=https://www.connaissancedesenergies.org/gaz-naturel-liquefie-gnl>.
- Corsmeir, U., et al. (2005). The Mistral and its effect on air pollution transport and vertical mixing. *Atmospheric Research*, 74(1-4), 275-302.
- Dahech, S., et al. (2005). Utilisation des données NOAA-AVHRR dans l'étude de la brise thermique et de l'îlot de chaleur : Exemple de Sfax. *Cybergeo : European Journal of Geography*.
- Dahech, S., et al. (2006). Brise de mer et pollution atmosphérique à Sfax (Tunisie). *Pollution Atmosphérique*, 190, 211-223.
- Dalstein-Richier, L., et al. (2005). État des forêts d'altitude en relation avec la pollution de l'air par l'ozone dans la région niçoise. *Pollution Atmosphérique*, 47(188), 503-520.
- Douabul, A. A. Z., et al. (2013). Gaseous pollutants in Basra City, Iraq. *Air, Soil and Water Research*, 6, 15–21.
- Doucet, R. (2006). *La science agricole : Le climat et les sols agricoles*. Berger.
- Duché, S. (2013). Air pollution in the Paris region: Exposure and perceptions at tourist sites. Paris, France : Institut Français de l'Environnement Urbain (IFEU).
- Dudouit, A., et al. (2006, 12–15 septembre). Pollution photochimique en région littorale : Exemple de la région caennaise [Communication orale]. 12ème Colloque International sur la Qualité de l'Air et le Littoral, La Baule, France.
- Etminan, M., et al. (2016). Radiative forcing of carbon dioxide, methane, and nitrous oxide: A significant revision of the methane radiative forcing. *Geophysical Research Letters*, 43(24), 12614-12623.
- Fiedler, F. (2003). Transport of pollutants along slopes [Lecture 3]. Summer School of Trento.
- Ghasemzade, R., et al. (2017). Estimation and modeling of gas emissions in municipal landfill (Case study: Landfill of Jiroft City). *Pollution*, 3(4), 689-700.

- Godard, A., et al. (1998). Les climats : Mécanismes et répartitions (3e éd.). Armand Colin.
- Hache, E. (2014). Apport de la bande de Chappuis pour la mesure de l'ozone depuis un satellite géostationnaire [Thèse de doctorat, Université Paul Sabatier-Toulouse III].
- Hufty, A. (2001). Introduction à la climatologie : Le rayonnement et la température, l'atmosphère, l'eau, le climat et l'activité humaine (2e éd.). De Boeck Supérieur.
- Jackson, R. B., et al. (2020). Increasing anthropogenic methane emissions arise equally from agricultural and fossil fuel sources. *Environmental Research Letters*, 15(7), 071002.
- Jalali, S. H., et al. (2019). The study of CO symptoms' impacts on individuals, using GIS and agent-based modeling (ABM). *Pollution*, 5(3), 463-471.
- Jones, A. M., et al. (2010). The wind speed dependence of the concentrations of airborne particulate matter and NO<sub>x</sub>. *Atmospheric Environment*, 44(13), 1682-1690.
- Karusisi, S. H. (2014). 20 years of urban pollution health risk monitoring and assessment. ORS Île-de-France.
- Katsouyanni, K., et al. (2009). Air pollution and health: A European and North American approach (APHENA). HEI Research Report.
- Koli Bi Zueli, B., et al. (2001). Initiation à la climatologie : Climatologie générale [Cours pédagogique, Université d'Abidjan].
- Lepeule, J., et al. (2018). Lung function association with outdoor temperature and relative humidity and its interaction with air pollution in the elderly. *Environmental Research*, 165, 110–117.
- Likus-Cieślak, J., et al. (2020). The current state of environmental pollution with sulfur dioxide (SO<sub>2</sub>) in Poland. *Environmental Pollution*, 258, 113559.
- Machin, A. B., et al. (2019). Effects of exposure to fine particulate matter in elderly hospitalizations due to respiratory diseases. *Brazilian Journal of Medical and Biological Research*, 52(2).
- Martin, M., et al. (2013). Hygroscopic properties of fresh and aged wood burning particles. *Journal of Aerosol Science*, 56, 15-29.
- Meersens. (2021). The impact of weather on air quality.  
<https://www.google.com/search?q=https://meersens.com/the-impact-of-weather-on-air-quality/>.
- Nester, K. (1995). Influence of sea breeze flows on air pollution over the Attica Peninsula. *Atmospheric Environment*, 24, 3655-3670.

- OMM. (2008). Guide to meteorological instruments and methods of observation (WMO-No. 8, 7ème éd.). Organisation Météorologique Mondiale.
- Pande, J. N., et al. (2002). Outdoor air pollution and emergency room visits at a hospital in Delhi. *The Indian Journal of Chest Diseases & Allied Sciences*, 44(1), 13–19.
- Petroff, A. M. (2008). Aerosol dry deposition on vegetative canopies. *Atmospheric Environment*, 42, 3625-3653.
- Philippe, C. (2004). Analysis of air pollution at local and regional scales [Thèse de doctorat, Université Pierre et Marie Curie]. Archive ouverte des thèses françaises..
- Piot, C. (2011). Pollutants atmosphériques organiques particulaires on Rhône-Alpes [Thèse de doctorat, Université de Grenoble]. URL.
- Poiton, J., et al. (2015). *Le climat : La Terre et les hommes*. EDP Sciences.
- Pro-Gas, LLC. (2023, 10 janvier). The liquefaction process for natural gas. <https://progasllc.com/the-liquefaction-process-for-natural-gas/>.
- Ramade, F. (1984). *Éléments d'écologie : Écologie fondamentale*. McGraw-Hill.
- Ramade, F. (2011). *Introduction à l'écochimie*. Tec & Doc.
- Romero, H., et al. (1999). Rapid urban growth, land-use changes and air pollution in Santiago, Chile. *Atmospheric Environment*, 33, 4039-4047.
- Salmabadi, H., et al. (2019). Monitoring of SO<sub>2</sub> column concentration over Iran using satellite-based observations. *Pollution*, 5(2), 257-268.
- Simpson, J. E. (1994). *Sea breeze and local winds*. Cambridge University Press.
- SONATRACH. (2010). Unit 30 operating manual: Reference GL1K (Manuel d'exploitation RA1K–SKIKDA). Division Liquéfaction et Transformation..
- Sportisse, B. (2008). *Air pollution: From processes to modeling*. Springer.
- Techinstro. (2017). Tedlar bag: Applications and advantages for gas sampling. <https://www.techinstro.com/tedlar-bag-applications-and-advantages/>.
- Technology Networks. (2020). Gas chromatography: How a gas chromatography machine works. <https://www.google.com/search?q=https://www.technologynetworks.com/analysis/articles/gas-chromatography-how-a-gas-chromatography-machine-works-338494>.
- Ung, A. (2003). Mapping urban air pollution using multi-source data [Thèse de doctorat, Paris 7].
- Vincent, A. (2002). Design and simulation of a wire-cylinder corona discharge reactor [Thèse de doctorat, Paris VI].
- Vincent, L. A., et al. (2013). Updated analyses of temperature and precipitation extreme

indices: The HadEX2 dataset. *Journal of Geophysical Research: Atmospheres*, 118(5), 2098-2118.