UNIVERSITY OF NOVA GORICA
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ASSESSING THE LEVEL OF OZONE POLLUTION IN URBAN AND SUB-URBAN TUNIS AREAS

MASTER'S THESIS

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Assessing the level of ozone pollution in urban and sub-urban Tunis areas

Abstract

The monitoring data analysis performed in this investigation focuses mainly on selecting statistically representative scenarios of ozone pollution in Tunisia. Measured data of ozone employed in this analysis were obtained from the monitoring stations of suburban Park Station El Mourouj. Computer programming language R was proposed to screen the ozone scenarios. Openair, an R package, was employed for the analysis of air pollution.

The analysis of spatial average ozone profiles, backward trajectories and statistical analysis could reveal features of selected ozone scenarios.

Keywords: Ozone, Air, Greater Tunis, standards, exceeded frequencies, pollution, climate change

Ocenjevanje stopnje onesnaževanja z ozonom v mestnih in primestnih območjih Tunisa

Povzetek

Spremljanje podatkov v tej preiskavi se osredotoča predvsem na izbiro statistično reprezentativnih scenarijev onesnaževanja z ozonom v Tuniziji. Izmerjeni podatki o ozonu, ki so bili uporabljeni v tej analizi, so bili pridobljeni iz merilnih postaj primestne postaje parka El Mourouj. Računalniški programski jezik R smo uporabili za spremljanje situacij ob različnih koncentracijah ozona. Uporaben je za spremljanje vrednosti ozona na prostem.

Analiza prostorskih povprečnih profilov ozona, presežnih koncentracij, onesnaženja in statistične analize lahko pokažejo značilnosti izbranih scenarijev ozona.

Ključne besede: Ozon, zrak, Greater Tunis, standardi, presežene frekvence, onesnaževanje, podnebne spremembe

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CORINAIR: Core Inventory of Air Emissions

RNSQA: National Network of monitoring air quality

WHO: World Health Organization

VOCs: Nitrogen oxides

NOx: and volatile organic compounds

PM10: Particulate Matter up to 10 micrometers in size

RACT: Reasonable available control technology

BACT: Best available control technology

LAER: Lowest achievable emission rates

GCT: Tunisian Chemical Group

ANPE: National Agency of Environmental Protection

PCN: Central National Station

SAM: measurement acquisition station

INS: National Institute of Statistic

ppb: parts per billion

Introduction

The air is an essential element for life; it is composed of 78% of nitrogen, 21% of oxygen and 1% of other gases. Although known quite a long time, air pollution has become an important issue in social life until the 1950s, marked by a series of major events ("smog" in London in 1952, Seveso accident in 1976 ...). The following decades were then marked by the awareness of health risks related to atmospheric pollution and preventive measures they imply. Knowledge about phenomena of air pollution and their biological and medical consequences were rapidly evolving [Wikipedia].

To better understand and control air pollution, it is necessary to know the sources of pollution, to identify and quantify. This knowledge can then take action to reduce emissions at source. Emission inventories are also a basic need to conduct assessments of air quality and estimate the impacts of air pollution on health, ecosystems...

Signed in 1979, the Geneva Convention on Long-range air pollution was the trigger for thoughts and attempts to organize and structure data on pollutant releases in the form of pollutant emission inventories. This dynamic was then relayed by a program of the European Commission Corinair, which has generated the first CORINAIR emission inventory.

Thus, communication policy in this issue is based on a problematic ambitious: to inform, educate, prevent and raise contribution of different actors. In this context, this work aims at makes aware public institutions and decision makers of the gravity of air quality degradation for human being.

It is within this context that this work is conducted, in order to provide an assessment of ozone, a major indicator of air pollution and precursors in Greater Tunis.

Initially, the bibliographic knowledge in terms of air pollution especially ozone and the statistic analyses of the situation in Tunis will be exposed.

The second part will outline some climatic parameters of the study area and how can they be a factor of ozone pollution.

In the third part, the special and temporal evolution of ozone pollution level will be illustrated, explained and compared with national and international overflow frequencies

The final chapter will seek to identify more closely the perceptions, needs and expectations in terms of information on ozone pollution.

Chapter I

Literature review

I. AIR POLLUTION

I.1 Definition

Air pollution is the condition in which air is contaminated by foreign substances, or the substances themselves.

Air pollution consists of gaseous, liquid, or solid substances that, when present in sufficient concentration, for a sufficient time, and under certain conditions, tend to interfere with human comfort, health or welfare, and cause environmental damage. Air pollution causes acid rain, ozone depletion, photochemical smog, and other such phenomena.

Several factors are considered air pollutants because they do not exist naturally in the air or not such a concentration, and they are harmful to the health of living beings.

These pollutants are gases which are often invisible such as carbon monoxide (CO), nitrogen oxides (NOx) and sulfur dioxide (SO_2) or ozone (O_3). There are also solid particles, more or less fine. They give their consistency and color of the fumes. These dusts are of mineral, organic or metallic origin [Lebron, 2012].

I.2 Origins

Air pollutants can be natural (volcanic emissions, pollen producing plants, lightning ...), but also due to human activities: transport, industry, incineration, heating of buildings or agriculture with the use of nitrogen fertilizers, pesticides and animal emissions

Finally, in confined spaces, use of cleaning products, adhesives, carpet, some furniture made of particleboard, domestic activities such as crafts can also emit pollutants.

I.3 Air pollution effects

I.3.1 Effects on human being

Adverse air quality can kill many organisms including humans. Every year, the health of countless people is ruined or endangered by air pollution. Many different chemicals in the air affect the human body in negative ways. Just how sick people will get depends on what chemicals they are exposed to, in what concentrations, and for how long.

Studies have estimated that the number of people killed annually in the US alone could be over 50,000. Older people are highly vulnerable to diseases induced by air pollution. Those with heart or lung disorders are under additional risk. Children and infants are also at serious risk [White, 1994].

Because people are exposed to so many potentially dangerous pollutants, it is often hard to know exactly which pollutants are responsible for causing sickness. Also, because a mixture of different pollutants can intensify sickness, it is often difficult to isolate those pollutants that are at fault.

Many diseases could be caused by air pollution without their becoming apparent for a long time. Diseases such as bronchitis, lung cancer, and heart disease may all eventually appear in people exposed to air pollution.

Air pollutants such as ozone, nitrogen oxides, and sulfur dioxide also have harmful effects on natural ecosystems [Romieu, 1993]. They can kill plants and trees by destroying their leaves, and can kill animals, especially fish in highly polluted rivers.

The presence of ozone is associated with the properties of other species such as acids or oxidizing aldehydes, organic nitro compounds, nitric acid, of hydrogen peroxide. This pollution occurs mainly in summer in suburban and rural areas downwind of cities, and contributes to the increase of background pollution by ozone (up approximately 1% per year over the entire the northern hemisphere).

Ozone and photochemical pollutants are also phyto-toxic species. Ozone can disrupt photosynthesis, alter plant resistance, reduce productivity, cause visible lesions (Bel W3 tobacco is sometimes used as bio-indicator of ozone).

Ozone also contributes to acid deposition and other adverse factors (drought, poor soils, etc ...) to forest disturbances observed in Europe and North America.

The ozone pollution remains a concern and every year, in summer, various regions undergoing situations of photochemical pollution peaks during which thresholds considered dangerous can be met or exceeded, both in relation to the health of the man plants. Such situations may occur 1 to 2 days per week in summer, particularly in the sunny regions. The ozone pollution (ozone peaks) is associated with an excess of ozone in the lower 20 layers of the atmosphere. This excess is harmful to the health of living organisms.

This problem is distinct from the hole in the ozone layer which corresponds to a lack of Ozone in the stratosphere for solar radiation barrier.

The main substances used in connection with the problems of acidification, eutrophication and photochemical are: SO_2, NOx, NH_3, NMVOC (including speciation over 200 compounds), CO.

Chemicals are sometimes converted into units such as acid equivalent indicators (Aeq) or potential for photochemical ozone creation (POCP).

I.3.2 Effects on materials

The materials are mainly affected by acid pollution (especially related to SO_2) which causes degradation of buildings, monuments and building facades. It is often the decomposition of some limestone under the influence of acids. Particles involved rather aspects of soiling of buildings. Air pollution threatens our cultural heritage and causes of costly building exterior work or restoration of monuments [Holland et al., 1996].

I.3.3 Effects on ecosystems: forest, freshwater reserve

Trees live and die of natural causes varied even that age.

The sudden decline observed since 1980 seems to be mainly causes quite unusual. Officials believe that air pollution is one of the many elements involved in forest dieback. Laboratory research has shown that the causes of forest decline are complex: poor soils, drought abnormal presence of pollutants in the atmosphere mainly acid pollution and ozone [Morrisey, 2007].

But close to some sites generate pollution (industrial site, big roads), we also observed lower yields of agricultural land [Emberson and Cinderby, 2007]. In addition, one can observe a local soil contamination which accumulate metals such as lead roadside.

The acidification of lakes and streams causes irreversible destruction sometimes to aquatic life. Besides the problem of eutrophication, decreasing pH causes the dissolution of metals contained naturally in the soil, such as aluminum, toxic dissolved for almost all living organisms.

Heavy metals also contaminate both soil and freshwater reserves. Accumulation in soil and water contamination let fear of the food chain.

This type of pollution is observed locally (near some sites), but also at the regional and continental levels, including some metals such as mercury.

I.3.4 Health Effects

Concentration limits in ambient air of certain pollutants (SO_2, dust, NO_2, Pb, O_3) imposed by European directives into account the health effects of certain substances. The World Health Organization (WHO) defines the rules that should be observed for several pollutants. Some effects are associated with thresholds, i.e. we can determine a value of concentration in air below which susbtance is not dangerous. For some substances, there is no threshold in the medical sense, but there are regulatory limits (acceptable pollution levels, but not without consequences). The health effects have been most studied are the short-term effects associated with high concentrations. Studies are also conducted to assess the long-term consequences of exposure to lower levels of pollution [Mckittrick, 1995].

I.4 Legislative framework

A substantial body of Community legislation has been adopted by the Council and the European Parliament in relation to ambient air quality. This is summarized below and links provided lead to the relevant documents.

The new Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe entered into force on 11 June 2008.

This new Directive includes the following key elements:

- The merging of most of existing legislation into a single directive (except for the fourth daughter directive) with no change to existing air quality objectives.
- New air quality objectives for PM2.5 (fine particles) including the limit value and exposure related objectives – exposure concentration obligation and exposure reduction target.
- The possibility to discount natural sources of pollution when assessing compliance against limit values.

- The possibility for time extensions of three years (PM10) or up to five years (NO_2, benzene) for complying with limit values, based on conditions and the assessment by the European Commission.

On 18 January 2011, the Commission discussed the progress on the EU's air policy with particular emphasis on the National Emission Ceilings Directive. As a result of this debate, the Commission agreed measures to improve air quality since action was recognized as a pressing need and a shared responsibility requiring our joint efforts.

Commission action will focus on a number of immediate measures and a more comprehensive review of EU's air policy by 2013 at the latest [WHO, 2011].

II. OZONE POLLUTION (O_3)

II.1 Definition

Ozone (O_3) is a gas that can form and react under the action of light and that is present in two layers of the atmosphere: the stratosphere and the troposphere [Carslaw, 2005].

Ozone is a colorless gas found in the air we breathe. Ozone can be good or bad depending on where it occurs:

- Ozone occurs naturally in the Earth's upper atmosphere (the stratosphere), where it shields the Earth from the sun's ultraviolet rays.
- At ground-level, ozone is an air pollutant that can harm human health.

II.2 Origins

However, in the lower atmosphere (troposphere), ozone (O_3) is the most important photochemical oxidant. There, it is a secondary pollutant formed when precursor pollutants such as nitrogen oxides (NOx) and volatile organic compounds react under the action of light [Monks, 2000].

Near strong emission sources of nitrogen oxides (NOx), where there is an abundance of NO, ozone is "scavenged" as it reacts with NO. As a result its concentrations are often low in busy urban centres and higher in suburban and adjacent rural areas. However, ozone is also transported long distances in the atmosphere and is therefore considered a trans-boundary problem.

Because the formation of ozone requires light, ozone concentrations fluctuate depending on season and time of day, with higher concentrations in the summer and in the afternoons. The correlation of O_3 with other pollutants varies by season and location.

Controlled exposure studies on humans and animals have provided evidence that ozone can cause adverse health effects. However, more research is needed, especially addressing the spatial and seasonal patterns of ozone exposure and related health effects.

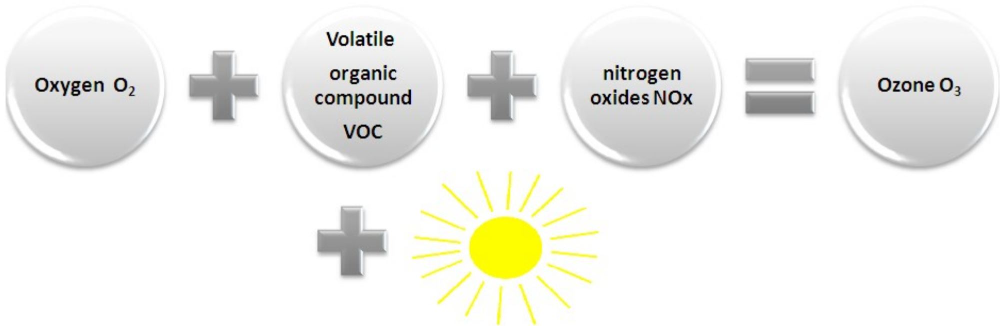

Figure 1. Ozone transformation in the atmosphere (www.earthobservatory.nasa.gov)

II.3 Formation and Removal of Tropospheric Ozone

The formation of ozone in the troposphere is a complex process involving the reactions of hundreds of precursors. The key elements [Finlayson-Pitts and Pitts 2000; Seinfeld and Pandis, 1998] are discussed below.

II.3.1 Nitrogen Cycle and the Photostationary-State Relationship for Ozone

The formation of ozone in the troposphere results from only one known reaction: addition of atomic oxygen (O) to molecular oxygen (O_2) in the presence of a third "body" (M). [M is any "body" with mass, primarily nitrogen or oxygen molecules, but also particles, trace gas molecules, and surfaces of large objects. M absorbs energy from the reaction as heat; without this absorption, the combining of O and O2 into O3 cannot be completed.

$$O + O_2 + M \rightarrow O_3 + M \qquad (1)$$

The oxygen atoms are produced primarily from photolysis of NO_2 by the ultraviolet portion of solar radiation ($h\nu$).

$$NO_2 + h\nu \rightarrow NO + O \qquad (2)$$

Reaction 3 converts ozone back to oxygen and NO back to NO_2, completing the "nitrogen cycle."

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (3)$$

Reactions 1 and 3 are comparatively fast. Therefore, the slower photolysis reaction 2 is usually the rate-limiting reaction for the nitrogen cycle and the reason why ozone is not formed appreciably at night. It is also one of the reasons why ozone concentrations are high during the summer months, when temperatures are high and solar radiation is intense. The cycle time for the three reactions described above is only a few minutes. Ozone accumulates over several hours, depending on emission rates and meteorological conditions. Therefore, the nitrogen cycle operates fast enough to maintain a close approximation to the following photostationary-state equation derived from the above reactions.

$$[O3]_{\text{photostationary-state}} = (k_2/k_3) \times [NO_2]/[NO] \qquad \text{(the brackets denote concentration)}$$

The ratio of the rate constants for reactions 2 and 3, (k_2/k_3), is about 1:100. Assuming equilibrium could be reached in the ambient air and assuming typical urban pollution concentrations, a NO_2 to NO ratio of 10:1 would be needed to generate about 0.1 ppm of ozone (a violation of the state one-hour ozone standard [0.09 ppm]). In contrast, the NO_2 to NO emission ratio is approximately 1:10; therefore, the nitrogen cycle by itself does not generate the high ozone concentrations observed in urban areas. The net effect of the nitrogen cycle is neither to generate nor destroy ozone molecules. Therefore, for ozone to accumulate according to the photostationary-state equation, an additional pathway is needed to convert NO to NO_2; one that will not destroy ozone. The photochemical oxidation of VOCs, such as hydrocarbons and aldehydes, provides that pathway.

II.3.2 The VOC Oxidation Cycle

Hydrocarbons and other VOCs are oxidized in the atmosphere by a series of reactions to form carbon monoxide (CO), carbon dioxide (CO_2) and water (H_2O).

Intermediate steps in this overall oxidation process typically involve cyclic stages driven by hydroxyl radical (OH) attack on the parent hydrocarbon, on partially oxidized intermediate compounds, and on other VOCs. The Hydroxyl radical is ever-present in the ambient air; it is formed by photolysis from ozone in the presence of water vapor, and also from nitrous acid, hydrogen peroxide, and other sources. In the sequence shown below, R can be hydrogen or virtually any organic fragment [Laaksonen, 2008]. The oxidation process usually starts with reaction 4, from OH attack on a hydrocarbon or other VOC:

$$RH + OH \rightarrow H_2O + R \qquad (4)$$

This is followed by reaction with oxygen in the air to generate the peroxy radical (RO_2).

$$R + O_2 + M \rightarrow RO_2 + M \qquad (5)$$

The key reaction in the VOC oxidation cycle is the conversion of NO to NO2. This takes place through the fast radical transfer reaction with NO.

$$RO_2 + NO \rightarrow NO_2 + RO \qquad (6)$$

R can also be generated by photolysis, which usually involves only VOCs with molecules containing the carbonyl (C=O) bond. The simplest VOC molecule that contains the carbonyl bond is formaldehyde (HCHO). Because formaldehyde enters into several types of reactions of importance for understanding ozone formation and removal, we will use it to help illustrate these reactions. The oxidation cycle for formaldehyde can be written in the following sequence of reactions.

$$OH + HCHO \rightarrow H_2O + HCO \qquad (7)$$
$$HCO + O_2 \rightarrow HO_2 + CO \qquad (8)$$
$$HO_2 + NO \rightarrow NO_2 + OH \qquad (9)$$

Hydroperoxyl radical (HO_2) is generated by reaction 8, and the hydroxyl radical (consumed in reaction 7) returns in reaction 9 to complete the cycle. In addition, reaction 9 produces the NO_2 required for ozone formation, as described above. Also, the carbon monoxide (CO) generated by reaction 8 can react like an organic molecule to yield another hydroperoxyl radical.

$OH + CO \rightarrow H + CO_2$ (10)

$H + O_2 + M \rightarrow HO_2 + M$ (11)

Another component that formaldehyde provides for smog formation is a source of hydrogen radicals.

$HCHO + h\nu \rightarrow H + HCO$ (12)

The hydrogen atom (H) and formyl radical (HCO) produced by this photolysis reaction yield two hydroperoxyl radicals via reaction with oxygen, as shown in reactions 8 and 11.

The reactions above comprise the simplest VOC oxidation cycle. Actually, hundreds of VOC species participate in thousands of similar reactions.

II.3.3 The Nitrogen Dioxide and Radical Sink Reaction

Another reaction is central to a basic understanding of ozone formation: the NO_2 plus radical sink reaction that forms nitric acid.

NO2 + OH + M à HNO3 + M (13)

The previous discussion can be used to explain the typical pattern of ozone concentrations found in the urban atmosphere. Nitric oxide concentrations are relatively high in the early morning because the free radicals needed to convert the NOx emissions (which are primarily NO) to NO_2 are not yet present in sufficient quantities. After sunrise, photolysis of formaldehyde (reaction 12) and other compounds starts the VOC oxidation cycle for the hundreds of organic gases present in the atmosphere. Subsequent NO to NO_2 conversion by the peroxy radical (reaction 6) results in NO_2 becoming the dominant NOx species. When the NO_2 to NO ratio becomes large enough, ozone builds up. In the South Coast Air Basin (Los Angeles area), the highest ozone concentrations are observed in the San Bernardino Mountains, many miles downwind from the highest concentration of emission sources (freeways, power generating facilities, and oil refineries along the coast), because the reactions involving the organic gases are relatively slow. Meanwhile, NO_2 concentrations decrease via the sink reaction 13 [Sebald, 2000].

Winds disperse and dilute both NOx and ozone. During the day, NOx is also diluted by the diurnal rising of the inversion layer, allowing for more mixing (see section 1.4 for further discussion). For ozone, however, the deepening mixing layer may cause its concentration to decrease on some days and increase on others. Although increased mixing almost always dilutes NOx, the effect of increased mixing on ozone concentrations depends upon whether higher concentrations of ozone are present aloft. Ozone that is trapped above the inversion layer overnight is available to increase the concentrations of ozone generated by the following day's emissions [Varotsos and Ondov, 2005].

During the night, NO and ozone combine to form NO_2 and oxygen via reaction 3 until either the NO or ozone is consumed. Nitrous acid or HONO is also present at night in polluted ambient air in California. Nitrous acid is produced from NO_2 and water, and is also emitted from various combustion sources. Its levels are low during the day because sunlight breaks it down rapidly. At sunrise, sunlight causes gas-phase HONO to react rapidly to provide NO and OH, two key reactants in the formation of ozone. In this way, they help initiate ozone formation in the morning by being available to react with VOCs as soon as their emissions increase due to an increase in human activity.

Nitric acid (HNO_3) was once thought to be a permanent sink for NOx and for radicals. However, nitric acid on surfaces may react with NO to regenerate NO_2, which would increase the ozone-forming potential of NOx emissions.

II.3.4 Ratio of Volatile Organic Compounds to Nitrogen Oxides in Ambient Air

Although VOCs are necessary to generate high concentrations of ozone, NOx emissions can be the determining factor in the peak ozone concentrations observed in many locations (Chameides, 1992; National Research Council, 1991). VOCs are emitted from both natural and anthropogenic sources. Statewide, natural VOC sources dominate, primarily from vegetation. However, in urban and suburban areas, anthropogenic VOC emissions dominate and, in conjunction with anthropogenic

NOx emissions, lead to the peak concentrations of ozone observed in urban areas and areas downwind of major urban areas.

The relative balance of VOCs and NOx at a particular location helps to determine whether the NOx behaves as a net ozone generator or a net ozone inhibitor. When the VOC/ NOx ratio in the ambient air is low (NOx is plentiful relative to VOC), NOx tends to inhibit ozone formation. In such cases, the amount of VOCs tends to limit the amount of ozone formed, and the ozone formation is called "VOC-limited". When the VOC/ NOx ratio is high (VOC is plentiful relative to NOx), NOx tends to generate ozone. In such cases, the amount of NOx tends to limit the amount of ozone formed, and ozone formation is called "NOx -limited". The VOC/ NOx ratio can differ substantially by location and time-of-day within a geographic area. Furthermore, the VOC/ NOx ratio measured near the ground might not represent the ratio that prevails in the air above the ground where most of the tropospheric ozone is generated.

II.3.5 Photochemical Reactivity

Photochemical reactivity, or reactivity, is a term used in the context of air quality management to describe a VOC's ability to react (participate in photochemical reactions) to form ozone in the atmosphere. Different VOCs react at different rates. The more reactive a VOC, the greater potential it has to form ozone. Examples of the more reactive VOCs in California’s atmosphere include propene, m-xylene, ethene, and formaldehyde. The ARB has helped to pioneer an approach to ozone control that considers the reactivity of each VOC constituent. In California’s urban areas, ozone formation tends to be limited by the availability of VOCs. Therefore, the reactivity-based regulatory approach has been applied in conjunction with reduction of NOx emissions. Reactivity-based regulations promote the control of those VOCs that form ozone most effectively, thereby guiding the affected industries (such as manufacturers

III. OZONE POLLUTION EFFECTS

Bad ozone is the ozone that is formed near the earth's surface. It is created when pollutants emitted from cars, chemicals, power plants, and other sources react chemically with the sunlight. It then damages crops, trees, and other vegetation, as well as becoming a part of what is known as smog. Ozone air pollution is a large problem during the summer months when the sun's rays are stronger and this increased level of ozone causes severe health effects for many people. Ozone can affect the environment as well as our health.

III.1 Environmental Effects

Ozone air pollution has many different effects on the environment. It can reduce the size of an agricultural crop, as well as a tree crop by reducing the number of seedlings and making the crops more susceptible to disease and pests. In the United States, it has been estimated that ozone air pollution causes up to $500 million in crop damage each year. Another effect on the environment is on the leaves and foliage of trees and other plants. This damage is seen in parks and yards across the country.

III.2 Health Effects

The number of health effects that ozone air pollution can cause is numerous. The most common way that ozone air pollution affects the body is in breathing. This is most evident in the summer, when the warm sun rays makes ozone pollution levels high and when people spend a great deal of time in the outdoors. The common symptoms that are seen include congestion, throat irritation, coughing, and even chest pain. If you have an underlying medical condition like asthma, then ozone air pollution can cause it to get worse significantly. Prolonged exposure to ozone air pollution can cause diminished lung capacity, lung inflammation, and scarring of the lung tissue.

IV. LEGAL FRAMEWORK

IV.1 Statutory and legal framework in force relating to air pollution

Many countries as well as the European Union have produced laws and are updating standards of air quality and thresholds relating in particular to ozone (eg threshold information in Europe is 180 $\mu g/m^3$, and should not exceed 120 $\mu g/m^3$ over 8 hours, from this threshold damage to health is certain). This allows the local or national authorities to prohibit or reduce certain activities (combustion of heavy fuel oil for example), or vehicle speed. WHO has also produced recommendations (guide values). Systems of fines and/or tax incentives or subsidies encourage local industry, communities and individuals to make more effort in reducing pollution. Some working time arrangements, telecommuting and devices thinning traffic help reduce emissions of ozone precursors at times when UV rays are most active.

In Europe, Warning networks and measurement of air quality devices are beginning to show their overall effectiveness, in 2007 summer ozone rates have been among the lowest in the past 10 years, especially in the countries of northern Europe where "no exceedances of the threshold value of information has occurred. " Italy is the country most exposed (479 μg/m³ were measured in Sicily; the second record on 2007 is 363 μg/m³ in Romania). Rates of 300 to 360 μg/m³ were measured 6 times in France, Greece, Italy and Romania and the threshold for long-term directive was largely exceeded in the EU, as in other European countries (including some have often exceeded the target value for the protection of human health). In 2007, 45% of total exceedances of information, 39% of exceedances of alert and 12% of exceedances of the long-term goal were observed between 14 and 21 July in Europe.

Each year they must provide additional information on ozone pollution, especially concerning exceedances of the long-term objective.

Table 1. Objectives of the Legal frameworks related of ozone pollution (WHO, 2011)

Objective	Value	Measured	Target/action
Information threshold	180 μg/m³	Hourly average	National authorities should inform the public and give advice immediately after an exceedance. Countries should report monthly on all exceedances
Alert threshold	240 μg/m³	Hourly average	National authorities should inform the public and give advice immediately after an exceedance. Countries should report monthly on all exceedances
Protect human health	120 μg/m³	8 hour average	Not to be exceeded on more than 25 days per year (to be met by 2010).

μg/m³: The concentration of an air pollutant (e.g. ozone) is given in micrograms (one-millionth of a gram) per cubic meter air or μg/m³.

IV.2 Tunisian standards on the AMBIENT AIR

The regulatory framework inherent in monitoring air quality and regulating air pollution in Tunisia is essentially by:

- Tunisian standard on the quality of ambient air: 106.04 NT (1994) on the protection of the environment and limit values for certain pollutants guides in the air.
- Tunisian standard on cement NT.106.05 (1995) on environmental protection emission limit values for polluting cement.
- Thresholds emission limits exhaust road transport vehicles (highway code 2004) and for carbon monoxide for petrol cars and opacity for diesel cars under Decree No. 2000-147 of 24 June 2000 laying down the technical and management.
- Law No. 2007-34 of 04 June 2007 on the quality of the air.

Table 2. Tunisian standard related to ozone pollution (ANPE, 2008)

Pollutant	Analysis Method	Type Average	Authorization exceeded	Limit values (health-related)	value Guide (relative to well-being)
O_3	NT .37.50	1 hour	2 times/30 days	0.12 ppm 235 g/m^3	0.077-0.102 ppm 150 to 200 µg/ m^3

O_3: Ozone

V. OZONE CONTROL STRATEGIES

V.1 European monitoring strategy

Reductions in air pollution can be achieved by a variety of methods including pollution prevention, control technologies, and control measures, and may be implemented through regulatory, market-based or voluntary programs. A control strategy may include a combination of different voluntary measures or mandatory controls.

Ozone control strategies generally target nitrogen oxides (NOx) and volatile organic compounds (VOCs), the primary contributors to ozone formation in the troposphere. Control strategies may comprise a set of regulations that specify emission limits and/or control equipment that are deemed to be reasonable available control technology (RACT), best available control technology (BACT), lowest achievable emission rates (LAER), depending on the severity of the air pollution problem in the area. NOx and VOC control equipment or programs may address specific industrial processes; on-road vehicles; non road equipment such as locomotives; or nonpoint sources such as small industrial boilers, dry cleaners, and consumer solvents. Pollution prevention measures such as use of non- or low-VOC content solvents and coatings can also be part of an effective ozone control strategy.

V.2 Tunisian monitoring strategy

The monitoring program of air quality provides data and scientific information, proposes scientific mechanisms to prepare and implement a clear strategy to protect and secure the quality and safety of the atmosphere. To this end, a national plan was developed which involves the installation of a network of fixed stations for continuous monitoring of the quality of atmospheric environment and to control sources of pollution. The National Agency for Environmental Protection (ANPE) has installed five new stations in Greater Tunis (Bab Alioua, Mannouba and Ghazela City), Gabes and Kairouan. Thus, the number of fixed stations monitoring air quality becomes 15 which are spread as follows:

- 9 stations in Greater Tunis: Bab Saadoun, Bab Alioua, El Mourouj, Ariana, El Nahli, Ben Arous, Rades, Cité Ghazela and Manouba
- 1 station in Bizerte
- 1 station Sousse
- 2 stations in Sfax: Sfax (city center), Sfax South
- 1 Station in Gabes
- 1 Station in Kairouan

Monitoring networks of air quality generally consist of several measuring stations spread over the geographical area in question. Outside air is drawn in a uniform and continuous manner then analyzed. Each station is equipped with one or more analyzers, each measuring a specific pollutant. Meteorological parameters must also be pursued.

The measuring stations are selected on the basis of specific and quantified criteria. A list of criteria allows classifying a measuring station among seven types: urban, suburban, regional rural, national rural, industrial, traffic, and observation and which can be classified into five categories such as:

- Urban and suburban stations

- Traffic stations
- Industrial stations
- Rural stations
- Observing stations

Currently, the National Network for Monitoring Air Quality is composed of ten stations:

1. The Ben Arous station is a nearly Industrial station: Category 3: it is located in the industrial area of the Ben Arous next to the great course No. 1 (GP1).
2. The Sfax station is a nearly traffic station: Categotry 2: it is located in a motorcar crossroad on the Grand Maghreb Square where the Route de Gabès, the Route Menzel Chaker, the Route de l'Aéoroport, l' Avenue des Martyrs, l'Avenue Farhat Hached and the Rue de Mauritanie all intersect.
3. The Radès station is a suburban base station: Category 1: it is located in the Olympic City of Radès.
4. The Bizerte station is an urban station: Category No. 1: It is located in the area of the municipality of Bizerte.
5. The Bab Saadoun station is a nearly traffic station: Category 2: it is located in a motorcar crossroad on the Bab Saadoun Square.
6. The Mourouj station is a suburban station: Category No. 1: it is located in the area of the El Mourouj Park.
7. The Nahli station is a suburban station: Category No. 1 is located in the area of the Nahli Park.
8. A new fixed station in the Cité des Sciences: Following the transfer of the headquarters of the National Agency for Environmental Protection to the Centre Urbain Nord Tunis, the monitoring air quality fixed station of reference has just been installed at the Cité des Sciences in Tunis. The station measures four key parameters: ozone, nitrogen oxides, nitric oxide and sulfur dioxide.

Work is underway to connect this station to the central station of the National Network for Monitoring Air Quality (RNSQA). The site was chosen following studies by the technical team in charge of air pollution, which identified several advantages such as:

- The proximity of a very important criterion which is the "Route X".
- The proximity of the headquarters of the ANPE thus the possibility of using this station for education (sensitization) and demonstration.

- The very important scientific input and the tight collaboration with the Sciences City.

9. The station of Sousse is a suburban base station: Category N 1: it will be located in the University Hospital of Farhat Hached.
10. The Sfax 02 station is a nearly Industrial station: Category 3: it will be located in the headquarters of the Tunisian Chemical Group (GCT), Gabès Road Km 3.

In addition, and as part of the partnership between institutions, ANPE has signed a cooperation agreement with the Tunisian Chemical Group (GCT). This agreement aims to connect the two fixed stations monitoring air quality installed by the Chemical Group of Gabès. Both stations are installed, one in the center of Gabès, and the other in the industrial area of Bouchamma.

The ANPE has signed a cooperation agreement with the Department of Environmental Health and Environment Protection. This agreement aims to connect the two fixed stations monitoring air quality installed in Gabès and Megrine under the supervision of the Ministry of Public Health.

On the other hand, and in order to ensure monitoring air quality throughout Tunisia, ANPE has a mobile laboratory which started operating in 1994. Currently, the aim of this truck laboratory is the control of the state of air quality throughout the territory of Tunisia, ensuring measurement campaigns in the vicinity of various sources (fixed and / or mobile) of atmospheric pollution. It produces pollution maps and identifies the sites most affected by pollution and which deserve continuous monitoring. Thus it serves to determine sites for new monitoring air quality stations of the RNSQA.

V.3 National Network for Monitoring Air Quality

Stations installed in the governorates of Tunis, Bizerte, Ariana, Ben Arous and Sfax include each a set of analyzers that can identify and measure the concentration levels of several air pollutants. These stations are also equipped with meteorological sensors to determine the parameters that are responsible for causing changes in physical and chemical phenomena of diffusion, dispersion or accumulation that may undergo atmospheric compounds, which are: the wind speed and direction, air temperature, air pressure, relative humidity and solar radiation.

Automatic measurements of the concentration of all pollutants and all meteorological parameters listed above are performed every 30 seconds and the data are stored after verification and processing every ¼ hour. Additional non-automatic measures are also provided for airborne dust, heavy metals ... All the analysis and measurement equipment are the subject of periodic calibrations, and routine checks of the sensitivity of the zero state and the drift of the baseline. These operations can be performed either in station or remotely (from the Central National Station for the various stations.

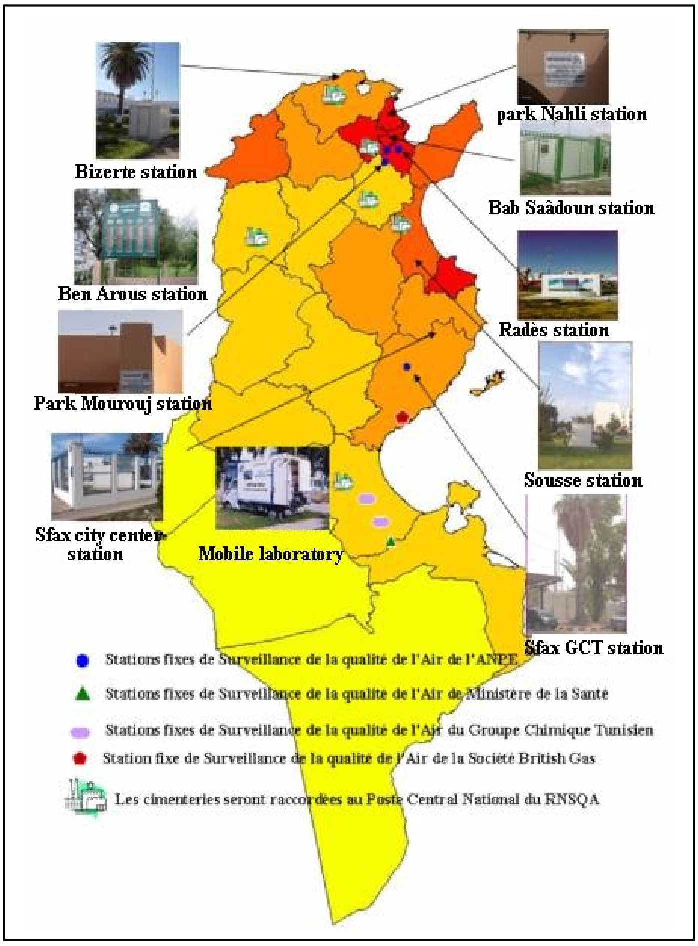

Figure 2. Geographical distribution of stations for monitoring the air quality in Tunisia (Source: RNSQA)

V.4 The National Central air quality Monitoring Station

All gas analyzers and solid particles and the atmospheric weather sensors are controlled by a measurement acquisition station (SAM) that provides data acquisition, the functioning and control of various devices in an automatic, autonomous and continuous way. Another computer station equipped with a transmission system (via modem) is connected to all the cabins and is the Central National Station (PCN).

This Station is able to perform remotely, the same analyzers' management and control operations and to ensure, real-time data acquisition regardless of the location of measuring stations.

The transmitted data are stored, checked, analyzed and validated through the implementation of powerful means.

Through the PCN, the recorded values are automatically compared with the Tunisian standard on the quality of ambient air (NT 05 106).

Chapter II

Description of the study area

I. PREFACE

In this study we focus in the urban and suburban areas of Greater Tunis. The Greater Tunis area has an area of about 300,000 hectares, 30,000 of which is urbanized, the rest being shared between bodies of water (20,000 hectares of lakes or lagoons) and agricultural or natural land (250,000 hectares). However, urban growth, which is estimated to be increasing by 500 hectares per year, is gradually changing the landscape with urban sprawl.

According to the 2004 census of the National Institute of Statistics of Tunis, this unit includes four governorates: Tunis, Ariana, Ben Arous, and Mannouba.

Population is 2.314.400 inhabitants, representing 22% of total population (2009 figure)

II. GEOGRAPHY

Greater Tunis is located in north-eastern Tunisia on the Lake of Tunis, and is connected to the Mediterranean Sea's Gulf of Tunis by a canal which terminates at the port of La Goulette / Halq al Wadi. The ancient city of Carthage is located just north of Tunis along the coastal part.

Greater Tunis area is consisting of four governorates (Tunis, Ariana, Ben Arous and Manouba the), it covers an area of 2726 km ², representing 1.6% of the total area of the country. It is a land to the relief sometimes flat, sometimes folded, mingling plains, hills and hills hardly exceeding 200 m in height, and bowls. Those of the Ben Arous Governorate are drained by wadis and Miliane el Hamma, those of Manouba Chafrou by the river.

The Municipality of Tunis is divided into fifteen districts municipaux11 Bab El Bhar, Bab Souika, Cité El Khadra, Jelloud Djebel El Kabaria El Menzah El Ouardia, Ettahrir, Ezzouhour, Hraïria, Medina, Al Omran El Omrane higher Séjoumi and Sidi Bashir.

Jebel Boukornine, a mountain which rises to 576 m, dominates the town of Hammam-lif, and beyond, the Gulf of Tunis. Jebel Ressas (805 m) side Mornag (Ben Arous), Jebel Kharrouba side of Ben Arous and Amar side Djebel Sidi Thabet (Ariana) are among the few mountains in Greater Tunis.

The majority of the country consists of natural or agricultural areas and water bodies. Only about one-tenth of the area is urbanized, a figure that continues to increase, however, at the expense of green spaces and even lakes.

Figure 3. Localization of different governorates in the area of study (Google Earth, 2012)

III. CLIMATE

Table 3. Climatic characteristics of the area study

Month	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct
Average high °C (°F)	15.7 (60.3)	16.5 (61.7)	18.1 (64.6)	20.7 (69.3)	24.9 (76.8)	29.0 (84.2)	32.6 (90.7)	32.7 (90.9)	29.7 (85.5)	25.2 (77.4)
Daily mean °C (°F)	11.5 (52.7)	12.0 (53.6)	13.2 (55.8)	15.6 (60.1)	19.3 (66.7)	23.2 (73.8)	26.3 (79.3)	26.8 (80.2)	24.4 (75.9)	20.4 (68.7)
Average low °C (°F)	7.2 (45.0)	7.4 (45.3)	8.3 (46.9)	10.4 (50.7)	13.7 (56.7)	17.3 (63.1)	20.0 (68.0)	20.8 (69.4)	19.0 (66.2)	15.5 (59.9)
Precipitation mm	59.3	57.0	47.2	38.0	22.6	10.4	3.1	7.1	32.5	65.5

Source: World Meterological Organization

Greater Tunis has a warm-summer Mediterranean climate characterized by a hot and dry season and a cool and rainy season. The local climate is also affected somewhat by the latitude of the city, the moderating influence of the Mediterranean Sea and the terrain of the hills.

Winter is the wettest season of the year, when more than a third of the annual rainfall falls during this period, raining on average every two or three days. The sun may still increase the temperature from 7 °C (45 °F) in the morning to 16 °C (61 °F) in the afternoon on average during the winter. Frosts are rare or nonexistent. In spring, rainfall declines by half. The sunshine becomes dominant in May when it reaches 10 hours a day on average. In March temperatures may vary between 8 °C (46 °F) and 18 °C (64 °F), and between 13 °C (55 °F) and 24 °C (75 °F) in May. However, it is common for temperatures to soar even as early as April with record temperatures reaching 40 °C (104 °F). In summer, rain is completely absent and the sunlight is at a maximum. The average temperatures in the summer months of June, July, August, and September are very high. Sea breezes may mitigate the heat, but sometimes the sirocco winds reverse the trend. In autumn, it begins to rain, often with short thunderstorms, which can sometimes cause flash floods or even flood some parts of the city. The month of November marks a break in the general heat with average temperatures ranging from 11 °C (52 °F) to 20 °C (68 °F).

IV. POPULATION

As capital of Tunisia, Tunis and the surrounding governorate forming the greater Tunis are the most populated zones.

Table 4. Population analysis of the Greater Tunis

Governorate	Population	Surface (km²)	Density (hab/km²)	Proportion %
Tunis	996400	356	2798.87	42
Ariana	483500	356	1358.14	20
Ben Arous	565500	790	715.82	23
Mannouba	363000	1204	301.49	15
Greater Tunis	2408400	2706	890.02	100

Source: INS_RGPH 1994-2004

The attraction of these areas is mainly explained by:

- Property factor: availability of lots with low prices which encourages middle and poor classes to settle especially in popular zones (Ettadhamen, Dar Fadhal, Soukra...)

- Proximity to the capital Tunis.

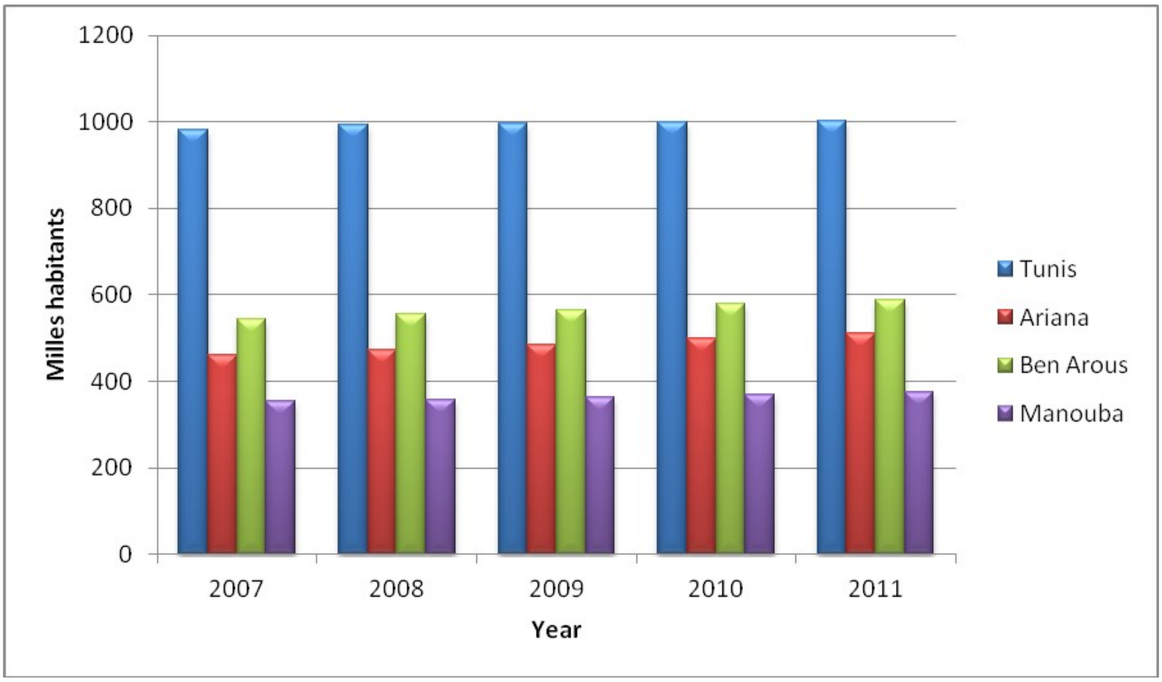

Figure 4. The population growth in Greater Tunis between 2007 and 2011 (Saad, 2012)

According to figures from the INS (National Institute of Statistics), the Tunisian population is estimated at 10,673,800 inhabitants representing an increase of 11% compared to 2011.

Greater Tunis is the most populated region in Tunisia with 2,477,400 inhabitants (h), followed Sfax 944 500 h 762 600 h with and Nabeul.

The data provided by the INS does not reflect intra-regional migration. Indeed, all regions experienced a positive evolution of the population, but it is reasonable to think that Tunis (+ 200 600) is the main city to which there is a shift of population from other regions.

The evolution of major cities has often been analyzed from a quantitative or spacial point of view. Anthropological and socio-urban approaches of the city are not numerous and require abundant research material and multidimensional observations. From this point of view, Greater Tunis is a region under-analyzed and understanding its evolution is dependent on the knowledge of the modes of decomposition and recomposition of social groups and their integration into the urban space.

Territoriality and centrality is a field from which it is possible to analyze the problem of membership of a population in relation to identity referents and in relation to urbanity.

V. URBANIZATION

Tunisia is a highly urbanized country with the urbanization rate reaching 66% in 2011. The urban population is projected to reach 70% by the year 2020. In fact, urbanization is a historic phenomenon; by 1975 50% of the country's population already lived in cities. This urbanization is characterized by:

- A pronounced coastal urbanization amounting to 75% of the total urban population grouped in a number of agglomerations less than 500,000 inhabitants each (with the exception of Greater Tunis),
- The preponderance of the agglomeration of Greater Tunis with 2.5 million inhabitants equivalent to 20% of the urban population, and
- The relative demographic growth of the smaller cities of the central Sahel. Finally, low fertility and rural to urban migration rates have stabilized urban growth.

Over the past forty years, the transformation of urbanization in Tunisia especially in Greater Tunis, were driven both by urban policies committed from the 70s and community strategies that, if not in line with these policies, have developed practices that have also contributed to the urbanization.

In the 60s, characterized by a development model based on the monopole state development, has had multiple negative and resulted in a deterioration of living conditions and living conditions of the population.

This system, called a socialist by its promoters, sinister helped the small farmers, to increase the breakdown of agrarian structures and boost the rural exodus to the cities. Treatment of urban issues has been achieved by coercion and repression, such as the demolition of and discharge gourbivilles occupants to their regions of origin.

Chapter III

Materials and methods

I. CONTEXT OF THE STUDY AND ISSUES

In this work we focus in the evaluation of ozone pollution in Greater Tunis, for that, we used a database collected from the central laboratory of air quality monitoring located in Park Mourouj and created by the National Agency of Environmental Protection (ANPE).

In order to perform a comparison between urban and suburban areas in terms of Ozone pollution, we process data on Ozone in the Greater Tunis from the year 2003 to the year 2011.

Concentration of ozone is expressed in mg/m^3. Eight stations were measuring these pollutants in the region of Grand Tunis (Table 5).

Table 5.Typology of monitoring stations of air quality in Greater Tunis

Station	**Radès**	**Ben Arous**	**Bab Saâdoun Tunis**	**Park Nahli Ariana**	**Park El Mourouj**	**Bab Alioua Tunis**	**Mannouba**	**El Ghazela**
Typology	urban	Near industrial zone	Near traffic	Suburban	Suburban	Near traffic	Near traffic	urban

An urban area assigned primarily to habitat, with shops, services public or private individuals and companies with a central character, offices, public facilities, craft activities.

Suburban areas are also seen as an interface between urban and rural areas, also called the transition zone or zone of interaction, where urban and rural activities are juxtaposed, and landscape features are subject to rapid changes, characterized by strong urban influences, easy access to markets, services and other service providers, a relative shortage of land and pollution risks, the problems of urban growth and waste disposal.

I.1 Selection criteria for stations

The choice of study area (monitoring stations) was based on:

- The geographic location which means the sort of the region (urban area, industrial areas, suburban areas).
- The availability of measures and data on the site.

▪ Accessibility of characteristic climatic as humidity, precipitations and wind direction that can influence the dispersion of the Ozone in the area.

I.2 Process steps

The RNSQA measure systematically a number of pollutants called "tracers" or "indicators" that reflect emissions from major sources of pollution. These are the main pollutants monitored by routine or regular measures companions by the National Network of monitoring air quality (RNSQA).

After being collected, data are defined and validated, then processed into information using the software R-Cran.

This tool helps us to get curves and graphs that describe better the distribution of ozone between urban and suburban areas.

I.3 Using R to analyze air pollution monitoring data

R is a computer programming language developed specifically for the purposes of analyzing data (R-project).

R is available as Free Software that is described as a statistical system, a system for statistical computation and graphics, and an environment for data analysis and statistics.

For air pollution purposes, R represents the ideal system with which to work. Core features such as effective data manipulation, data/statistical analysis, high quality graphics and visualization lend themselves to analyzing air pollution data.

While R began and is probably best known as a statistical programming language, its strong capability of working with data in general means that it has a much wider impact, covering a very wide range of disciplines. The ability to develop one's own analyses, invent new approaches etc. using R means that advanced tools can be quickly developed for specific purposes. The use of R ensures that analyses and graphics are not constrained to "of the shelf" tools. These tools will often contain functionalities that are either part of the R base system or that exist through specific packages.

Another key strength of R is its package system. The base software, which is in itself highly capable (e.g. offering for example linear and generalized linear models, nonlinear regression models, time series analysis, classical parametric and nonparametric tests, clustering and smoothing), has been greatly extended by additional functionality. Packages are available to carry out a wide range of analyses including: generalized additive models, linear and non-linear modeling, regression trees, Bayesian statistics etc.

II. DATA DESCRIPTION

We have collected data from the national urban park of Mourouj. The park is situated on the southwest of the city of Tunis; with a surface of 100 ha the park was built on the former landfill on the el Yahoudia under banks of sabkhet Séjoumi. Until now just 30% of surface is developed however 70% is under study planning.

Figure 5. Localisation of Park Mourouj where data was collected

All given information in terms of ozone concentrations in the atmosphere in different station in greater Tunis was gathered from fixed station stated in different urban and sub-urban sites then transmitted to super sites put in a hard driver connected to information system in the park of Mourouj.

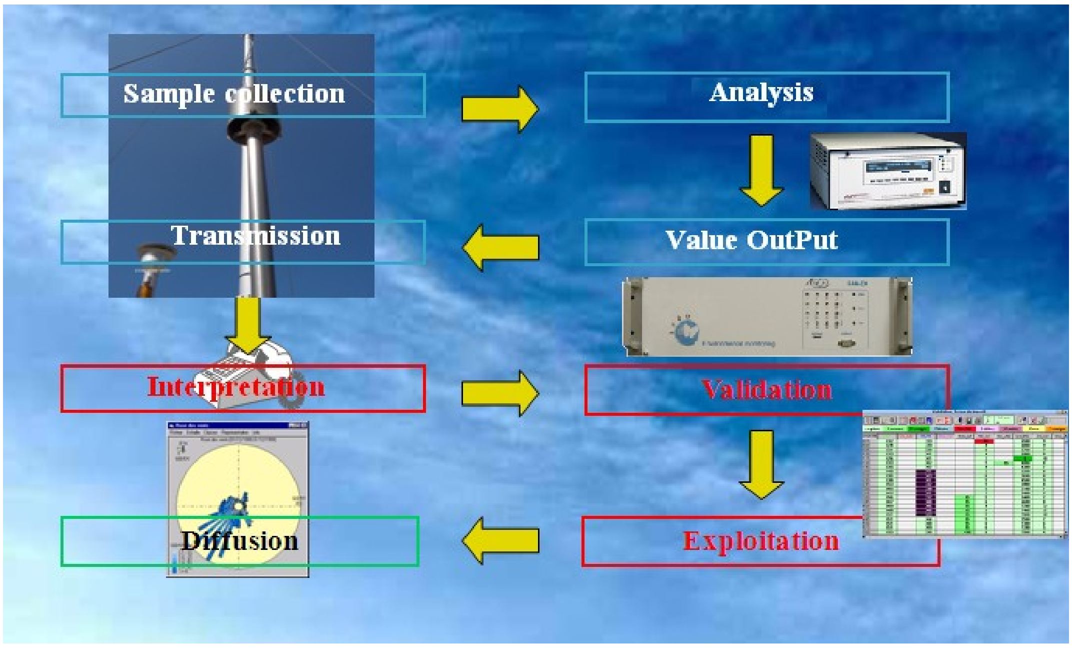

Figure 6. Chain of environmental information (Source: RNSQA)

During January 2010, the Super Site or reference site was implemented and entered into operation. We should bring to mind that the Super Site is funded under the Tunisian-Korean cooperation. This site has analyzers PM10, PM2.5, NOx, SO_2, CO and O_3 as well as a gas chromatograph that will measure volatile organic compounds (VOCs).

So with this new achievement, the National Network for Monitoring Air Quality expand its field of intervention research on ozone and volatile organic compounds.

Figure 7. Information system and new supersite station installed in 2010 in Park Mourouj (Source: RNSQA)

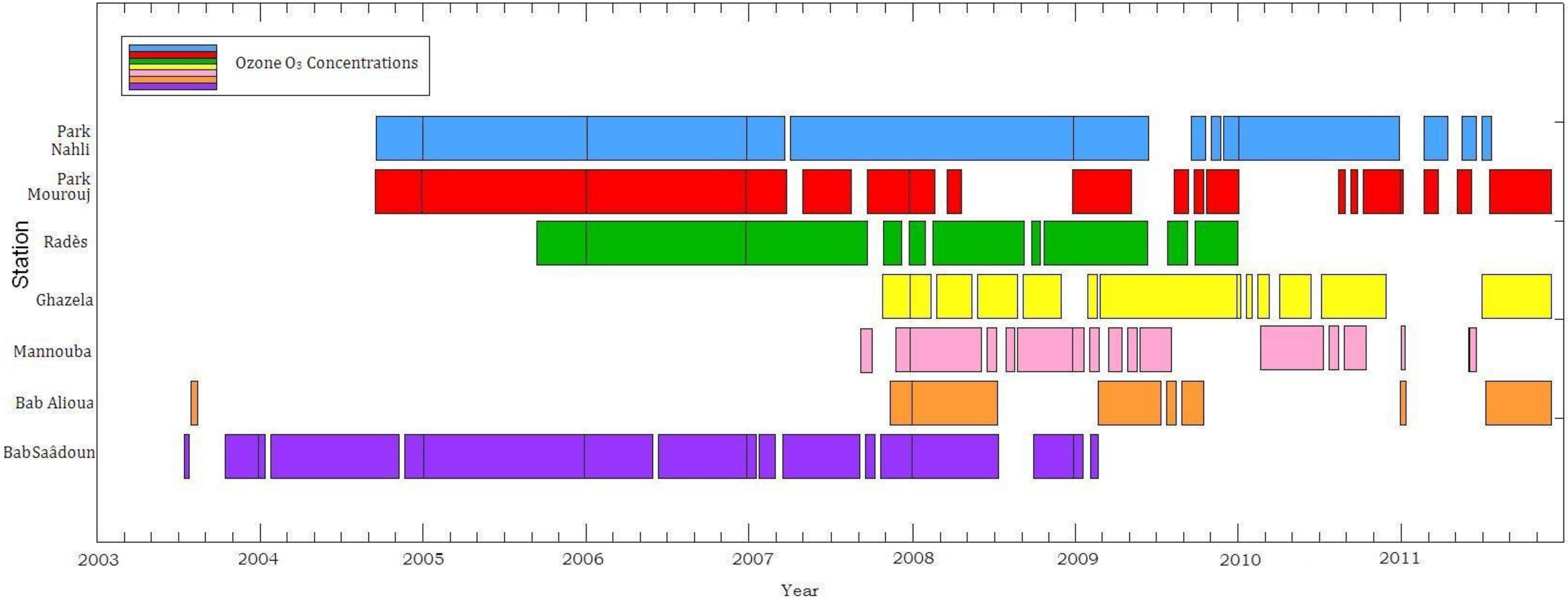

Figure 8. Data availability in the study area (Saad, 2012)

III. STATISTIC DESCRIPTION ANAYSIS

In ozone pollution, the variation of a pollution level by time of day and day of week can reveal useful information concerning the likely sources. For example, road vehicle emissions tend to follow very regular patterns both on a daily and weekly basis. By contrast some industrial emissions or pollutants from natural sources (e.g. sea salt aerosol) may well have very different patterns.

The **time Variation** function produces four plots: day of the week variation, mean hour of day variation and a combined hour of day – day of week plot and a monthly plot. Also shown on the plots is the 95 % confidence interval in the mean. These uncertainty limits can be helpful when trying to determine whether one candidate source is different from another.

The uncertainty intervals are calculated through bootstrap re-sampling, which will provide better estimates than the application of assumptions based on normality, particularly when there are few data available. The function can consider one or two input variables. In addition, there is the option of “normalizing” concentrations (or other quantities). Normalizing is very useful for comparing the patterns of two different pollutants, which often cover very different ranges in concentration. Normalizing is achieved by dividing the concentration of a pollutant by its mean value. Note also that any other variables besides pollutant concentrations can be considered e.g. meteorological or traffic data.

There is also an option difference which is very useful for considering the difference in two time series and how they vary over different temporal resolutions.

To better describe typical day, week and month curves, we referred to the year in which we dispose more available data. For this, we choose the year 2008 to describe behavior of the time series of ozone pollution in urban and suburban areas in order to read and interpret better ozone pollution levels. The following shows the function applied to concentrations of O_3 concentration (ppb) on the year 2008 (Figure 9).

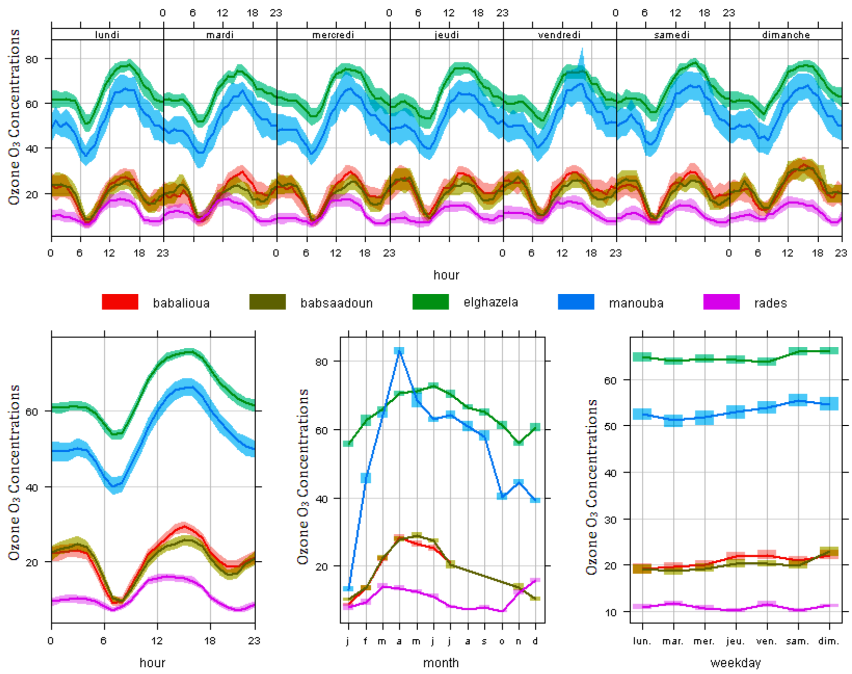

Figure 9. Plot using the timeVariation function (Rcran) to plot O_3 concentration (ppb) in urban stations (Saad, 2012)

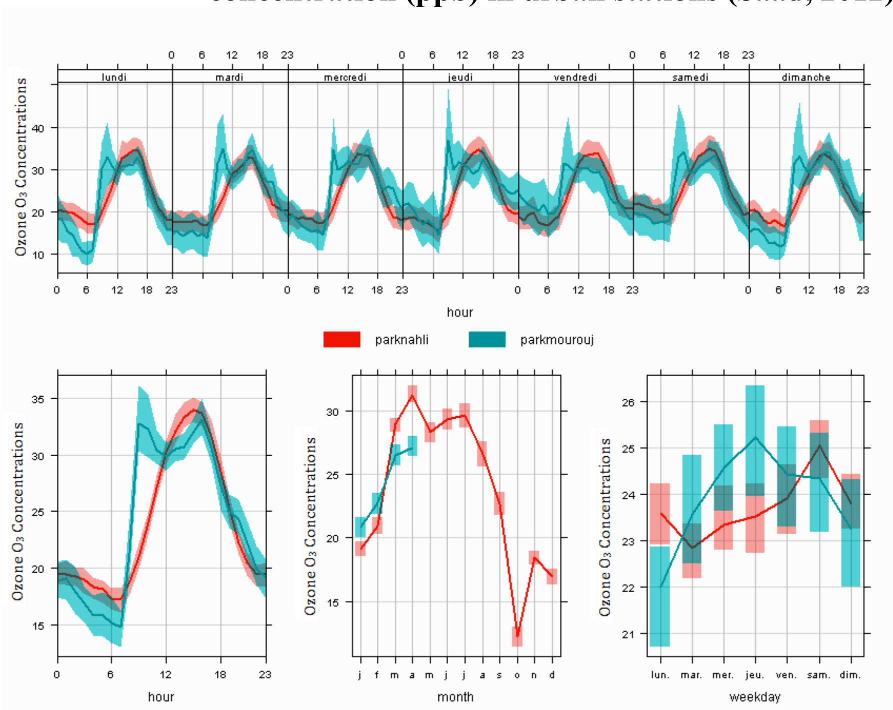

Figure 10. Plot using the timeVariation function (Rcran) to plot O3 concentration (ppb) in suburban stations (Saad, 2012)

These plots show both sets of information together to provide an overview of how concentrations vary.

III.1 Typical day curve

The graph of the typical day summaries statistics shows the average behavior of a pollutant during a day (24 hours). Curve of typical day is a series of 24 averages. Each value (e.g. 13 to 14h) is the average of all hourly averages 13 to 14h recorded daily throughout the period.

III.1.1 Urban area

In this part, we choose the year 2008 in order to describe typical day curve in urban area regarding data availability and accessibility, that's why we present the concentration of O_3 as following typical day curve recorded in urban stations; Bab Alioua, Bab Saâdoun, Radès, Elghazela and Mannouba.

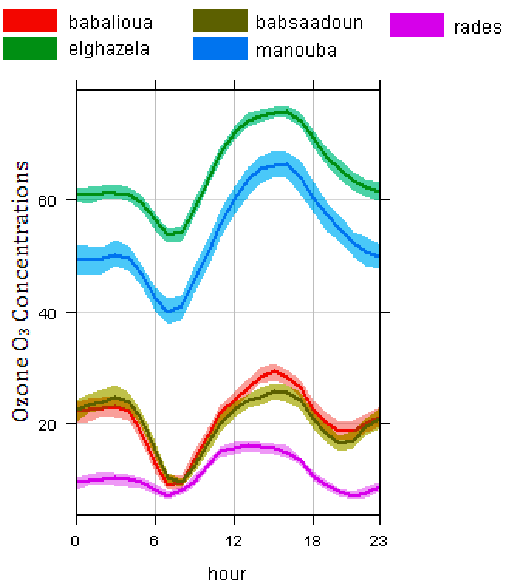

Figure 11. Typical day curve related to considered urban stations (Bab Alioua, Bab Saâdoun, Radès, Elghazela and Mannouba) recorded in 2008

The plot clearly shows the markedly different temporal trends in concentration.

As shown in figure 11, concentrations of ozone increase during rush hours in midday when traffic road is maximal.

In urban areas, ozone is destroyed again at night; the lack of sunlight prevents the formation of ozone in the presence of nitric oxide (NO) from road traffic. At this time, the results of the chemical reaction are reversed. Ozone concentrations in urban areas may be lower than the rates recorded in the surrounding countryside, where there is not enough nitric oxide to reduce ozone.

We note that ozone concentrations are higher in Mannouba and Elghazela stations given they are near traffic locations.

III.1.2 Suburban area

We present the concentration of O_3 in 2008 given data availability as following typical day curve recorded in suburban stations; Park Mourouj and Park Nahli.

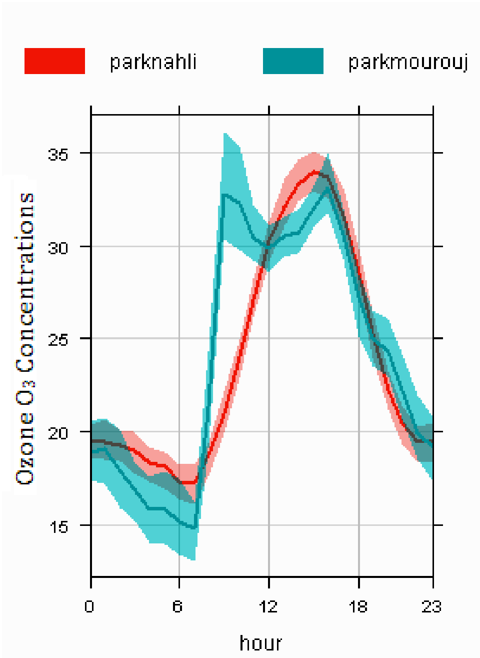

Figure 12. Typical day curve related to considered suburban stations (Park Nahli and Park Mourouj) recorded in 2008

The plot shown in figure12 shows the diurnal variation of concentrations for all days. It shows that O_3 concentrations tend to peak around 9 am and 2 pm. The shading shows the 95 % confidence intervals of the mean.

III.2 Typical week curve

The curve summaries statistics shows the average behavior of a pollutant during a week (7 days). The typical week curve represents a series of seven averages (Monday to Sunday). Each value (e.g. Monday) is the average of all daily medium recorded on Mondays during the period concerned.

III.2.1 Urban area

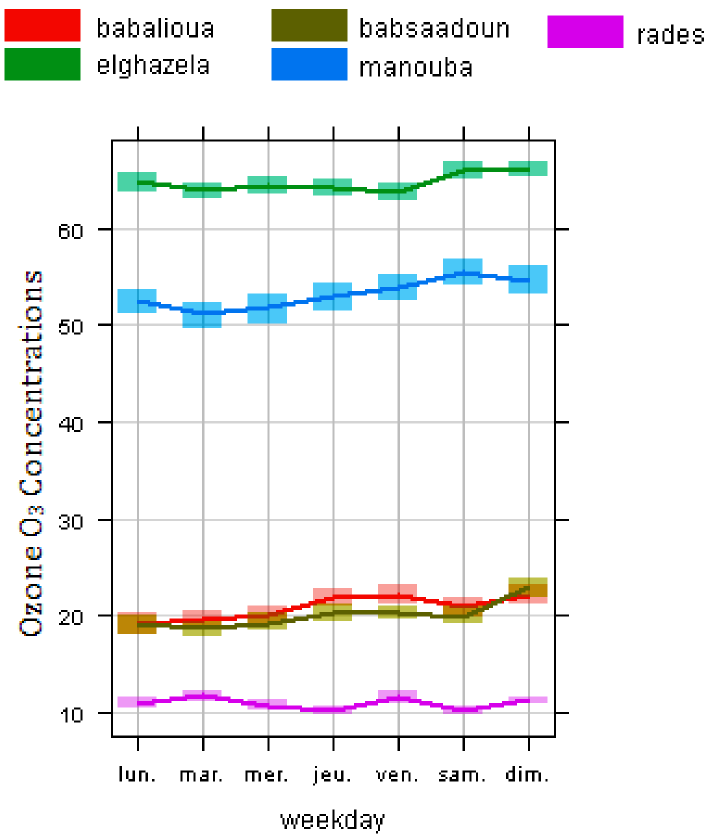

Figure 13. Typical week curve related to considered urban stations (Bab Alioua, Bab Saâdoun, Radès, Elghazela and Mannouba) recorded in 2008

The plot of typical week curve (figure 13) shows how O_3 concentrations vary by day of the week. The weekly cycle is unique among the ozone periodicities in that it is explicitly driven by human activities.

Since the atmospheric variables are not expected to vary from one day of the week to another, the weekly cycling of the ozone signal provides an outstanding opportunity to study the man-induced ozone contribution. The weekly pattern analysis reveals the consequences of emission reductions from weekday to weekends. It represents an emission reduction scenario that can be verified by the available data.

III.2.2 Urban area

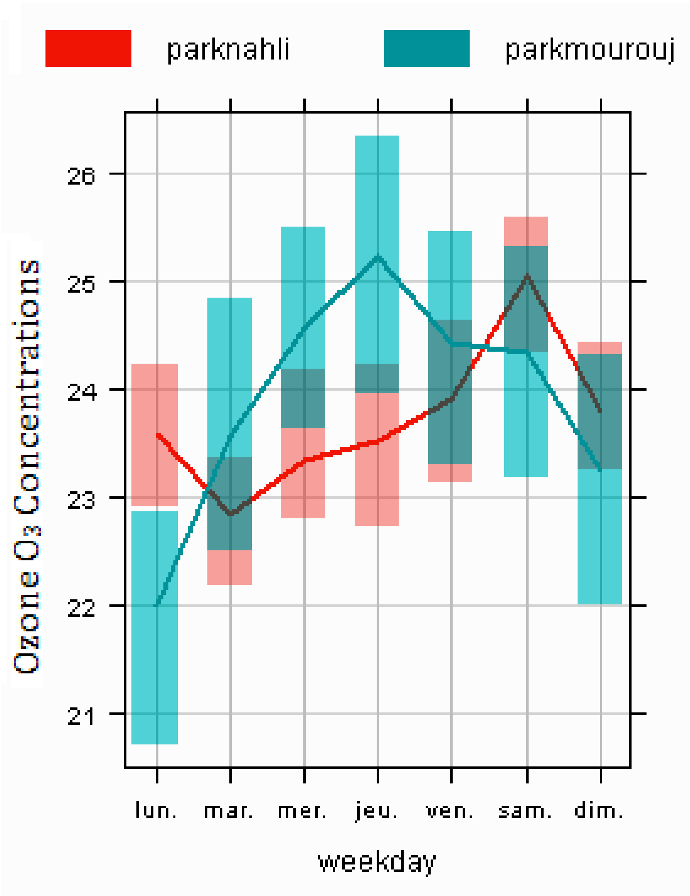

Figure 14. Typical week curve related to considered suburban stations (Park Nahli and Park Mourouj) recorded in 2008

Here there is strong evidence that O_3 is much lower at the weekends and that there is a significant difference compared with weekdays. It also shows that concentrations tend to increase during the weekdays.

III.3 Typical month curve

The curve of the monthly evolution highlights trends of monthly averages of pollutant throughout the year. This curve focuses on the behavior of pollutants according to the seasons.

III.3.1 Urban area

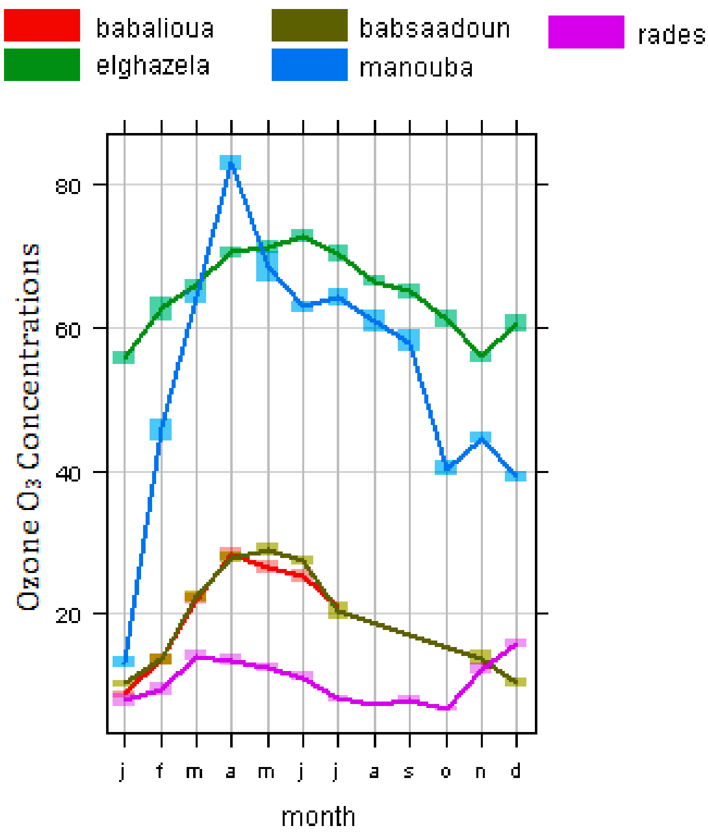

Figure 15. Typical month curve related to considered urban stations (Bab Alioua, Bab Saâdoun, Radès, Elghazela and Mannouba) recorded in 2008

In summer when solar radiation is intense, VOCs emitted by conifers allow the formation of ozone. The urban average monthly concentrations are shown in figure 15. A great dispersion is observed among the values measured in summer compared with the ones obtained in winter months. The month that shows the lowest range is January with 10 µg m^{-3}, June is the month with the greatest range exceeding 85 µg m^{-3}.

From the same figure, we can infer that ozone concentration starts to increase slowly from January to June. In June the highest value is reached and the ozone value starts to decrease. The lowest value is reached in November.

III.3.2 Urban area

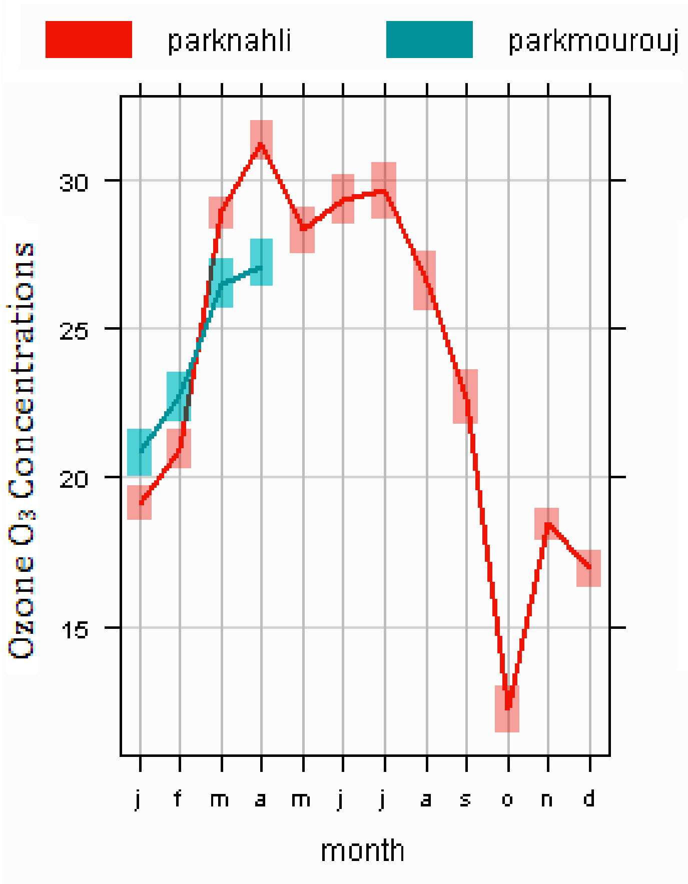

Figure 16. Typical month curve related to considered suburban stations (Park Nahli and Park Mourouj) recorded in 2008

For urban areas, the same as for suburban, the highest levels are found in the spring/summer, and the lowest in the autumn, because strong sunlight and hot weather result in harmful ozone concentrations.

The summer months represent the group of greatest interest in the study of the behavior of photochemical origin due to the favorable meteorological conditions that are produced in this season, such as strong sunshine that provokes the start of chemical reactions with the precursors and the limited atmospheric diffusion that favors the accumulation of ozone in the layers close to the ground.

III.4 Conclusion

From the figures described previously, we notice a similarity on the evolution of ozone concentrations in urban and suburban areas. In fact, plots clearly show the markedly different temporal trends in concentration. There is a very pronounced increase in O_3 concentrations during the peak pm rush hour. The other important difference is on midday when O_3 concentrations are relatively much higher than other hours of the day. This is because flows of cars (mostly petrol). There are important difference in how these emissions vary by hour of day and day of week. In addition, ozone levels are higher on hot, sunny summer days especially during episodes of stagnant air. In urban and suburban areas, high-ozone days tend to occur more frequently on weekdays than on weekends, however, in some urban areas (Bab Saâdoun, Bab Alioua and Radès), ozone concentrations tend to be higher on weekends than on weekdays, despite what are believed to be lower emissions of ozone precursors on weekends. This phenomenon is known as the “weekend effect.” Numerous hypotheses to explain the weekend effect have been proposed, but a detailed understanding of it has been lacking.

Chapter IV

Results and discussion

I. INTRODUCTION

This study summarizes the measures observed by the National Network for Monitoring Air Quality (RNSQA) from the year 2003 to 2011.

The principal pollutant analyzed in this report is ozone (O_3) correlated with various pollutants such as nitrogen dioxide (NO_2), sulfur dioxide (SO_2), dust (PM10) and in accordance with Tunisian standard NT.106.04 (1994) on the air current.

Space and time are the most important variables considered in the analysis. This analysis involves three phases:

Phase 1: Spatial Analysis

This phase provides a comparative view of the measures RNSQA from the year 2003 to the year 2011, to take the peculiarities and critical situations initially and compare compared to the Tunisian standard.

Phase 2: Temporal Analysis

This phase is to monitor ozone level over time, i.e. the development of one month to another, and one hour to the next. This phase is important because it allows one to draw relevant information on the hourly evolution of different pollutants and to detect the effect of seasonal changes on the evolution of ozone concentrations.

Phase 3: Influence of the meteorological parameters

In this phase, the analysis focused on supposed critical situations, otherwise the particularities compared to normal situation or measures of the highest levels compared to others, and by coupling with the pollutant meteorological parameters.

The box mustache is a simple graphical tool, accurate and efficient briefly displays the dispersion of a series of observations. The graph includes among other various indicators of position (1st and 3rd quartile, median...) as shown in the following chart.

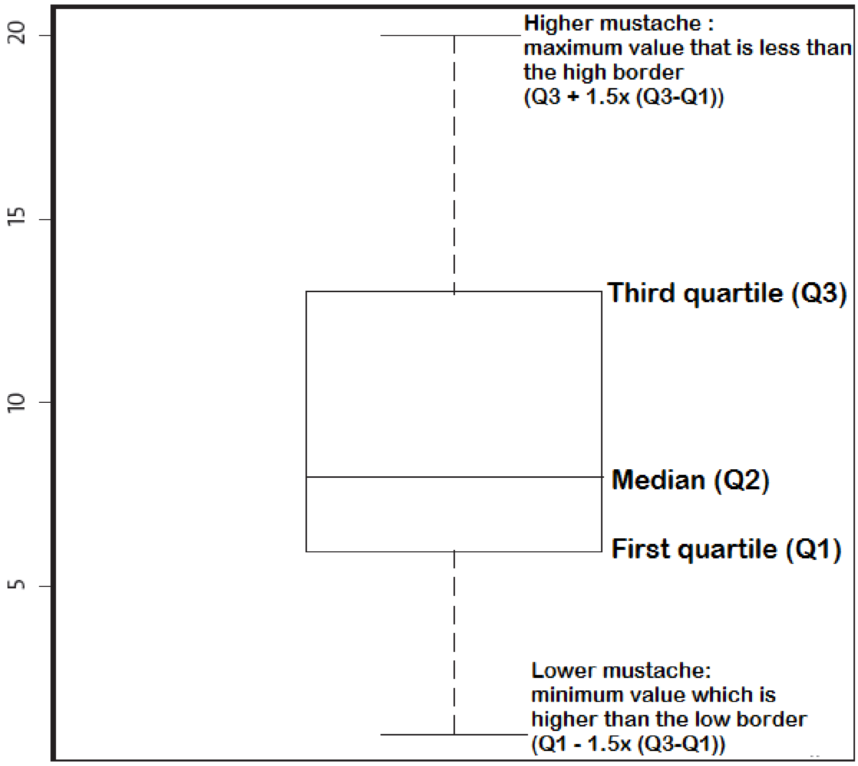

Figure 17. Box plot with the software R

II. SPATIAL ANALYSIS

The National Network for Monitoring Air Quality records by monitoring stations:

- 26 exceedances of the limit value on health (120 ppb),
- 119 exceedances of the guideline value on the welfare and during 2008.

All exceedances of the limit value were observed by the monitoring station located at Mannouba.

The lowest values were recorded by the measuring station of Radès and some exceedances of the guideline values at the following stations: ElGhazela, Park Mourouj and Park Nahli.

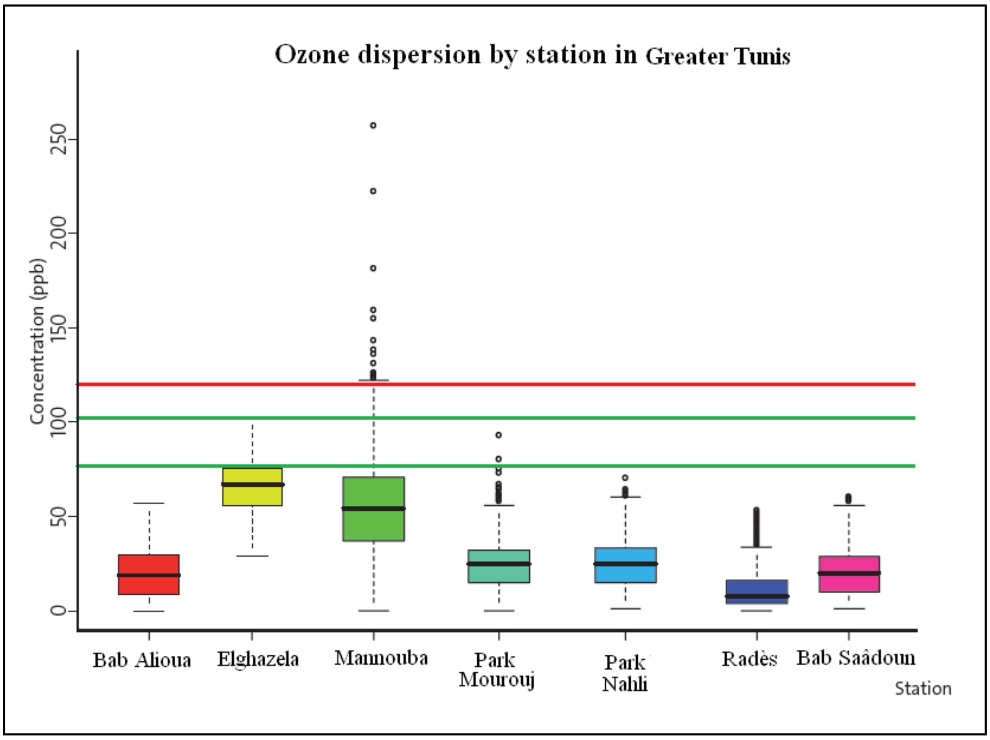

Figure 18. Spatial evolution of O_3 in 2008

The measurement stations installed in Manouba and Ghazela record respectively the highest values of ozone during 2008. We recorded 26 exceedances limit value and 112 exceedances of the guideline value. At level of temporal evolution of ozone concentrations, the highest value was observed in the summer, especially during the afternoon.

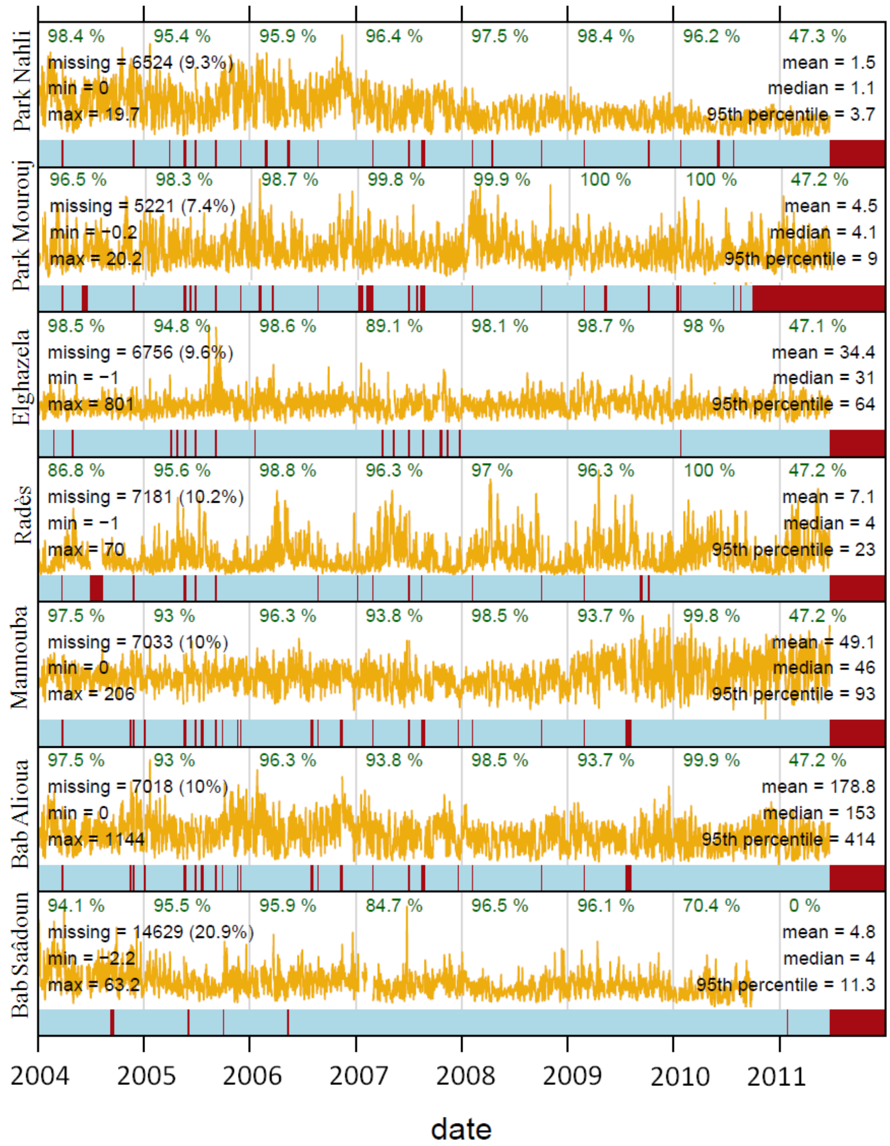

Figure 19. Temporal evolution of O_3 levels between 2004 and 2011 in different stations

The plots in the left panel show the time series data, where blue shows the presence of data and red missing data. The daily mean values are also shown in pale yellow scaled to cover the range in the data from zero to the maximum daily value. As such, the daily values are indicative of an overall trend rather than conveying quantitative information. For each station, the overall summary statistics are given. For each year the percentage data capture is shown in green font. The panels on the right show the distribution of each species using a histogram plot. A slight increase in average ozone during the summer of 2010 was recorded compared to the year 2008.

III. TEMPORAL ANALYSIS

III.1 Temporal evolution in urban areas

III.1.1 Mannouba Station

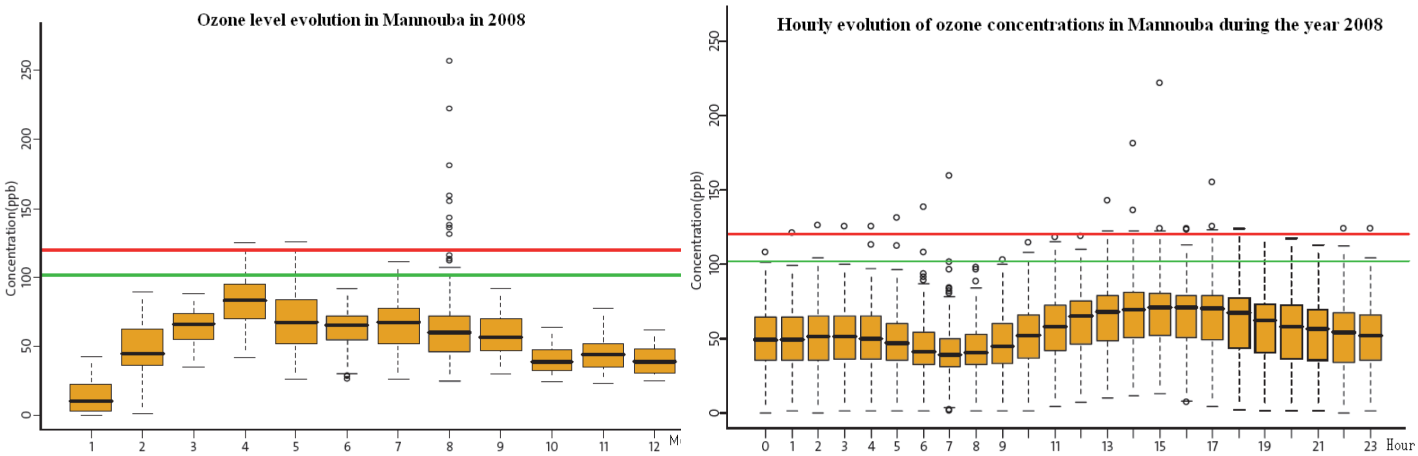

Figure 20. Temporal evolution in Mannouba station in 2008

In Manouba, April and May have recorded the highest values of ozone, however the values sup measured is observed during the August. The following table shows the number of value guide exceedings and limit observed by the station measure of Mannouba, for the year 2008. Using the statistical model CART, a day is over three phases perspective ozone observed value:

1. From midnight to 10: 30 h> mean (ozone) = 46.5 ppb
2. From 10: 30 am to 18: 30h> mean (ozone) = 63 ppb
3. From 18: 30 to midnight> mean (ozone) = 53 ppb

Month	1	2	3	4	5	6	7	8	9	10	11	12
exceedings number of Value limits	0	0	0	13	4	0	0	13	0	0	0	0
exceedings number of value guide	0	0	0	82	19	0	3	9	0	0	0	0

III.1.2 Bab Saâdoun Station

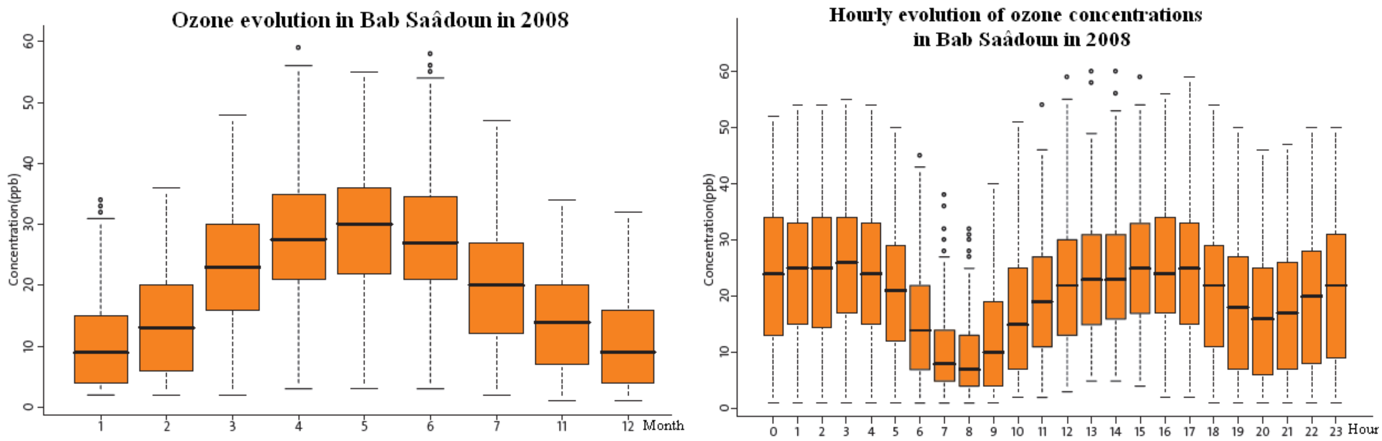

Figure 21. Temporal evolution in Bab Saâdoun station in 2008

In Bab Saadoun, concentrations of ozone have undergone a gradual increase on January until May and then decreased until the end of the year. O_3 concentrations are symmetrical in May.

April, May and June marked the highest values of ozone in Bab Saadoun during 2008. This chart allows for the dispersion of ozone each hour of the day.

Ozone concentrations reach maximum values in the afternoon, when general weather conditions are favorable for ozone photochemistry.

III.1.3 Elghazela Station

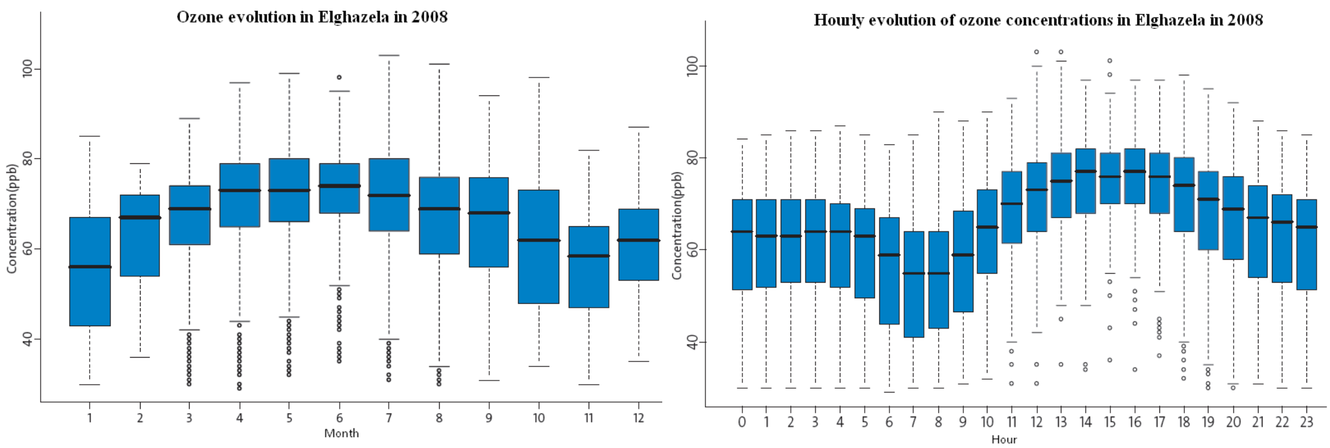

Figure 22. Temporal evolution in Elghazela station in 2008

No exceedances of the guideline value or the value limit in Elghazela station for the year 2008 have been recorded. The highest values were observed during April, May, June and July. At night there is a background level decrease. The morning, with the increase in traffic, the maximum is reached (especially in the afternoon).

III.1.4 Bab Alioua Station

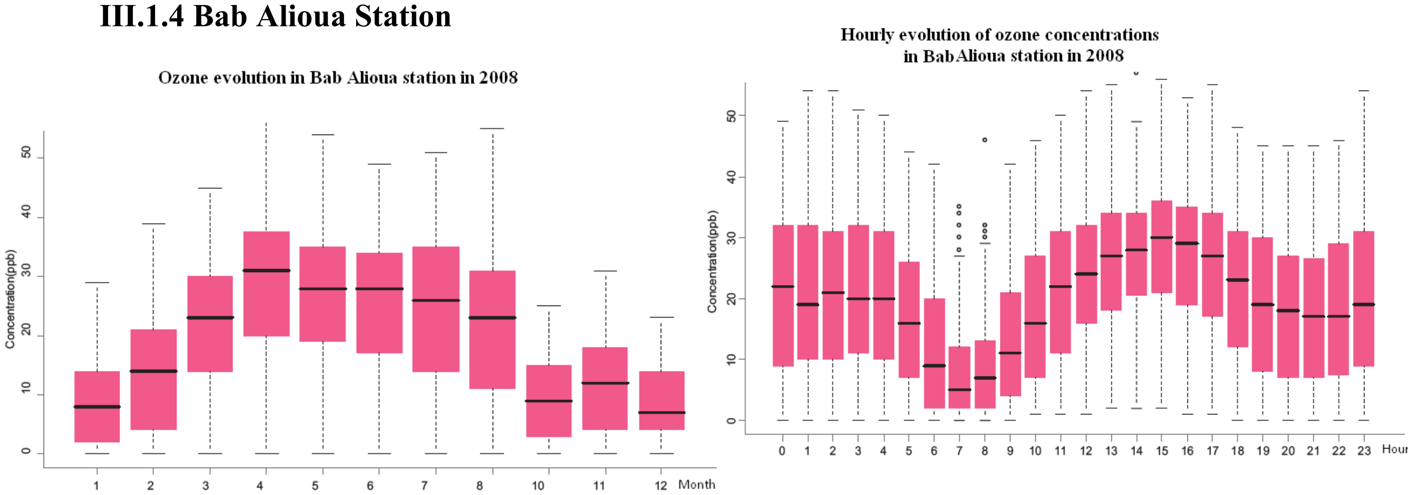

Figure 23. Temporal evolution in Bab Alioua station in 2008

The highest values of O_3 were marked between the March and August. This shows the effect of factor season on the evolution of the ozone. In fact, highest values were observed during the summer season.

Ozone concentrations in Bab Aliwa are among the lower compared to other stations. The shape of the curve profile of ozone seems to be typical.

III.1.5 Radès station

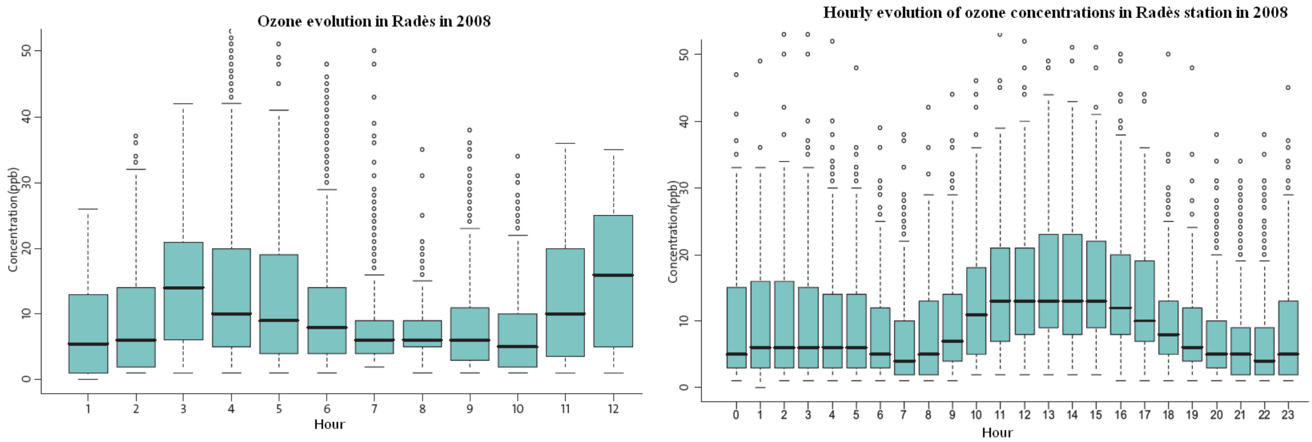

Figure 24. Temporal evolution in Radès station in 2008

The graph in Figure 24 shows the evolution of the ozone from one month to another during the year 2008 in Radès. An increase of O_3 concentration is observed during March compared with to the first two months of the year, followed by a decrease until October, and then increased until the end of year. In Radès, the third quartile of recorded values is less than 16 ppb. The highest values were observed during the afternoon.

III.2 Temporal evolution in suburban areas

III.2.1 Park Mourouj station

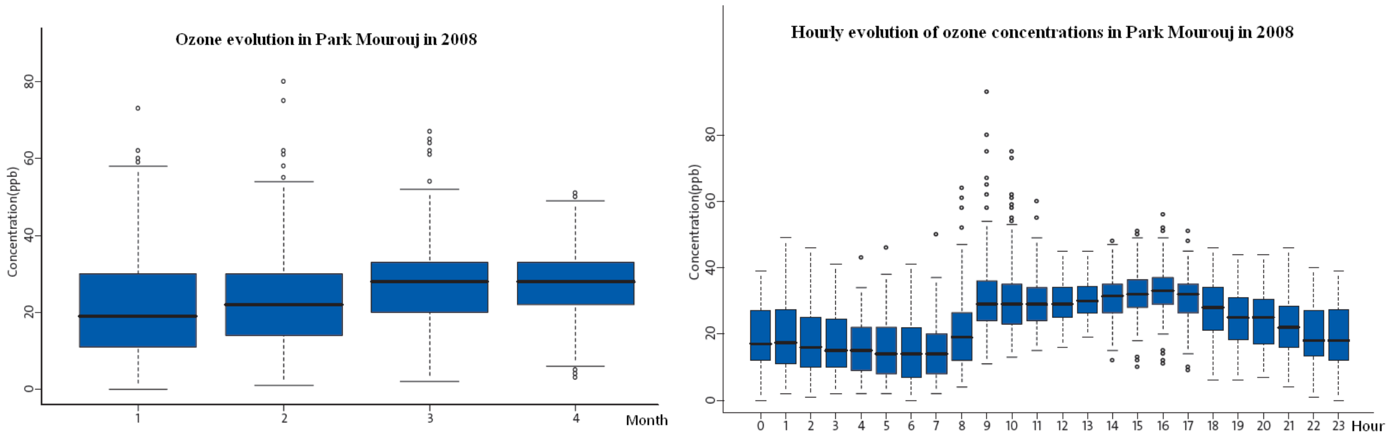

Figure 25. Temporal evolution in Park Mourouj station in 2008

Only during the first four months of the year we recorded values by station installed Mourouj Park. A slight increase concentrations of O_3 was marked in both last month compared to other months.

The information provided by this graph on the hourly evolution fo ozone level in Park Mourouj is not very relevant and comprehensive for the whole year, because measures were only available for four first months of year 2008.

III.2.2 Park Nahli station

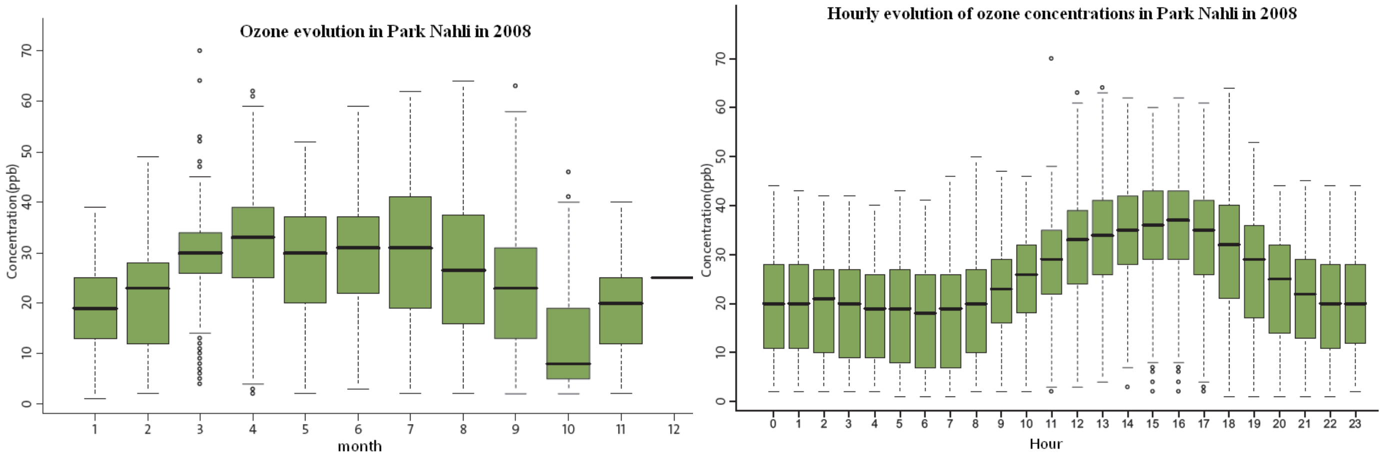

Figure 26. Temporal evolution in Park Nahli station in 2008

The graphs above (Figure 26) illustrate the evolution of ozone concentrations, by month in Park Nahli during the year 2008. We observed a gradual increase in ozone concentrations during the first four months of the year, then stability until August, followed by a decrease from one month to another until October. And finally an increase was recorded on November. The highest values occur during the afternoon and lowest around 8:00 am.

IV. INFLUENCE OF THE METEOROLOGICAL PARAMETERS

In this part, we study the Influence of meteorological parameters on the evolution of O_3 in Mannouba given it is characterized by a high level of ozone concentrations and for the reason that we have sufficient available data in this station.

The direction and strength of the wind also affect ozone concentrations. Based on worldwide climate patterns, western coasts at California's latitude tend to have high-pressure areas over them, especially in summer. By preventing the formation of storms, and by promoting the sinking of very warm air, these high-pressure areas are associated with light winds and temperature inversions, both of which limit dispersion of pollutants.

IV.1 Influence of wind direction

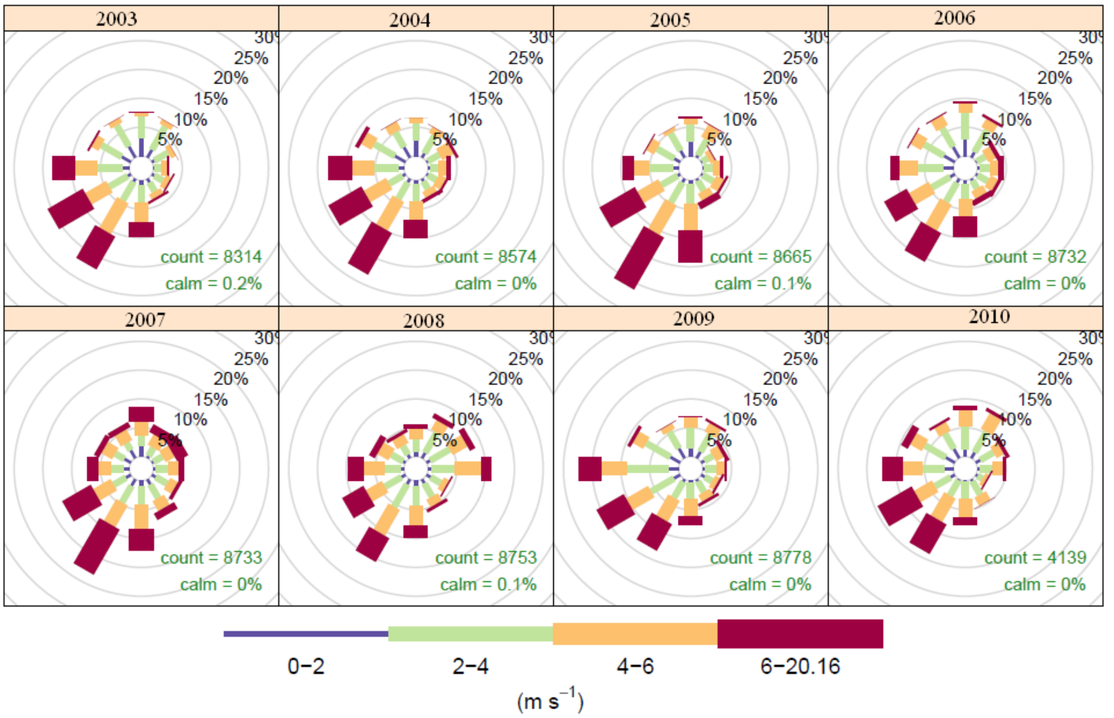

Figure 27. Frequency of counts by wind direction (%)

The case study of Mannouba by bivariate and multiple regressions reveal the overall heaviness of meteorological variables measured and the respective heaviness of each of them. The degree of binding (threshold 95%) is high: 77% and 60% of the variance is explained. The predominant variables (bivariate regressions) are related directly or indirectly to radiation balance (moisture, direct radiation, air temperature and dew point) or wind.

Mannouba station which is enclosed is less ventilated. It is downwind of a huge urban mass. This region receives pollution from its own suburb and from elsewhere.

Winds E and NE directions put it under the wind across the northern and eastern part of the city. The following explains the higher number of exceedances significantly in Mannouba. The case of the year 2008 illustrates the effect of this type of flow micro spatial scale.

IV.2 Influence of wind speed

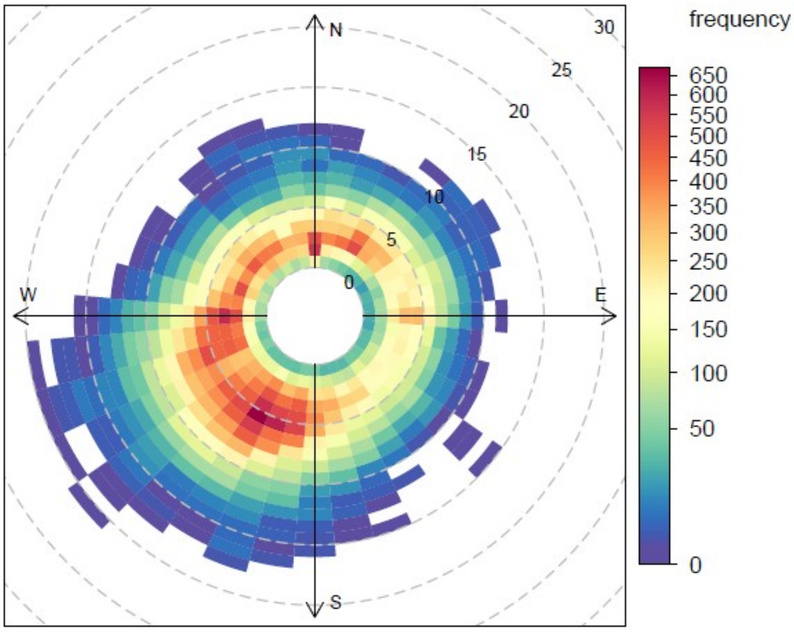

Figure 28. Frequency of counts by wind speed/direction (%)

Exceedances of the limit value and the guide value have been recorded. When wind speed is between 0 and 4 m/s.

These are a few reasons why concentrations can change with increasing wind speeds.

- Buoyant plumes from tall stacks can be brought down to ground-level resulting in high concentrations under high wind speed conditions.
- Particle suspension increases with increasing wind speeds e.g. PM10 from spoil heaps and the like.
- "Particle" suspension can be important close to coastal areas where higher wind speeds generate more sea spray.
- The wind speed dependence of concentrations in a street canyon can be very complex: higher wind speeds do not always results in lower concentrations due to re-circulation. Bivariate polar plots are very good at revealing these complexities.
- As Carslaw et al. (2006) showed, aircraft emissions have unusual wind speed dependence and this can help distinguish them from other sources. If several

measurement sites are available, polar plots can be used to triangulate different sources.

- Concentrations of NO_2 can increase with increasing wind speed — or at least not decline steeply due to increased mixing. This mixing can result in O_3-rich air converting NO to NO_2.

IV.3 Influence of temperature

Temperature and long term urban warming have a serious impact on urban pollution, resulting in higher ozone concentrations, as heat accelerates the chemical reactions in the atmosphere (Clark and Karl 1982; Walcek and Yuan 1999). Higher ozone concentration values in urban environments are mainly caused by solar radiation and pollutants. Air temperature acts as a proxy parameter, representing the diurnal variation of solar radiation. Urban areas accumulate greater amounts of heat than the surrounding rural country, resulting in higher air temperature values in densely populated and built areas. This phenomenon, which is widely known as the "heat island effect", is mainly caused by the differences in the thermal structure between urban and rural environments that are associated with thermal properties of urban materials, urban geometry, air pollution and the anthropogenic heat released by urban activities (Oke 1987; Mihalakakou et al. 2004, Park 1986). The urban heat island phenomenon may occur during day or night-time periods and its patterns are strongly controlled by the unique characteristics of each urban area (Oke et al. 1991). It is usually developed during clear, calm evenings and nights and is normally a result of delayed cooling of the city compared to surrounding rural areas (Barring et al. 1985).

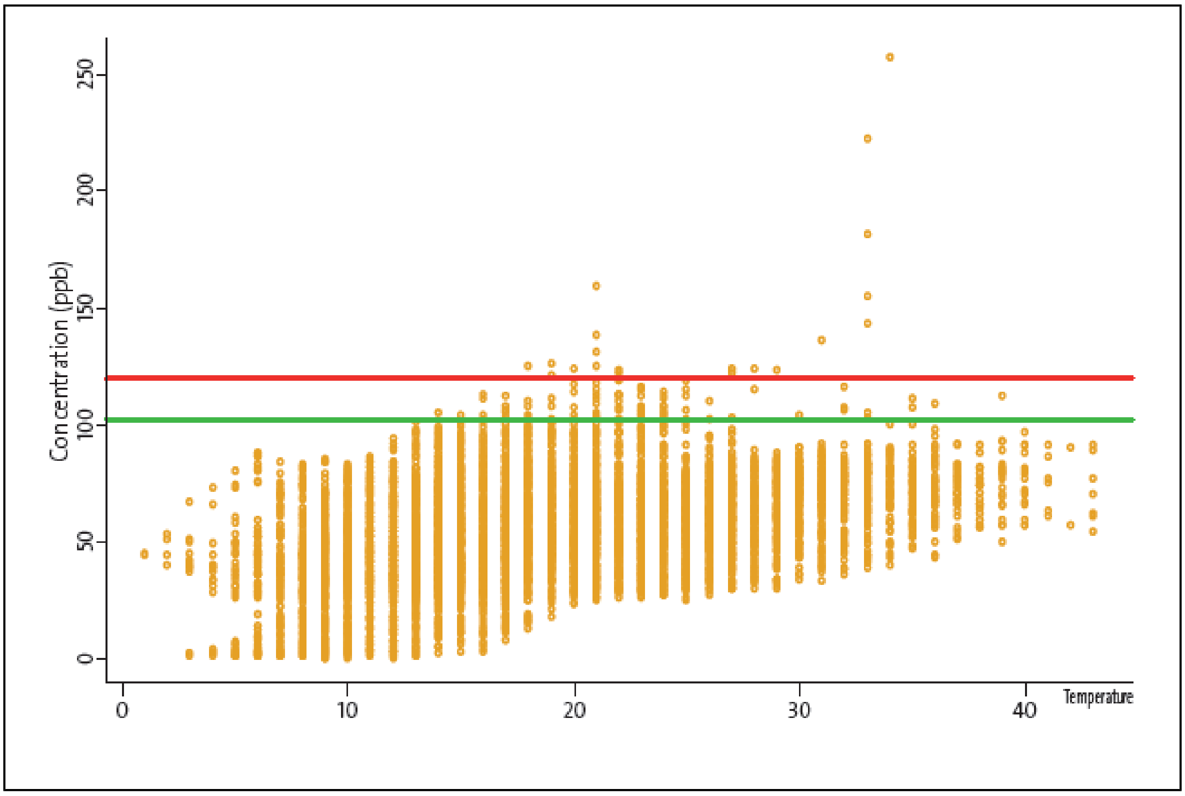

Figure 29. Influence of Temperature on the evolution of the ozone concentrations in Mannouba

This graph (Figure 29) shows a mixture between ozone level and temperature in Mannouba, for the year 2008. The highest values of O_3 correspond to a temperature of 34 ° C.

IV.4 Effect of Vegetation on Ozone Concentrations

Vegetation can reduce ozone concentrations by providing cooling and by removing pollutants. The shade provided by trees lowers ozone concentrations in several ways. It reduces the pollutant emissions from many sources (such as less evaporation of fuel from cooler parked vehicles). By cooling homes and offices, tree shade lowers emissions coupled with electricity generation because less power is needed for air conditioning. In addition, cooling reduces the speed of chemical reactions in ambient air that lead to the formation of ozone.

Vegetation can also enhance the removal of ozone through deposition on plant surfaces. The surfaces of leaves and pine needles allow for deposition of ozone and NO_2. Several different factors affect pollutant removal, such as how long a parcel of air is in contact with the leaf and the total leaf area available for deposition. Also, rain tends to reduce ambient ozone concentrations by washing out atmospheric gases as well as gases deposited on leaves and needles.

Other processes involving vegetation can lead to higher concentrations of ozone. For example, trees and other types of vegetation emit biogenic VOCs, such as isoprene, pinenes, and terpenoid compounds. These biogenic VOCs can react with NOx emitted from sources such as cars and power plants to form ozone. Many biogenic VOCs are highly reactive (i.e., especially efficient in reacting to form ozone); some VOCs are even more efficient in forming ozone than those emitted from cars and power plants. In addition, VOCs can be emitted from decomposing leaves.

V. CLIMATE CHANGE COULD WORSEN OZONE POLLUTION

Climate change and air pollution are closely coupled. Just as air pollution can have adverse effects on human health and ecosystems; it can also impact the Earth's climate. When energy from the sun reaches the Earth, the planet absorbs some of this energy and radiates the rest back to space as heat. The Earth's surface temperature depends on this balance between incoming and outgoing energy. Atmospheric greenhouse gases (GHGs) like carbon dioxide (CO_2) and methane (CH_4) can trap this energy and prevent the heat from escaping.

Because climate represents meteorological conditions over a long period of time, it is difficult to identify a climate fingerprint in the current trends in air quality discussed earlier in this report. Given the general improvement in air quality over the past decade, it appears that emissions reductions from air quality regulations are outpacing any climate-driven impacts.

Given the strong dependence of ozone formation on temperature, a changing climate can make ozone pollution worse. As temperatures increase in a warmer world, days that are conducive to ozone formation are likely to be more frequent. Temperatures in Tunisia have already increased more than 1.5°F over the past century because of human-caused emissions of carbon dioxide and other heat-trapping gases. The amount of warming this century depends heavily on the amount of heat-trapping gases we emit today. Even if emissions of all heat-trapping gases were to stop immediately, warming would still be "locked in" for years afterward because carbon dioxide resides in the atmosphere a very long time. As such, temperatures will remain elevated for at least the next decade and possibly longer (Armour and roe 2011; Gillett et al. 2011; solomon et al. 2009).

In addition to bad air quality, climate change poses other threats to the health and well-being of Americans. This report addresses just one public health threat associated with climate change, but there are numerous others, including heat waves, elevated allergen levels, more occurrences of waterborne diseases, changing disease vectors, and degraded water quality. The good news is that both ozone pollution and climate change are fundamentally caused in large part by the same activities: human beings burning fossil fuels to generate electricity and run their vehicles. Therefore we can address both ozone pollution and climate change by implementing practical policies and programs and changing individual behaviors. For example, we can reduce both ozone-precursor and carbon emissions from power plants, refineries, and vehicles by:

•Investing in more fuel-efficient cars and reducing miles driven

•Developing fuels that are less carbon-intensive

•Providing good public transit and other commuting and travel alternatives

•Increasing energy efficiency at industrial and commercial facilities

•Developing and retrofitting homes and buildings to be more efficient

•Using more renewable energy resources such as wind, solar, and geothermal to generate electricity

•Ensuring that ozone- and carbon-reduction standards are strong enough to be truly protective of public health

•Working collaboratively with global partners to reduce carbon emissions from other countries.

CONCLUSION

Ozone measurements that are still very little used, reflects the multitude of factors that affect the spatial variability of secondary pollutant in urban and suburban areas. The impact of each is impossible to quantify and order in absolute terms, but as a general statement more air circulation is low more the surrounding environment will have more weight on the level of pollution. From one street to ozone level may double or triple depending on attendance lanes, strength and direction of the wind, the background level of ozone in the day, human exposure varies strongly. In addition, when ozone concentrations are very low in downtown, they do not necessarily reflect good air quality but probably a strong primary pollution. The measurement of ozone in urban areas may seem unnecessary, but it indirectly indicates the levels of nitrogen oxides.

As you can see, ozone air pollution is a big problem to both the environment and our health. The EPA (Environmental Protection Agency) has enacted many regulations to help decrease ozone air pollution. They have also set standards to help residents know when it is safe to spend time outdoors. This has helped to decrease some of the health effects. By lowering the emissions from your vehicle by carpooling, using alternative fuels, and decreasing your car usage, you can help decrease some of the emissions that are involved in the chemical process of creating ozone air pollution. Decreasing your use of VOCs (Volatile Organic Compounds) is another way you can decrease the creation of ozone. By learning more about the causes of ozone air pollution, you can become part of the key to helping decrease the amount of bad ozone in the air.

The Law on Air Quality of June 4, 2011 enlightened the National Agency for the Protection of the Environment to undertake a number of actions to reduce air pollution, including the quality control air and its impacts on health and the environment, the creation of a National Network for Monitoring Air Quality (RNSQA), the development of conservation plans for quality air in some cities, the limitation of emissions from mobile sources and stationary sources and the fight against crime, etc ...

In order to control and reduce pollution toward air quality and public health conditions improvement in Tunisia, and even before the extension of the said Act, the RNSQA works in a fully automatic and autonomous and results presented in this report are the result of the operation of the network throughout many years.

Following this work, we can conclude that the results obtained show a marked variability in air pollution levels, according to various influences. The highest levels of air emissions are recorded in the industrial centers in Mannouba, including for the following pollutants, namely Ozone, Sulphur Dioxide, Nitrogen Dioxide and dust.

In urban areas, highest air pollution levels are measured closer to road emissions for urban stations near automobiles. Road traffic causes pollution levels more or less important depending on the number of channels and traffic flow. The planning and topography also play an important role in the level of atmospheric emissions and contribute significantly to the degradation of air quality in Bab Saadoun, especially dust. Finally, meteorological factors and photochemical reactivity generally have a prominent impact on the state of air quality and are more particularly, to the origin of the formation of secondary pollutants. Given the above, development projects and research programs in the field of air quality, is the best way to understand our atmospheric environment.

Under Article 4 of the law on air quality, promulgated on June 4, 2007, the National Agency for the Protection of the environment make up one's mind to develop Conservation Plans of Air Quality, called PCQA. These plans are a tool for information, consultation and guidance for preserving the air quality, as was mentioned by law and will mark a new milestone for the promotion of the right to a healthier environment and better quality of life and by measures in general or particular character and respect for standards balance the natural environment.

Local communities, structures and institutions public concerned are called upon to contribute in the preparation of these plans especially for urban areas whose population exceeds a fixed number and areas record exceeded or are likely to exceed the limit values or alert thresholds for the air quality. The choice of Greater Tunis was the result of a concerted for the development of the foreground and seems suitable and for two reasons:

- Its economic and demographic importance.
- The availability of data in this area (mapping, 9 fixed stations, one DOAS ...)

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